รายงานฉบับสมบูรณ์
ทุนส่งเสริมกลุ่มวิจัย สกว. ประจำปี 2552
สำนักงานกองทุนสนับสนุนการวิจัย

เลขที่สัญญา RTA5280008

วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง
Hybrid Materials & Processing Development for Plastic and Rubber Composites (Hy-MAC)

โดย ศาสตราจารย์ ดร.ณรงค์ฤทธิ์ สมบัติสมภพ และคณะ
สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ
มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
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ประกอบด้วย

- รายงานฉบับสมบูรณ์ของโครงการวิจัย
- รายงานการเงินของโครงการวิจัย

รายงานฉบับสมบูรณ์ของโครงการวิจัย
สัญญาเลขที่ RTA5280008
วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง
Hybrid Materials & Processing Development for Plastic and Rubber Composites (Hy-MAC)

รายงานในช่วงวันที่ 31 กรกฎาคม 2552 ถึง 31 สิงหาคม 2555
ระยะเวลาโครงการ 37 เดือน
ชื่อหัวหน้าโครงการ ศ.ดร. ณรงค์ฤทธิ์ สมบัติสมภพ
(Prof. Dr. Narongrit Sombatsompop)

รายชื่อนักวิจัย

1. ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ (KMUTT)	หัวหน้าโครงการ
2. รศ.ดร.ชาคริต สิริสิงห (MU)	นักวิจัยร่วม
3. ผศ.ดร.ณฐินี โล่ห์พัฒนานนท์ (PSU)	นักวิจัยร่วม
4. ผศ.ดร.พูนทรัพย์ ตรีภพนาถกูล (SU)	นักวิจัยร่วม
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10. ผศ.ธีระศักดิ์ หมากผิน (KMUTT)	นักวิจัยร่วม
11. ผศ.ดร.ทวิช พูลเงิน (KMUTT)	นักวิจัยร่วม
12. ดร.ศิรินทร ทองแสง(KMUTT)	นักวิจัยร่วม
13. นายวิชัย โรซาพิทักษ์ (VP Wood Co., Ltd.)	ผู้ร่วมวิจัยและผู้ร่วมทุนวิจัย (in cash) ภาคเอกชน
14. นักศึกษาปริญญาโทและเอก (จาก มจธ. และ ม.เครือข่าย) อีก 24 คน	

1. ผลการดำเนินงาน : ☑ ได้ดำเนินงานตามแผนงานที่ได้วางไว้ทุกประการ
โครงการย่อยทุกโครงการ ได้ outputs สูงกว่าแผนที่วางไว้ โดยมีข้อสรุปดังนี้

1.1 จำนวนบทความวิจัยที่ตีพิมพ์ในวารสารวิชาการนานาชาติ (+impact factors) **จำนวน 25 บทความ**
1.2 การนำผลจากโครงการไปใช้ประโยชน์ (Royalty) **จำนวน 300,000 บาท**
1.3 จำนวนบทความวิจัยฉบับเต็มที่เสนอในที่ประชุมวิชาการนานาชาติ**จำนวน 8 บทความ** ใน 4 ประเทศ
1.4 จำนวนบทความวิจัยฉบับเต็มที่เสนอในที่ประชุมวิชาการในประเทศ **จำนวน 7 บทความ**
1.5 จำนวนนักศึกษาบัณฑิตศึกษา (เฉพาะโทและเอก) ภายใต้โครงการฯ **จำนวน 24 คน**
1.6 จำนวนทุนการศึกษาของนักศึกษาที่เชื่อมต่อกับโครงการฯ **จำนวน 6 ทุน**การศึกษา
1.7 จำนวนรางวัลที่บุคลากรในโครงการได้รับจากภายนอก **จำนวน 1 รางวัล**
1.8 จำนวนการจัดประชุมประจำปีของโครงการฯ **จำนวน 2 ครั้ง**

การประสานงานในรอบ 37 เดือน

- ☑ ติดต่อทางโทรศัพท์ / โทรสาร กับผู้ร่วมทุน 97 ครั้ง
- ☑ ประชุมร่วมกับผู้ร่วมทุน 25 ครั้ง
- ☑ ประชุมทีมวิจัย 185 ครั้ง เป็นเรื่อง
  - ☑ วางแผนและทบทวนงาน 57 ครั้ง
  - ☑ หารือปัญหาการทำวิจัย 64 ครั้ง
  - ☑ วิเคราะห์ผล 32 ครั้ง
  - ☑ มอบหมายงาน 32 ครั้ง

2. ผลงานวิจัย

2.1 ผลงานตีพิมพ์ "เฉพาะ" ในวารสารวิชาการนานาชาติ (ตามเอกสารแนบหมายเลข 1)

ขณะนี้โครงการวิจัยมีบทความวิจัยเพื่อลงพิมพ์ในวารสารวิชาการนานาชาติ (ที่มีค่า journal impact factors) จากทุกโครงการย่อยรวมกันจำนวน 25 บทความ โดยสถานภาพของบทความวิจัย เป็นดังนี้

O	บทความวิจัยที่ได้ตีพิมพ์แล้ว (Published)	จำนวน 22	บทความ
O	บทความวิจัยที่ได้รับการตอบรับแล้ว (Accepted/in-press)	จำนวน 3	บทความ
O	บทความที่อยู่ระหว่างการพิจารณา (Under review)	จำนวน 0	บทความ

2.1.1 Taptim K & **Sombatsompop N** (2012) Effect of UV weathering on mechanical and anti-bacterial performances for peroxide-cured silicone rubber with HPQM – ***Journal of Vinyl & Additive Technology*** (Accepted) [JIF = 0.878]. จากโครงการย่อย RCT

2.1.2 Jai-eau K, Wimolmala E & **Sombatsompop N** (2012) Cure Behavior and Antimicrobial Performance of Sulfur-Cured NR Vulcanizates Containing 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate or Silver Substituted Zeolite- ***Journal of Vinyl & Additive Technology*** (in press) [JIF = 0.878]. จากโครงการย่อย RCT

2.1.3 Taptim K & **Sombatsompop N** (2012) Anti-microbial Performance and Cure & Mechanical Properties for Peroxide-Cured Silicone Rubber Compounds – ***Journal of Vinyl & Additive Technology*** 18: (in press) [JIF = 0.878]. จากโครงการย่อย RCT

2.1.4 Hatthapanit K, Saeoui P, Sombatsompop N & **Sirisinha C** (2012) Enhancement of Rubber-Carbon Black Interaction by Amine-Based Modifiers and Their Effect on Viscoelastic and Mechanical Properties, ***Journal of Applied Polymer Science***, 126 (S2): E315-321 [JIF = 1.289]. จากโครงการย่อย RCT

2.1.5 Hamaviriyapornwattana N, Sombatsompop N, Markpin T, Kositchaiyong A & **Wimolmala E**, (2012) Solar Reflectance, Surface Adhesion and Thermal Conductivity of Wood/NR Composite Sheet with TiO_2/PU Topcoat for Roofing Applications – ***Journal of Vinyl & Additive Technology*** 18 (3): 184-191 [JIF = 0.878]. จากโครงการย่อย RCT

2.1.6 Prapruddivongs C & **Sombatsompop N** (2012) Roles and Evidences of Wood Flour as Anti-bacterial Promoter for Triclosan Filled Poly(lactic acid) – ***Composites: Part B. Engineering***, 43 (7): 2730-2737 [JIF = 1.731]. จากโครงการย่อย WPC and BPC

2.1.7 Jeamtrakull S, Kositchaiyong A, Markpin T, Rosarpitak V & **Sombatsompop N** (2012) Effects of Wood Constituents and Content, and Glass Fiber Reinforcement on Wear Behavior of Wood/PVC Composites – ***Composites: Part B. Engineering***, 43 (7): 2721-2729 [JIF = 1.731]. จากโครงการย่อย WPC

2.1.8 Saowapark T, Sae-oui P, Sombatsompop N & **Sirisinha C** (2012) Storage Instability of Fly Ash Filled Natural Rubber Compounds – ***Applied Rheology*** 22 (5): 55414 [JIF = 1.000]. จากโครงการย่อย RCT

2.1.9 **Lopattananon N**, Thongpin C & Sombatsompop N (2012) Bioplastics from Blends of Cassava Rice and Flour: The Effect of Blend Composition – ***International Polymer Processing*** 27 (3): 334-340 [JIF = 0.345]. จากโครงการย่อย BPC

2.1.10 **Thongsang S**, Vorakhan W, Wimolmala E & Sombatsompop N (2012) Dynamic Mechanical Analysis and Tribological Properties of NR Vulcanizates with Fly Ash/Precipitated Silica Hybrid Filler – ***Tribology International*** 53 (1): 134-141 [JIF = 1.553]. จากโครงการย่อย RCT

2.1.11 Kanking S, Niltui P, **Wimolmala E** & Sombatsompop N (2012) Use of Bagasse Fiber Ash as Secondary Filler in Silica or Carbon Black Filled Natural Rubber Compound – ***Materials and Design***, 41 (1): 74-82. [JIF = 2.200]. จากโครงการย่อย RCT

2.1.12 Kaiyaded W, Wimolmala E, Harnnarongchai W, Sithicharoen W, Intawong N-T, & **Sombatsompop N** (2012) Rotating Die Technique for Sharkskin Minimization in Highly Viscous Wood/PP Composite Melt in an Extrusion Die – ***Journal of Applied Polymer Science*** 125 (3): 2312–2321 [JIF = 1.289]. จากโครงการย่อย WPC and PPR

2.1.13 Kaewkanokslip C, Patcharaphun S, Apimonsiri, W & **Sombatsompop N** (2012) Rheological Properties and Melt Strength of LDPE During Coextrusion Process – ***Journal of Applied Polymer Science*** 125 (3): 2187–2195 [JIF = 1.289]. จากโครงการย่อย PPR

2.1.14 Sithicharoen W, Harnnarongchai W, Intawong N-T, & **Sombatsompop N** (2012) Melt Strength, Local Velocity, and Elongational Viscosity Profiles of Low-Density Polyethylene Filaments Affected by the Die Design and Process Conditions – ***Journal of Applied Polymer Science*** 124 (5): 3751-3764. [JIF = 1.289]. จากโครงการย่อย PPR

2.1.15 Chaochanchaikul K, Jayaraman K, Rosarpitak V & **Sombatsompop N** (2012) Influence of Lignin Content on Photodegradation in Wood/HDPE Composites under UV Weathering – ***BioResources*** 7 (1): 38-55 [JIF = 1.328]. จากโครงการย่อย WPC

2.1.16 Hatthapanit K, Nillawong M, Sombatsompop N, **Sirisinha C** & Saeoui P (2011) Rubber-filler Interaction, Cure and Viscoelastic Properties in Black Filled Nitrile Rubber (NBR) Compounds Modified by Functionalized Liquid Polybutadiene – ***KGK - Kautschuk Gummi Kunststoffe*** 64 (10): 54-60 [JIF = 0.345]. จากโครงการย่อย RCT

2.1.17 **Threepopnatkul P**, Teppinta W & Sombatsompop N (2011) Effect of Co-monomer Ratio in ABS and Wood Content on the Processing and Properties in Wood/ABS Composites – ***Fibers and Polymers*** 12 (8): 1007-1013. [JIF = 0.836]. จากโครงการย่อย WPC

2.1.18 Harnnarongchai W, Sithicharoen W, Intawong N-T & **Sombatsompop N** (2011) Mechanical Strengths of Molten and Solidified LLDPE/LDPE Blends and Wood/LDPE Composite under Tensile Deformation – ***Journal of Vinyl & Additive Technology*** 17 (3): 164-176. [JIF = 0.878]. จากโครงการย่อย PPR

2.1.19 Chaochanchaikul K, Rosarpitak V & **Sombatsompop N** (2011) Structural and Thermal Stabilizations of PVC and Wood/PVC Composites by Metal Sterates and Organotin – ***BioResources*** 6 (3): 3115-3131. [JIF = 1.328]. จากโครงการย่อย WPC

2.1.20 Chaochanchaikul K & **Sombatsompop N** (2011) Stabilizations of Molecular Structures and Mechanical Properties of PVC and Wood/PVC Composites by Tinuvin and TiO_2 Stabilizers – ***Polymer Engineering and Science*** 51 (6): 1354-1365 [JIF = 1.302]. จากโครงการย่อย WPC

2.1.21 Harnnarongchai W, Intawong N-T & **Sombatsompop N** - Effects of Roller Speed, Temperature, Volumetric Flow Rate and Multiple Extrusions on Mechanical Strength of Molten and Solidified LDPE under Tensile Deformation– ***Journal of Macromolecular Science: Part B. Physics*** 50 (6): 1074 – 1086. [JIF = 0.739]. จากโครงการย่อย PPR

2.1.22 **Pulngern T**, Padyenchean C, Rosarpitak V, Prapruit W & Sombatsompop N (2011) Flexural and Creep Strengthening for Wood/PVC Composite Members using Flat Bar Strips – ***Materials and Design*** 32 (6): 3431-3439 [JIF = 2.200]. จากโครงการย่อย WPC

2.1.23 Silapasorn K, Sombatsompop K, Kositchaiyong A, Markpin T & **Sombatsompop N** (2011) Effect of Chemical Structure of Thermoplastics on Anti-bacterial Activity and Physical Diffusion of Triclosan Doped in Vinyl Thermoplastics and Their Composites with $CaCO_3$- ***Journal of Applied Polymer Science*** 121 (1): 253-261 [JIF = 1.289]. จากโครงการย่อย WPC

2.1.24 Intawong N-T, Kantala C, Toataison W & **Sombatsompop N** (2011) A Die Rotating System for Moderations of Extrusion Load and Pressure Drop Profiles for Molten PP and Wood/PP Composites in Extrusion Processes – ***Journal of Applied Polymer Science***, 120 (2): 1006-1016. [JIF = 1.289]. จากโครงการย่อย PPR และ WPC

2.1.25 Sithicharoen W, Intawong N-T & **Sombatsompop N** (2010) An Experimental Apparatus for Measurement of Elongational Flow Properties for LDPE Melt and the Effect of Testing Conditions – ***Polymers and Polymer Composites*** 18 (7): 359-368 [JIF = 0.326]. จากโครงการย่อย PPR

สรุปผลงานวิจัยในแง่จำนวนและการเป็น Corresponding author (เฉพาะนักวิจัยโดยไม่นับรวม นศ.)

รายชื่อนักวิจัยในโครงการ	**ต้นสังกัดนักวิจัย**	**จำนวนผลงานตีพิมพ์** (เรื่อง)	**จำนวนผลงานที่เป็น Corresponding author**
ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ	ม.พระจอมเกล้าธนบุรี	25	16
รศ.ดร.ชาคริต สิริสิงห	ม.มหิดล	3	3
ผศ.ดร.จันทร์ฉาย ทองปิ่น	ม.ศิลปากร	1	-
ผศ.ดร.พูนทรัพย์ ตรีภพนาถกูล	ม.ศิลปากร	1	1
ผศ.เอกชัย วิมลมาลา	ม.พระจอมเกล้าธนบุรี	5	2
ผศ.ธีระศักดิ์ หมากผิน	ม.พระจอมเกล้าธนบุรี	3	-
ผศ.ดร.ทวิช พูลเงิน	ม.พระจอมเกล้าธนบุรี	1	1
ดร.สมเจตน์ พัชรพันธ์	ม.เกษตรศาสตร์	1	-
ผศ.ดร.ณฐินี โล่ห์พัฒนานนท์	ม.สงขลานครินทร์	1	1
ดร.นเรศ อินต๊ะวงค์	ม.ราชมงคล ล้านนา	6	-
ดร.ศิรินทร ทองแสง	ม.พระจอมเกล้าธนบุรี	1	1
นายวิชัย โรซาพิทักษ์ (ผู้ร่วมทุนภาคเอกชน)	บ.วี พี วู๊ด จำกัด	4	-

2.2 ความก้าวหน้าในการสร้างทีมวิจัย

2.2.1 โครงการนี้ได้รับนักวิจัยรุ่นใหม่ในรูปของนักศึกษาระดับปริญญาโทและเอก เพื่อเข้าร่วมทีมศึกษาวิจัย 24 คน (2551-2554) โดยแบ่งเป็นปริญญาเอก 6 คน และปริญญาโท 18 คน ซึ่งมีรายชื่อนักศึกษา ดังนี้

1. นายวัชรินทร์ สิทธิเจริญ (นศ. ป.เอก 2551)
2. นายวัลลภ หาญณรงค์ชัย (นศ. ป.เอก 2551)
3. นายชนะ ประพฤกษ์วงศ์ (นศ. ป.เอก 2552)
4. นางสาวกุลนิดา เทพทิม (นศ. ป.เอก 2552)
5. นายอภิสิทธิ์ โฆษิตชัยยงค์ (นศ.ป.เอก ปี 2553)
6. นายสิทธิพงค์ มหาธนบดี (นศ.ป.เอก ปี 2554)

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7. นายชัชชัย พัดเย็นชื่น (นศ.ป.โท ปี 2551)
8. นางสาวกรรณิกา หัตถะปะนิตย์ (นศ.ป.โท ปี 2552)
9. นายอธิป บุญบำรุง (นศ.ป.โท ปี 2552)
10. นายศิริชัย ก้านกิ่ง (นศ.ป.โท ปี 2552)
11. นางสาวรัชนี ฉิมกมลทอง (นศ.ป.โท ปี 2552)
12. นายอัฐพงษ์ กิตติ์ชัยวัชร์ (นศ.ป.โท ปี 2552)
13. นายคณิศร ใจเอื้อ (นศ.ป.โท ปี 2552)
14. นายวีรพล อภิมนสิริ (นศ.ป.โท ปี 2552)

15. นายเชษฐ์ภรณ์ แก้วกนกศิลป์ (นศ.ป.โท ปี 2552)
16. นางสาวสุปรีดา เจียมตระกูล (นศ.ป.โท ปี 2552)
17. นางสาวปาริชาติ ยศแก้ว (นศ.ป.โท ปี 2553)
18. นางสาวปวีณา แตงอุดม (นศ.ป.โท ปี 2553)
19. นางสาวจันทราพร พรหมฉิม (นศ.ป.โท ปี 2553)
20. นายปรีชา แก้วกัลยา (นศ.ป.โท ปี 2554)
21. นางสาวอริยา ศรีบุตร (นศ.ป.โท ปี 2554)
22. นางสาวชิตสุปรีย์ กตาธิการกุล (นศ.ป.โท ปี 2554)
23. นายจุมพล เล็กเริงสินธุ์ (นศ.ป.โท ปี 2554)
24. นายภาณุ กนกศิลปธรรม (นศ.ป.โท ปี 2554)

2.2.2 การเลื่อนตำแหน่งวิชาการของนักวิจัยในโครงการระหว่างดำเนินโครงการ

รายชื่อนักวิจัยในกลุ่มวิจัย	**ตำแหน่งเดิม**	**ตำแหน่งใหม่** (ระหว่างทุน)	**สถานภาพ/ช่วงเวลาที่เลื่อนตำแหน่ง**
นายเอกชัย วิมลมาลา	นักวิจัย (มจธ.)	ผศ.วิจัย	สิงหาคม 2552
นายธีระศักดิ์ หมากผิน	นักวิจัย (มจธ.)	ผศ.วิจัย	สิงหาคม 2552
ดร.พูนทรัพย์ ตรีภพนาถกูล	อาจารย์ (ม.ศิลปากร)	ผศ.	ธันวาคม 2553
ดร.ณฐินี โล่ห์พัฒนานนท์	อาจารย์ (ม.สงขลาฯ)	ผศ.	กันยายน 2553
ดร.ทิพบรรณ ปะละไทย	อาจารย์ (มจธ.)	ผศ.	กันยายน 2553
ดร.ทวิช พูลเงิน	อาจารย์ (มจธ.)	ผศ.	ธันวาคม 2553
ดร.สมเจตน์ พัชรพันธ์	อาจารย์ (มจธ.)	ผศ.	มกราคม 2553
ดร.นเรศ อินต๊ะวงค์	อาจารย์ (มทร. ล้านนา)	ผศ.	มิถุนายน 2553

2.3 การนำผลจากโครงการไปใช้ประโยชน์

ทางบริษัท วี พี วู๊ด จำกีด นำผลวิจัยจากโครงการ WPC จัดทำเป็นเอกสารประชาสัมพันธ์ผลิตภัณฑ์ของบริษัทฯ และขณะนี้ สกว. และ มจธ. ได้ผลตอบแทนจากการนำสิทธิบัตรไปใช้ประโยชน์ เป็นเงินในงวดแรกปี 2554 จำนวน 300,000 บาท (เอกสารหลักฐานที่ สกว.)

3. กิจกรรมอื่น ๆ ที่เกี่ยวข้อง

3.1 ผลงานอื่น ๆ เช่น การไปเสนอผลงานในที่ประชุม การได้รับเชิญไปเป็นวิทยากร การได้รับรางวัล

3.1.1 ส่งผลงานไปเสนอในที่ประชุมวิชาการ**ระดับนานาชาติ** จำนวน 8 เรื่องใน 4 ประเทศ (มีบทความฉบับเต็มทุกบทความ และ Proceedings indexed อยู่ในฐานข้อมูล Scopus)

3.1.1.1 Kositchaiyong A & Sombatsompop N (2012) Anti-fungal and Anti-algal Performances of Biocides filled PVC and Wood/PVC Composites - ***Advanced Materials Research***, Vol. 410: 75-78. (Presented at ***Twentieth International Symposium on Processing and Fabrication of Advanced Materials (PFAM XX)***, 15-18 December 2011, Hong Kong, Paper No. PFAM-033

3.1.1.2 Prapruddivongs C & Sombatsompop N (2012) Effect of wood flour on structural and thermal properties and antibacterial activity of PLA filled with triclosan - ***Advanced Materials Research***, Vol. 410: 67-70. (Presented in ***Twentieth International Symposium on Processing and Fabrication of Advanced Materials (PFAM XX)***, 15-18 December 2011, Hong Kong, Paper No. PFAM-027

3.1.1.3 Taptima K & Sombatsompop N (2012) UV Weathering Effect on Antibacterial Performance in Silicone Rubber Compounds-***Advanced Materials Research***, Vol.410: 325-328.(Presented at ***Twentieth International Symposium on Processing and Fabrication of Advanced Materials (PFAM XX)***, 15-18 December 2011, Hong Kong, Paper No. PFAM-031

3.1.1.4 Kulnida Taptim and Narongrit Sombatsompop (2011) Mechanical properties and antimicrobial performance evaluations for silicone rubber compounds, ***5th International Conference on Materials Processing Technology***, June 2-3, 2011, Phuket, Thailand.

3.1.1.5 Chaochanchaikul K, Sombatsompop N & Rosarpitak V (2011) Thermal Stabilizations of PVC and Wood/PVC Composites under Thermal Ageing by Metal Stearate and Organotin - ***Processing and Fabrication of Advanced Materials XIX:*** 14-17 January 2011, The University of Auckland, Auckland, New Zealand, pp. 986-997.

3.1.1.6 Sitticharoen W, Intawong N, Harnnarongchai W & Sombatsompop N (2011) Radial Velocity Profiles and Melt Strength of LDPE Melt under Elongational Flow in Circular Die - ***Processing and Fabrication of Advanced Materials XIX:*** 14-17 January 2011, The University of Auckland, Auckland, New Zealand, pp. 322-333.

3.1.1.7 Thongsang S, Vorakhan W, Wimolmala E & Sombatsompop N (2011) Dynamic Mechanical Analysis and Tribological Properties of Fly Ash/Precipitated Silica Hybrid Filled-NR Composites - ***Processing and Fabrication of Advanced Materials XIX***: 14-17 January 2011, The University of Auckland, Auckland, New Zealand, pp. 264-275.

3.1.1.8 Jeamtrakull S, Kositchaiyong A, Markpin T & Sombatsompop N (2010) Effects of Wood Constituents and Content, and Glass Fiber Reinforcement on Wear Behavior of Wood/PVC Composites - ***The 7th Asian-Australasian Conference on Composite Materials (ACCM - 7):*** 15-18 November 2010, Taipei, Taiwan.

3.1.2 ส่งผลงานไปเสนอในที่ประชุมวิชาการ**ระดับชาติ** จำนวน 7 เรื่อง (มีบทความฉบับเต็มทุกบทความ)

3.1.2.1 เชษฐ์ภรณ์ แก้วกนกศิลป์, วีรพล อภิมนสิริ และ สมเจตน์ พัชรพันธ์ (2554) การศึกษาสมบัติการไหลของพอลิเอธีลีนหลอมเหลวในระหว่างกระบวนการอัดรีดร่วม - **การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยี ครั้งที่ 9 "วิทยาศาสตร์และวิทยาศาสตร์สุขภาพ",** 30 มิถุนายน - 1 กรกฎาคม 2554, คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยธรรมศาสตร์ ศูนย์รังสิต, กรุงเทพฯ, หน้า 157-163.

3.1.2.2 ศิริชัย ก้านกิ่ง, ศิรินทร ทองแสง, ณรงค์ฤทธิ์ สมบัติสมภพ, ชาคริต สิริสิงห และ เอกชัย วิมลมาลา (2554) อิทธิพลของแหล่งชานอ้อยและปริมาณของซิลิกาในผงเถ้าชานอ้อยที่มีต่อสมบัติการบ่มสุกและเชิงกลของวัสดุเชิงประกอบยางธรรมชาติ - **การประชุมทางวิชาการครั้งที่ 49 มหาวิทยาลัยเกษตรศาสตร์**, 2-4 กุมภาพันธ์ 2554, มหาวิทยาลัยเกษตรศาสตร์ กรุงเทพฯ, หน้า 89-95.

3.1.2.3 รัชนี ฉินกมลทอง, ขวัญเนตร สมบัติสมภพ, อภิสิทธิ์ โฆษิตชัยยงค์, ธีระศักดิ์ หมากผิน และ ณรงค์ฤทธิ์ สมบัติสมภพ (2554) ผลของการบ่มเร่งจากรังสียูวี ที่มีต่อประสิทธิภาพการยับยั้งเชื้อแบคทีเรียของพอลิเอทิลีนและพอลิไวนิลคลอไรด์ที่ผสมซิลเวอร์คอลลอยด์ - **การประชุมวิชาการระดับชาติ มหาวิทยาลัยราชภัฏ ครั้งที่ 2**, 14-17 มกราคม 2554, มหาวิทยาลัยราชภัฏพิบูลสงคราม, พิษณุโลก, หน้า 188-194.

3.1.2.4 Karn Silapasorn, Kwannate Sombatsompop, Apisit Kositchaiyong, Ekachai Wimolmala, Teerasak Markpin and Narongrit Sombatsompop (2010) Effects of Triclosan and CaCO3 Incorporations on Antibacterial Performance for Thermoplastic Films Having Different Molecular Structures - **6th Thailand Materials Science and Technology Conference (MSAT-6)**, 26-27th August 2010, Miracle Grand Convention Hotel, Bangkok.

3.1.2.5 วีรยา วรคันธ์, ณรงค์ฤทธิ์ สมบัติสมภพ, เอกชัย วิมลมาลา และ ศิรินทร ทองแสง (2553) การเสริมแรงของสารประกอบยางธรรมชาติด้วยซิลิกาผสมระหว่างเถ้าลอยและพรีซิพิเทตซิลิกา - **การประชุมวิชาการ มอบ. วิจัย ครั้งที่ 4**, 9-10 สิงหาคม 2553, มหาวิทยาลัยอุบลราชธานี, อุบลราชธานี

3.1.2.6 สุปรีดา เจียมตระกูล, อภิสิทธิ์ โฆษิตชัยยงค์, เอกชัย วิมลมาลา, ธีระศักดิ์ หมากผิน และ ณรงค์ฤทธิ์ สมบัติสมภพ (2553) ผลของเส้นใยไม้ธรรมชาติและเส้นใยแก้วสังเคราะห์ที่มีต่อการต้านทานการสึกหรอของวัสดุเชิงประกอบพีวีซี - **การประชุมวิชาการ มอบ. วิจัย ครั้งที่ 4**, 9-10 สิงหาคม 2553, มหาวิทยาลัยอุบลราชธานี, อุบลราชธานี

3.1.2.7 ณฐิตา เหมะวิริยาพรวัฒนา, เอกชัย วิมลมาลา, ธีระศักดิ์ หมากผิน และ ณรงค์ฤทธิ์ สมบัติสมภพ (2553) อิทธิพลความหนาผิวเคลือบพอลิยูริเทนและปริมาณผงไททาเนียมไดออกไซด์ในผิวเคลือบ ที่มีต่อการสะท้อนรังสีอาทิตย์และการยึดเกาะของแผ่นวัสดุยางธรรมชาติผสมขี้เลื่อยไม้ - **การประชุมทางวิชาการเสนอผลงานวิจัยระดับบัณฑิตศึกษา ครั้งที่ 11**, 12 กุมภาพันธ์ 2553, มหาวิทยาลัยขอนแก่น, ขอนแก่น

3.1.3 ศาสตราจารย์ ดร. ณรงค์ฤทธิ์ สมบัติสมภพ หัวหน้าโครงการวิจัย และหัวหน้ากลุ่มวิจัยการผลิตและขึ้นรูปพอลิเมอร์ (Polymer PROcessing and Flow (P-PROF) Research Group ได้รับ **รางวัลนักวิจัยดีเด่นแห่งชาติ ประจำปี 2553 (สาขาวิศวกรรมศาสตร์และอุตสาหกรรมวิจัย)** พิธีมอบรางวัลมีขึ้นในวันที่ 2 กุมภาพันธ์ พ.ศ. 2554 โดยมี ฯพณฯ ท่านนายกรัฐมนตรี เป็นผู้มอบรางวัล
รายละเอียดสามารถเยี่ยมชมได้ที่ http://www.kmutt.ac.th/p-prof/Event53_Dec10.html

3.2 กิจกรรมที่เกี่ยวข้องกับการนำผลจากโครงการไปใช้ประโยชน์

3.2.1 ชิ้นงานไม้เทียม (WPC) ถูกนำไปใช้เป็นองค์ประกอบหนึ่งในการสร้างสนามเด็กเล่นในรายการคิดข้ามเมฆ ร่วมกับ บริษัท เชฟรอน (ประเทศไทย) จำกัด ได้ทำโครงการนี้ขึ้น

3.2.2 ทางบริษัท วี พี วู๊ด จำกีด นำผลงานวิจัยจากโครงการ WPC ไปปรับปรุงเอกสารประชาสัมพันธ์ผลิตภัณฑ์ของบริษัทฯ (อยู่ระหว่างดำเนินการ)

3.2.3 ผลงานวิจัยเรื่อง Wood Polymer Composites เผยแพร่ในรายการวิจัยไทยคิด ของ สกว. โดยออกอากาศเมื่อวันที่อาทิตย์ที่ 27 มิถุนายน 2553

3.2.4 ผลงานวิจัยเรื่อง Wood Polymer Composites เผยแพร่ในงานแสดงผลงานวิจัยของโครงการมหาวิทยาลัยวิจัยแห่งชาติ ระหว่างวันที่ 27-28 กรกฎาคม 2554 ณ ศูนย์การค้าแฟชั่นไอร์แลนด์ รามอินทรา กรุงเทพฯ

3.3 การเชื่อมโยงทางวิชาการกับนักวิชาการอื่น ๆ ทั้งในและต่างประเทศ

3.3.1 คณะวิจัยฯ ได้ทำการปรึกษาหารือกับ รศ.ดร. ปราณี ภิญโญชีพ (คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล) ในเรื่องเกี่ยวกับการปฏิบัติการด้านปรับปรุงโครงสร้างของ Liquid Polybutadiene เพื่อให้มี Functional groups ตามต้องการ โดยมีผู้ประสานงานคือ รศ.ดร. ชาคริต สิริสิงห

3.3.2 คณะวิจัยฯ ได้ทำการปรึกษาหารือกับ รศ.ดร. เบญจภรณ์ ตั้งภักดี (คณะสิ่งแวดล้อมและทรัพยากรศาสตร์ มหาวิทยาลัยมหิดล) ในเรื่องเกี่ยวกับการปฏิบัติการด้านการเลี้ยงเชื้อแบคทีเรีย เชื้อราและสาหร่าย ในวัสดุ wood polymer composites โดยมีผู้ประสานงานคือ ศ.ดร. ณรงค์ฤทธิ์ สมบัติสมภพ (ตลอดโครงการ)

3.3.3 คณะวิจัยฯ ได้มีความร่วมมือกับ Professor Dr. Krishnan Jayaraman, Department of Mechanical Engineering, The University of Auckland ประเทศ New Zealand ในการส่งนางสาวกัลทิมา เชาว์ชาญชัยกุล ไปทำวิจัยที่ The University of Auckland เป็นเวลา 6 เดือน

(มกราคม – มิถุนายน 2554) และมีผลงานวิจัยตีพิมพ์ร่วมกันในวารสารวิชาการนานาชาติ BioResources 7(1): 38-55 (2012) [JIF = 1.328] และอยู่ระหว่างวางแผนงานวิจัยในอนาคตร่วมกัน

3.3.4 คณะวิจัยฯ ได้มีความร่วมมือกับ Prof. Dr. rer. nat. Dirk W. Schubert, Department of Polymer Science, Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nürnberg ประเทศ Germany ในการส่ง นายวัลลภ หาญณรงค์ชัย ไปทำวิจัยเป็นเวลา 6 เดือน (สิงหาคม 2554 – มกราคม 2555) ขณะนี้อยู่ระหว่างเขียนบทความวิจัยเพื่อตีพิมพ์ร่วมกันในวารสารวิชาการนานาชาติ และอยู่ระหว่างวางแผนงานวิจัยในอนาคตร่วมกัน

3.4 การได้รับทุนอื่น ๆ จากทั้งในและต่างประเทศ (เช่น คปก.)

3.4.1 ทุนวิจัยของนักศึกษาจากศูนย์ความเป็นเลิศด้านนวัตกรรมทางเคมี PERCH-CIC สำหรับ นายอธิป บุญบำรุง (ภายในการดูแลของ รศ.ดร.ชาคริต สิริสิงห)

3.4.2 ทุนวิจัยจากโครงการ คปก. ปี 2553 สำหรับ นายอภิสิทธิ์ โฆษิตชัยยงค์ นศ. ป.เอก ร่วมกับโครงการเมธีวิจัยอาวุโส สกว. (ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)

3.4.3 ทุนวิจัยคณะพลังงานสิ่งแวดล้อมและวัสดุ มจธ. ปี 2554 สำหรับนายศิริชัย ก้านกิ่ง นศ. ป.โท ร่วมกับโครงการเมธีวิจัยอาวุโส สกว. (ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)

3.4.4 ทุนวิจัยคณะพลังงานสิ่งแวดล้อมและวัสดุ มจธ. ปี 2554 สำหรับนางสาว ปวีณา แตงอุดม นศ. ป.โท ร่วมกับโครงการเมธีวิจัยอาวุโส สกว. (ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)

3.4.5 ทุนวิจัยมหาบัณฑิต สกว. (ด้านวิทยาศาสตร์และเทคโนโลยี) ปี 2553 จำนวน 2 ทุน เป็นทุนวิจัยสำหรับ นางสาว โสมธิดา ลิขิตเลิศ และ นางสาว จันทราพร พรหมฉิม นศ. ป.โท ร่วมกับโครงการเมธีวิจัยอาวุโส สกว. (ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)

3.4.6 ทุนวิจัยมหาบัณฑิต สกว. (ด้านวิทยาศาสตร์และเทคโนโลยี) ปี 2554 จำนวน 1 ทุน เป็นทุนวิจัยสำหรับ นางสาว ปาริชาติ ยศแก้ว ร่วมกับโครงการเมธีวิจัยอาวุโส สกว. (ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)

3.4.7 ทุนวิจัยจากโครงการมหาวิทยาลัยวิจัยแห่งชาติ (NRU) มจธ. ปี 2554-2556

4. การจัดประชุมประจำปีของโครงการฯ

4.1 การจัดประชุมประจำปี ครั้งที่ 1

เมื่อวันศุกร์ที่ 17 กันยายน พ.ศ. 2553 นักวิจัยทุนเมธีวิจัยอาวุโส สกว. ได้จัดการประชุมเสนอผลงานวิชาการ ในการประชุมดังกล่าวถือเป็น**การจัดประชุมประจำปีครั้งที่ 1** เพื่อรายงานความก้าวหน้าผลการวิจัยที่ได้รับการสนับสนุนจากทุนเมธีวิจัยอาวุโส สกว. ประจำปี พ.ศ. 2552 ที่มี ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ เป็นผู้รับทุนดังกล่าว รวมถึงการประเมินผลงานจากผู้ทรงคุณวุฒิในสาขาวิชาที่เกี่ยวข้องอีกด้วย สำหรับกำหนดการประชุมเริ่มตั้งแต่เวลา 9:00-17:00 น. ณ ห้องประชุมปรีดา วิบูลย์สวัสดิ์ อาคารคณะพลังงานสิ่งแวดล้อมและวัสดุ (ชั้น 2) มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี รายชื่อผู้ทรงคุณวุฒิประกอบด้วย **รศ.ดร.วิรัญญา แก้ววัฒนะ** ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ **รศ.ดร.ดวงดาว อาจองค์** ภาควิชาวัสดุศาสตร์ คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย และ **ผศ.ดร.ทิพบรรณ ปะละไทย**

สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี สำหรับหัวข้องานวิจัยที่เสนอในที่ประชุมมีทั้งสิ้น 8 เรื่อง ดังนี้

1. **หัวข้อบรรยายเรื่องที่ 1** "Wear Behavior of Wood/PVC Composites" โดย ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
2. **หัวข้อบรรยายเรื่องที่ 2** "Flexural and Creep Strengthening of Wood/PVC Composite Members using Flat Bar Strips" โดย ผศ.ดร.ทวิช พูลเงิน มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
3. **หัวข้อบรรยายเรื่องที่ 3** "Rubber-filler interaction, cure and viscoelastic properties in black filled nitrile rubber (NBR) compounds modified by functionalized liquid polybutadiene"
   โดย รศ.ดร.ชาคริต สิริสิงห มหาวิทยาลัยมหิดล
4. **หัวข้อบรรยายเรื่องที่ 4** "Use of Hybrid Silica-Based Fillers in Natural Rubber Composites"
   โดย ผศ.เอกชัย วิมลมาลา มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
5. **หัวข้อบรรยายเรื่องที่ 5** "Bioplastics from Blends of Cassava Flour and Rice Flour: Effect of Blend Composition" โดย ผศ.ดร.จันทร์ฉาย ทองปิ่น มหาวิทยาลัยศิลปากร
6. **หัวข้อบรรยายเรื่องที่ 6** "Effect of Molecular Structures of Thermoplastics on Anti-bacterial Performance of Triclosan/Nano-silver Doped in Thermoplastics"
   โดย คุณอภิสิทธิ์ โฆษิตชัยยงค์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
7. **หัวข้อบรรยายเรื่องที่ 7** "Melt strength measurement of co-extrudates" โดย ดร.สมเจตน์ พัชรพันธ์ มหาวิทยาลัยเกษตรศาสตร์
8. **หัวข้อบรรยายเรื่องที่ 8** "A Die Rotating System for Moderations of Extrusion Loads and Pressure Drop Profiles for Molten PP and Wood/PP Composites in Extrusion Processes" โดย ดร.นเรศ อินต๊ะวงค์ มหาวิทยาลัยเทคโนโลยีราชมงคลล้านนา

ภาพบรรยากาศ สามารถเยี่ยมชมได้ที่ http://www.kmutt.ac.th/p-prof/P-PROF%20website

4.2 การจัดประชุมประจำปี ครั้งที่ 2

คณะวิจัยฯ ได้กำหนดให้วันพฤหัสบดีที่ 11 สิงหาคม พ.ศ. 2554 เป็นกำหนดการการจัดการประชุมเสนอผลงานวิชาการในการประชุมทุนเมธีวิจัยอาวุโส สกว. ประจำปี พ.ศ. 2552 ที่มี **ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ** เป็นผู้รับทุน โดยถือเป็นการจัดประชุมประจำปีครั้งที่ 2 เพื่อรายงานความก้าวหน้าผลการวิจัย ที่ได้รับการสนับสนุนจากทุนเมธีวิจัยอาวุโส สกว. โดยครั้งนี้ จัดการประชุมวิชาการประจำปีร่วมกับการจัดประชุมประจำปีครั้งที่ 1 ที่มี **ศ.ดร.รัตนา จิระรัตนานนท์** เป็นนักวิจัยทุนเมธีวิจัยอาวุโส สกว. ผู้รับทุนประจำปี 2553 โดยมีผู้ทรงคุณวุฒิจากสาขาวิชาเทคโนโลยีร่วมกับวิศวกรรมเคมี สำหรับกำหนดการประชุมเริ่มตั้งแต่เวลา 08.30-16:00 น. ณ ห้องประชุมสนั่น สุมิตร ชั้น 9 อาคารสำนักงานอธิการบดี มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี รายชื่อผู้ทรงคุณวุฒิประกอบด้วย **ศ.ดร.สุเมธ ชวเดช** วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย **รศ.ดร.วิรัญญา แก้ววัฒนะ** ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ และ **รศ.ดร.ศราวุธ ริมดุสิต** ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย สำหรับหัวข้องานวิจัยที่เสนอในที่ประชุมมีทั้งสิ้น 12 เรื่อง โดยมีกำหนดการจัดประชุม ดังนี้

การนำเสนอผลงานทุนเมธีวิจัยอาวุโส สกว. ครั้งที่ 2 (ปี 2554)
“การศึกษาหลักการพื้นฐานและการประยุกต์ใช้เทคโนโลยีเมมเบรนในอุตสาหกรรมและสิ่งแวดล้อม”
ร่วมกับ “วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง”
วันที่ 11 สิงหาคม 2554 เวลา 8.30-16.00 น.
ห้องประชุมสนั่น สุมิตร ชั้น 9 อาคารสำนักงานอธิการบดี
มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

8.30 – 9.00 น. ลงทะเบียน

9.00 – 9.15 น. พิธีเปิด **“การนำเสนอผลงานทุนเมธีวิจัยอาวุโส สกว. ประจำปี 2554”**
ประธานในพิธี ศาสตราจารย์ ดร. สมชาย ชูชีพสกุล
ที่ปรึกษาอาวุโสอธิการบดี มจธ.
ผู้กล่าวรายงาน ศาสตราจารย์ ดร.รัตนา จิระรัตนานนท์
หัวหน้าโครงการ “การศึกษาหลักการพื้นฐานและการประยุกต์ใช้เทคโนโลยีเมมเบรนในอุตสาหกรรมและสิ่งแวดล้อม”

9.15 – 9.40 น. Analytical and numerical results of strengthened wood/poly(vinyl chloride) (WPVC) composite members by using flat bar strips
โดย ผศ.ดร.ทวิช พูลเงิน ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มจธ.

9.40 – 10.05 น. Rubber content recovery from skim latex suspension by microfiltration process: the investigation of operating conditions and fouling characteristics
โดย รศ.ดร.พรทิพย์ ศรีแดง ภาควิชาวิทยาศาสตร์สิ่งแวดล้อม คณะวิทยาศาสตร์ มหาวิทยาลัยศิลปากร

10.05 – 10.30 น. Roles and evidence of wood flour as an antibacterial promoter for triclosan-filled poly(lactic acid)
โดย นายชนะ ประพฤกษ์วงศ์ สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มจธ.

10.30 – 10.45 น. พักรับประทานอาหารว่าง

10.45 – 11.10 น. Modification of ultrafiltration membranes by blending and coating with polyvinyl-alcohol (PVA)
โดย นายณัฐพงศ์ เที่ยงตรง ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มจธ.

11.10 – 11.35 น. Rheological properties and melt strength of LDPE during the co-extrusion filament winding process
โดย ดร.สมเจตน์ พัชรพันธ์ ภาควิชาวิศวกรรมวัสดุ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเกษตรศาสตร์

11.35 – 12.00 น. Cascade design of hollow fiber membrane contacting process for CO_2 absorption by MEA

โดย นายสมนึก บริบุตร ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

12.00 – 13.00 น. **พักรับประทานอาหารกลางวัน**

13.00 – 13.25 น. Effect of die rotation mode on rheological properties and swelling behavior of HDPE melt flowing in an annular die in single screw extruder
โดย ดร.นเรศ อินต๊ะวงค์ สาขาวิชาวิศวกรรมอุตสาหการ มหาวิทยาลัยเทคโนโลยีราชมงคลล้านนา

13.25 – 13.50 น. Extractive Fermentation of Ethanol using Vacuum Fractionation Technique
โดย ผศ.ดร.อภิชาติ บุญทาวัน สาขาเทคโนโลยีชีวภาพ สำนักวิชาเทคโนโลยีการเกษตร มหาวิทยาลัยเทคโนโลยีสุรนารี

13.50 – 14.15 น. A development of nitrile rubber-carbon black interaction: Effect on viscoelastic behavior
โดย รศ.ดร.ชาคริต สิริสิงห ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

14.15 – 14.30 น. **พักรับประทานอาหารว่าง**

14.30 – 14.55 น. Trends in research and development of membrane bioreactor (MBR) process for wastewater treatment
โดย ดร.จิรโชติ ภัทรนาวิก บริษัท เอสซีจี เคมิคอลส์ จำกัด

14.55 – 15.20 น. Investigation of friction and wear behavior of natural rubber filled with silica hybrid fillers
โดย ดร.ศิรินทร ทองแสง ภาควิชาวิศวกรรมเครื่องมือและวัสดุ
คณะวิศวกรรมศาสตร์ มจธ.

15.20 – 15.45 น. Fouling Effect of Nanofiltration Membrane by Combined Carbonate Species and Natural Organic Matter (NOM)
โดย นายชฤพนธ์ เจริญสุข ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยอุบลราชธานี

15.45 – 16.00 น. กล่าวปิดโดย ศาสตราจารย์ ดร. ณรงค์ฤทธิ์ สมบัติสมภพ
หัวหน้าโครงการ "วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง"

ภาพบรรยากาศ สามารถเยี่ยมชมได้ที่ http://www.kmutt.ac.th/p-prof/P-PROF%20website_thai%20version/Activity/2554/August/15_Aug_54/Event54_Aug15.html

4.3 การจัดประชุมประจำปี ครั้งที่ 3 (ปิดโครงการวิจัย)

เมื่อวันจันทร์ที่ 30 กรกฎาคม พ.ศ. 2555 กำหนดให้มีการจัดการประชุมเสนอผลงานวิชาการในการประชุมทุนเมธีวิจัยอาวุโส สกว. ประจำปี พ.ศ. 2552 ที่มี **ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ** เป็นหัวหน้าโครงการผู้รับทุน โดยถือเป็นการจัดประชุม ครั้งที่ 3 (ปิดโครงการวิจัย) การจัดประชุมสัมมนาทางวิชาการเพื่อเป็นการเผยแพร่ผลงานวิจัยในโครงการที่ได้รับการสนับสนุนจากทุนเมธีวิจัยอาวุโส สกว. นำเสนอใน

รูปแบบการบรรยายออกสู่สาธารณะ โดยครั้งนี้ มีจัดการประชุมวิชาการประจำปีร่วมกับการจัดประชุมรายงานความก้าวหน้าผลการวิจัยประจำปีครั้งที่ 2 ที่มี **ศ.ดร.รัตนา จิระรัตนานนท์** เป็นนักวิจัยทุนเมธีวิจัยอาวุโส สกว. ผู้รับทุนประจำปี 2553 โดยมีผู้ทรงคุณวุฒิจากสาขาวิชาเทคโนโลยีร่วมกับวิศวกรรมเคมี สำหรับกำหนดการประชุมเริ่มตั้งแต่เวลา 08.30-16:00 น. ณ ห้องประชุมสนั่น สุมิตร ชั้น 9 อาคารสำนักงานอธิการบดี มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี รายชื่อผู้ทรงคุณวุฒิประกอบด้วย **ศ.ดร.สุเมธ ชวเดช** วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย **รศ.ดร.อิทธิพล แจ้งชัด** ภาควิชาเคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง และ **รศ.ดร.ศราวุธ ริมดุสิต** ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย สำหรับหัวข้องานวิจัยที่เสนอในที่ประชุมมีทั้งสิ้น 11 เรื่อง โดยมีกำหนดการจัดประชุม ดังนี้

การประชุมวิชาการโครงการทุนเมธีวิจัยอาวุโส สกว. ประจำปี 2555 (ครั้งที่ 3)
โครงการ "วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง"
และ "การศึกษาหลักการพื้นฐานและการประยุกต์ใช้เทคโนโลยีเมมเบรนในอุตสาหกรรมและสิ่งแวดล้อม"
วันที่ 30 กรกฎาคม 2555 เวลา 8.30-16.00 น.
ณ ห้องประชุมสนั่น สุมิตร ชั้น 9 อาคารสำนักงานอธิการบดี
มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

8.30 – 9.00 น.	ลงทะเบียน	
9.00 – 9.15 น.	พิธีเปิด "ประชุมวิชาการโครงการทุนเมธีวิจัยอาวุโส สกว. ประจำปี 2555"	
	ประธานเปิดการประชุม	ดร.พัฒนะ รักความสุข คณบดี คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
	ผู้กล่าวรายงาน	ศาสตราจารย์ ดร.ณรงค์ฤทธิ์ สมบัติสมภพ หัวหน้าโครงการ "วัสดุลูกผสมและการพัฒนากระบวนการผลิตสำหรับวัสดุเชิงประกอบพลาสติกและยาง"
9.15 – 9.40 น.	นำเสนอภาพรวมของงานวิจัยและสรุปผลงานทั้งหมด โดย ศาสตราจารย์ ดร.ณรงค์ฤทธิ์ สมบัติสมภพ	
9.40 – 10.05 น.	A novel surface modification of PVDF hollow fiber membrane to enhance hydrophobicity using organosilanes โดย นายเสริมพงศ์ สายเรียม สาขาวิชาการจัดการสิ่งแวดล้อม จุฬาลงกรณ์มหาวิทยาลัย	
10.05 – 10.30 น.	Investigation on the influence of wood on anti-algal performance of wood/poly(vinyl chloride) composites โดย นายอภิสิทธิ์ โฆษิตชัยยงค์ สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี	
10.30 – 10.45 น.	**พักรับประทานอาหารว่าง**	

10.45 – 11.10 น.	Simultaneous absorption of CO_2 and H_2S from biogas by capillary membrane contactor โดย นายสมนึก บริบุตร จากภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
11.10 – 11.35 น.	Use of bagasse fiber ash as secondary filler in silica or carbon black filled natural rubber compound โดย ผศ. เอกชัย วิมลมาลา และ นายศิริชัย ก้านกิ่ง สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
11.35 – 12.00 น.	Extractive fermentation of bio-ethanol from concentrated sweet sorghum juice using vacuum fractionation technique โดย ผศ.ดร. อภิชาติ บุญทาวัน สาขาเทคโนโลยีชีวภาพ สำนักวิชาเทคโนโลยีการเกษตร มหาวิทยาลัยเทคโนโลยีสุรนารี
12.00 – 13.00 น.	**พักรับประทานอาหารกลางวัน**
13.00 – 13.25 น.	Assessment and characterization of anti-fungal and anti-algal performances for biocide-enhanced linear low-density polyethylene โดย นายอัฐพงษ์ กิตติ์ชัยวัชร์ สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
13.25 – 13.50 น.	Concentration of skim latex suspension by microfiltration process: fouling characteristics and latex properties โดย นางสาวนฤมล ทองมาก สาขาวิศวกรรมสิ่งแวดล้อม คณะวิศวกรรมศาสตร์ มหาวิทยาลัยสงขลานครินทร์
13.50 – 14.15 น.	Shear flow and elongational flow properties of peroxide modified wood/LDPE composite melts โดย นายวัลลภ หาญณรงค์ชัย สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
14.15 – 14.30 น.	พักรับประทานอาหารว่าง
14.30 – 14.55 น.	The effect of pH on nanofiltration by combined carbonate species and natural organic matter โดย รศ.ดร. สุพัฒน์พงษ์ มัตราช ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยอุบลราชธานี
14.55 – 15.20 น.	Experimental and computational investigations on creep behavior of strengthened wood/PVC composite members โดย ผศ.ดร.ทวิช พูลเงิน ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

15.20 – 15.45 น. Surface modification of PVDF membrane by bilayer coating with chitosan and poly (vinyl alcohol) for reducing protein fouling
โดย ผศ.ดร. อำไพ ชนะไชย ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

15.45 – 16.00 น. กล่าวปิดโดย ศาสตราจารย์ ดร.รัตนา จิระรัตนานนท์
หัวหน้าโครงการ “การศึกษาหลักการพื้นฐานและการประยุกต์ใช้เทคโนโลยีเมมเบรนในอุตสาหกรรมและสิ่งแวดล้อม”

ภาพบรรยากาศ สามารถเยี่ยมชมได้ที่ http://www.kmutt.ac.th/p-prof/P-PROF%20website_thai%20version/Activity/2555/August/1_Aug/Event55_Aug1.html

(ศ.ดร.ณรงค์ฤทธิ์ สมบัติสมภพ)
หัวหน้าโครงการวิจัยฯ
31 สิงหาคม 2555

Effect of UV weathering on mechanical and anti-bacterial performances for peroxide-cured silicone rubber with HPQM

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Keywords:	Silicone rubber, Crosslink density, Anti-microbial activity, UV effect

Effect of UV weathering on mechanical and antibacterial performances for peroxide-cured silicone rubber with HPQM

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Abstract

2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQM) was used as biocide in silicone rubber compound. Antibacterial and mechanical performances of silicone rubber compound were assessed before and after exposure to UV light at different times. Drop-plate and halo tests were employed to qualitatively and quantitatively evaluate the antibacterial performance of silicone rubber compound against *Escherichia coli* (*E.coli*, ATCC 25922) and *Staphylococcus aureus* (*S.aureus*, ATCC 25923). The results suggested that the cure characteristics, and physical and mechanical properties for the HPQM added silicone rubber compound were strongly affected by the UV light. The tensile properties and hardness increased with UV aging. The lightness (L^*) for the silicone rubber compound without HPQM did not change with UV light, whereas that for the silicone with HPQM decreased with UV light. The longer the contact time the better the killing ability of the bacteria. Experiencing the initial UV aging of 3 days, the rubber compound with HPQM showed an effective killing ability of bacteria. However, under prolonged UV exposure, the antibacterial efficacy reduced as a result of HPQM removal from the rubber surface during the condensation stage, and a post-curing reaction of the residual peroxide in the rubber compound. The silicone rubber compound with HPQM under UV light had more preference for killing the *E.coli*.

Key words: Silicone rubber, Crosslink density, Anti-microbial activities, UV weathering aging

Introduction

Silicone rubber is excellent for oil resistance, thermal stability, oxidation resistance, and biocompatibility due to strong silicon-oxygen (Si-O) and carbon-carbon (C-C) bonds. As a result, it is often used in food packaging, and medical house-ware applications (children's toys, computer keyboards, phone keypad, ear plugs, ear phones and watch) which are likely to contact with the human body. Therefore, antimicrobial performance of the silicone rubber appears to be very important in order to prevent infection of harmful microorganism. Microorganisms are usually referred to as bacteria, algae and fungi that are commonly found in the ground, water, air, and in other living organisms. For example, the infection of *Escherichia coli (E.coli)* can result in food poisoning problem.[1-2] Most species of bacteria can be grouped into two categories based on their membrane structure and their responses to a laboratory technique, these being referred to as gram-positive and gram-negative bacteria.[3-4]

One of the most common techniques to achieve antibacterial properties in materials is to incorporate an antibacterial agent into the material. Antibacterial agents are, in general, divided into 2 types that are inorganic and organic agents. The inorganic antibacterial agents are used for hundreds of years in human history, such as, ammonium salts, metal salt solutions, antibiotics and nano silver particle, whereas the organic antibacterial agents are most widely used such as alcohol solution applications. Such antibacterial agent can kill both gram-positive and gram-negative bacteria by attacking cell walls, destroying bacteria metabolisms and interacting with functional DNA inside Prokaryotic cell of bacteria.[5] One good thing is that these bacterial agents do not have an effect on the human body.[6-7]

Available studies in the literature [8-10] have used a wide range of antibacterial agents in polymers, both thermoplastics and rubbers, for achieving the antibacterial performances which led to some value-added polymers. The antibacterial agents used including nano-Ag colloids, silver substituted Zeolite compound (SSZ) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQM). In terms of silicone rubber compound, work by Taptim and Sombatsompop [8] clearly suggested that HPQM was the most effective antibacterial agent when comparing with nano-silver colloids and SSZ agents due to its organic structure and chemical compatibility with the silicone. This statement contradicted with the work of Kaali et al [11] who found that addition of Ag+ loaded zeolite in silicone rubber improved the anti-microbial performance of the silicone which was caused by the formation of OH bond occurring due to moisture contact with Ag+ loaded zeolite.

It is essential to know of how long the added antibacterial agent could be effective in polymers, specifically in silicone rubber compound. The question has been approached by a number of studies under the effects of aging under a wide range of conditions [12-14]. Work by Oldfield and Symes [12] studied long-term natural aging in hot-wet and hot-dry environments using different silicone elastomers. A satisfactory durability for prolonged antibacterial performance was found at room temperature aging. Gorur et al [13] studied the effect of outdoor aging on physical and chemical changes in silicone rubber, and observed some permanent changes, which included a depletion of low molecule weight polymer change on surface, de-polymerization, surface roughness, increased surface crystallization. The damaging and degradation mechanisms, resulting in deteriorations in mechanical properties of silicone rubber, via proton radiation were suggested by Zhang et al [14] and Belhaneche-Bensemra [15], Benavides et al [16].

This present work was an extending part of ongoing investigations into mechanical and anti-microbial properties for silicone rubber compound cured by peroxide [8]. This present study focused on the effects of HPQM loading and UV aging time on the antibacterial and mechanical performance changes. The contact time between the bacteria used and the HPQM was also varied from 30 to 210 mins. The main highlight of this work was to propose possible causes and explanations for the changes in antibacterial and mechanical performances of silicone rubber vulcanizates after experiencing UV light at different aging times from 1 to 21 days. The results were explained quantitatively by independent experimental evidences, such as contact angle and post-curing measurements (peroxide loading effect).

Experimental

Materials and Chemicals

The rubber used in this study was silicone rubber (KE-951-U), which was supplied by Shin-Etsu Chemical Co., Ltd., (Japan). The curing agent, 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane (designated as TRigonox®101-45s-ps) was supplied by Akzo Noble Polymer Chemicals Ltd., (Shanghai, China). The antibacterial agent was 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (designated as HPQM), that was supplied by Micro Science Tech Co., Ltd, (South Korea). The HPQM was supplied in liquid form which had a pH value of 12. *Escherichia coli* (*E.coli*, ATCC 25922) and *Staphylococcus aureus* (*S.aureus*, ATCC 25923) were used as testing bacteria.

Sample preparation

In order to produce silicone rubber vulcanizates, 100 phr silicone rubber were added with required contents (0.5, 1.0 or 1.5 phr) of 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane and then mixed on a two roll mill (Yong Fong Machinary Co., Ltd., Thailand). The silicone rubber was first masticated for 5 minutes, and then compounded with peroxide and HPQM for a further 10 minutes before being cured using a hydraulic hot press (LAB TECH Co., Ltd., Bangkok, Thailand) at a 90% cure, using a curing pressure of 170 kg/cm^2 with 165°C curing temperature in order to produce vulcanized silicone rubber compound. After that, the silicone rubber vulcanizates were placed in UV weathering machine (Q-Panel Lab Products Co., Ltd., USA) which followed ASTM G 154 (2006) whose conditions were UVA 0.77 W/m^2/nm 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.

Cure characteristics and crosslink density

Cure time and delta torque (differences in maximum and minimum torques) of the silicone rubber compounds were assessed using an Oscillating Disk Rheometer (Model ODR GT 7070-S2, GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 165°C. After that, the vulcanized silicone rubber sample was cut into 2 cm width × 2 cm length before being immersed into toluene and the crosslink density was calculated using Flory-Rehner equation as expressed by **Equation 1** [17]

$$v = \frac{-[\ln(1-v_2)+v_2+\chi v_2^2]}{2V_1(v_0^{2/3}v_2^{1/3}-v_2/2)} \qquad \text{(Eqn. 1)}$$

where v is the moles of crosslinks per unit volume of polymer, v_2 is the volume fraction of polymer in the swollen sample, V_1 is the molar volume of the solvent and v_0 is the volume fraction of polymer at the time of crosslinking. The v_0 term is used to correct for material that is extracted by the solvent. χ is the rubber-solvent interaction parameter (0.499 in this case).

Mechanical properties

Tensile modulus at 200% elongation, tensile strength and elongation at break were of our interests for mechanical property evaluations, following the ASTM methods (ASTM D 412-92(1998)) using dumbbell-shaped samples and a universal testing machine (Auto-graph AG-I, Shimadzu, Tokyo, Japan). A hardness durometer (Shore A) Model 475, PTC instruments, (MA, USA) was used for hardness evaluation in accordance with ASTM D 2240-03 (2003). All reported data were averaged from at least five independent experiments.

Antibacterial performance

The anti-microbial performance for the silicone rubber compounds were examined quantitatively and qualitatively through Drop-plate and Halo test methods, respectively. *Escherichia coli* (*E.coli*, ATCC 25922) and *Staphylococcus aureus* (*S.aureus*, ATCC 25923) were used as testing bacteria. Both of bacteria were first incubated in nutrient broth for 24 h at 37 ^{o}C prior to use.

- *Halo test*: The test was commenced by mixing the nutrient agar and the nutrient broth (1:1 in ratio) and incubated testing bacterial solution (OD_{600} = 0.1). The mixture was then poured into sterilized Petri dishes. The silicone rubber samples of 6 mm in diameter were gently placed over the solidified agar. After that, Petri dishes were incubated at 37 ^{o}C for 24 h for inhibition zone measurement.
- *Drop-plate-method:* The method followed ASTM E 2149 (2001). That was, 5 mL of incubated bacteria were diluted with 45 mL of peptone water in a flask. The silicone rubber sample of 5×5 cm in dimensions was dropped into the flask. The flask was then shaken by 30, 90, 150 and 210 minutes. Dilution factors of n4 and n5 were considered depending on the preferred number of initial bacteria colony (which should range from 3 to 30 colonies when n is a dilution factor). 10 µL of the solution was dropped on agar into sterilized Petri dishes incubated at 37 ^{o}C for 24 h. The results were reported in terms of viable cell count of the bacteria

Discoloration testing

UV-Vis Spectrophotometer Model UV-3100, Shimadzu Co., Ltd. (Japan) was utilized to monitor color changes of silicone rubber samples with the addition of HPQM agent through the CIELAB color system. Values of $L^*a^*b^*$ coordinates of silicone rubber specimens were considered based on a D65 light source. L^* represents the lightness whereas a^* and b^* are the chromaticity coordinates. In this work, only lightness (L^*) change of the silicone rubber with various HPQM loadings and UV aging times were of our interests. The higher the L^* value the lighter the rubber sample. All reported experimental data were averaged from at least five independent determinations.

Measurement of water contact angle

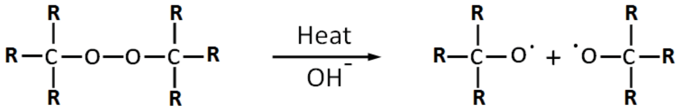
Contact angle measurements indicate quantitaive changes in sensitivities of material surface properties which are usually referred to as roughness and chemistry modifications. In this work, the contact angle of deionized water on silicone rubber surfaces was assessed by a drop method using a Contact Angle Goniometer (Model 100-00 from Ramé-hart Instrument Co., Ltd, New Jersey, USA). The wettability was evaluated comparing between neat silicone rubber and silicone rubber added with HPQM agent with and without experiencing the UV light. The results were given by microscopic images and the contact angle values for advancing stages of drops for 5 times/100 μL droplets with three independent samples.

Results and Discussion

Cure characteristics, and physical & mechanical properties

Table 1 shows the effect of HPQM loading on cure time, delta torque, torque maximum, torque minimum and crosslink density (before and after UV light of 21 days), for the silicone rubber vulcanizates using the peroxide content of 0.5 phr. It can be seen that the addition of HPQM had an impact on the vulcanizing reaction, which was evidenced by significant changes in 90% cure time and delta torque. The addition of HPQM at 15 phr increased the cure time from 2:20 to 3:18 min:sec, and decreased the delta torque from 53.08 to 47.79 dN/m. The decreases in the delta torque probably involved a plasticization effect occurring. During the compounding process, the silicone rubber became softened while blending with the HPQM. This was also evidenced by the decreases in minimum torque with HPQM content. When considering the crosslink density results in **Table 1**, it can be seen that the crosslink density of the neat silicone vulcanizates before and after UV ageing were not different as compared with those for the HPQM added silicone vulcanizates. The reason was because the peroxide left in the neat silicone vulcanizates was unlikely to generate free radicals at low temperature (at 60°c in the UV weathering machine), and thus the post-curing effect was insignificant. However, in the case of the HPQM added silicone vulcanizates, the post-curing effect appeared to be apparent due to that the HPQM could induce the free radicals generation of the peroxide added. The work by Su et al [18] suggested that the addition of peroxide in basic condition (OH^-) would result in generation of free radicals to induce crosslinking process whose chemical reaction is given in **Equation 2**. In relation to this work, the silicone rubber with HPQM would be more likely to encounter a post-curing effect under UV aging as compared with the rubber without HPQM. This was because the HPQM could promote the basicity in the compound, and then generate the free radicals from the peroxide. This was why the increase in crosslink density of the silicone rubber with

HPQM was observed after 21 days of UV light. This clearly suggests that HPQM play an important role on the changes in material properties after UV aging rather than the silicone rubber itself. It may also be related to the pH of HPQM which was experimentally measured to be 12.



$$R_3C{-}O{-}O{-}CR_3 \xrightarrow[OH^-]{Heat} R_3C{-}O^{\cdot} + {}^{\cdot}O{-}CR_3$$

(Eqn. 2)

Figure 1 shows the results of ultimate tensile strength and elongation at break for the silicone rubber vulcanizates at different loadings of HPQM before and after UV aging at 21 days. It was found that HPQM loading had no effect on the changes in ultimate tensile strength and elongation at break. On the contrary, UV light at 21 days exhibited a significant effect by improving the tensile properties, especially the elongation at break. The increased tensile properties may be caused by the increase in crosslink density as mentioned in **Table 1**. **Figure 2** shows tensile modulus at 200% elongation and hardness for the silicone rubber vulcanizates at different loadings of HPQM agent before and after UV aging at 21 days. It can be seen that the tensile modulus at 200% elongation and the hardness of the silicone rubber vulcanizates increased with UV light because of the increase in crosslink density as previously discussed. In summary, the results suggested that the UV light improved the tensile and hardness properties.

The physical appearances of the silicone rubber compounds were considered by lightness (*L**). The color changes for silicone rubber vulcanizates before and after UV aging for 21 days are shown in **Table 2**. It was clearly observed that the lightness (*L**) for the silicone rubber without HPQM did not change with UV light, whereas that for the silicone with HPQM decreased with UV light. In general, silicone rubber has relatively excellent resistance to UV light [19]. The decrease in the lightness by the HPQM addition may be caused by a degradation of HPQM on the rubber surface under UV aging.

Antibacterial performance

Figures 3a and 3b show the results of inhibition zone from halo test for silicone rubber vulcanizates incorporated with a fixed HPQM of 15 phr at various UV aging times of 0, 3, 5, 7, 14 and 21 days against *E. coli* and *S. aureus* bacteria, respectively. For comparison purposes, a filter paper doped with $CuSO_4$ (positive control, C^+) and a blank filter paper (negative control, C^-) were employed. It was observed that without UV light (0 days), a large inhibition zone was apparent, but as the aging time was increased the inhibition zone decreased noticeably, suggesting that the UV light worsened the ability of the HPQM to bacteria killing. The inhibition zone seemed to disappear when the UV aging times after 7 and 1 days for *E. coli* and *S. aureus* bacteria, respectively. This indicates that the UV aging had a prolonged effect on the killing of *E. coli*. This may be expected since the peptidoglycan thickness of *E. coli* is far thinner than that of *S. aureus* structure, and this would then be much easier for HPQM to penetrate into the cell to kill the *E.coli*. [20] The quantitative results for antibacterial performances of silicone rubber vulcanizates added with different loadings of the HPQM are given in **Figure 4,** the results being assessed as a function of aging time and contact time. The results suggested that the cell counts for *E. coli* appeared to decrease with increasing contact time, but this was not the case for *S. aureus*. This re-stressed the above statement that the *E.coli* was more sensitive to the HPQM and UV effect than the *S. aureus*. With presence of HPQM, the cell counts of *E. coli* and *S. aureus* bacteria were much lower. This indicates that the bacteria's killing has occurred for the silicone rubber vulcanizates with

HPQM without UV. It was interesting to note that the viable cell counts decreased at the initial stage of UV exposure of 3-5 days and then started to increase, but still lower than the rubbers without aging. This observation from the drop-plate test corresponded to that from the halo test in **Figure 3**. No bacteria's killing was observed under UV exposure for *S.aureus*. The cell count for *E.coli* after UV aging was lower than that for *S. aureus.* The reason was based on the thinner peptidoglycan thickness of *E. coli* structure as compared with that of *S. aureus* structure. [20]

The experimental results in **Figures 3 and 4** clearly indicate that the antibacterial activities of silicone rubber vulcanizates with HPQM loading significantly reduced with increasing UV aging time. Therefore, it is very essential to introduce the causes for this observation. In this work, two possible reasons were proposed; (i) HPQM removal on the rubber surface and (ii) post-curing effect as a result of residual peroxide in the rubber samples.

- The first reason could be experimentally proven by considering the contact angle on the silicone surface. **Table 3** shows the contact angle values for the silicone rubber vulcanizates without and with HPQM loading of 15 phr, before and after UV aging at 21 days. It was found that the contact angle values for the silicone rubbers with HPQM significantly decreased from 111.8°±2.3 to 67.2°±5.3, indicating more hydrophilic structure of the HPQM/silicone compound since HPQM is a hydrophilic structure whereas the silicone is hydrophobic in nature [21]. Therefore, the contact angle reduction in this case may imply a migration of the HPQM to kill the bacteria on the silicone rubber surface. This explains why the antibacterial efficacy of the silicone rubber was improved with the HPQM. However, when experiencing the UV light at 21 days, the contact angle value appeared to increase from 67.2°±5.3 to 96.9°±4.1, but still lower than the neat silicone rubber (111.8°±2.8).This was because that UV-conditioning of the silicone rubber had removed the HPQM resided on the silicone rubber surfaces, probably occurring during the condensation stage at 60 °C for 8 h. This explains why the antibacterial efficacy decreased with increasing UV aging.

- The second explanation for the antibacterial efficacy reduction by UV aging was associated with the post-curing reaction. In order to substantiate this claim, an additional and independent experiment was carried out by producing silicone rubber vulcanizates with different crosslink densities. This was achieved by varying the peroxide loadings (TRigonox®101-45s-ps) from 0.5 to 1.5 phr, and the antibacterial performance (via both halo and drop plate tests) was re-evaluated against *E.coli* and *S.aureus.* The results are given in **Figures 5 and 6** for inhibition zone and viable cell count tests, respectively. **Table 4** shows the cure characteristics of the silicone rubber vulcanizates incorporated with 10 phr of HPQM for different peroxide loadings. It was anticipated that the delta torque and crosslink density increased as a direct function of peroxide loading. The results in **Figure 5** shows that the inhibition zone apparently decreased with increasing peroxide content, confirming that the higher the crosslink density the lower the antibacterial performance. This claim was re-confirmed by a slight increase in viable cell count with increasing peroxide content especially at the contact times of 150 and 210 min, as illustrated in **Figure 6**. Again, as expected, the viable cell counts for *S.aureus* were higher than those for *E.coli* for any given peroxide contents and contact times. In relation to the results in **Figures 3 and 4**, it was suggested that increasing the crosslink density in the silicone rubber made it more difficult for the HPQM to transfer onto the silicone surface to kill the bacteria. **Figure 7** shows a model of HPQM transfer from the inside of silicone rubber sample to the surface to kill the bacteria with (left) low peroxide content or crosslink density, and (right) high peroxide content or crosslink density, the right sample being the case for the cured silicone sample under the prolonged UV light.

In summary, it was suggested that HPQM incorporated silicone rubber compounds exhibited effective antibacterial performance with mechanical property improvement at the initial stage of UV exposure. Under prolonged UV light, the efficacy of the antibacterial properties appeared to diminish as a result of HPQM removal during condensation and post curing effect.

Conclusions

The experimental results in this work suggested that the UV light had a greater effect on cure characteristics, and physical and mechanical properties for the HPQM added silicone rubber compounds as compared to the neat silicone rubber compound. The tensile properties and hardness were found to improve with UV aging. The lightness (L^*) for the silicone rubber was affected by HPQM addition, and decreased with UV light. The antibacterial performance was improved by HPQM loading and by increasing contact time. The silicone rubber with HPQM under UV light had ability to kill the *E.coli* in the initial stage, and the *E.coli* killing efficacy became diminished under prolonged UV aging of longer than 3 days. The rubber compound with HPQM under UV aging showed a better killing efficacy for the *E.coli* as compared with that for the *S. aureus*. The antibacterial performance reduction was caused by HPQM removal from the silicone rubber surface during the condensation stage of the UV exposure, and a post-curing reaction of the peroxide-cured silicone rubber compound.

Acknowledgments

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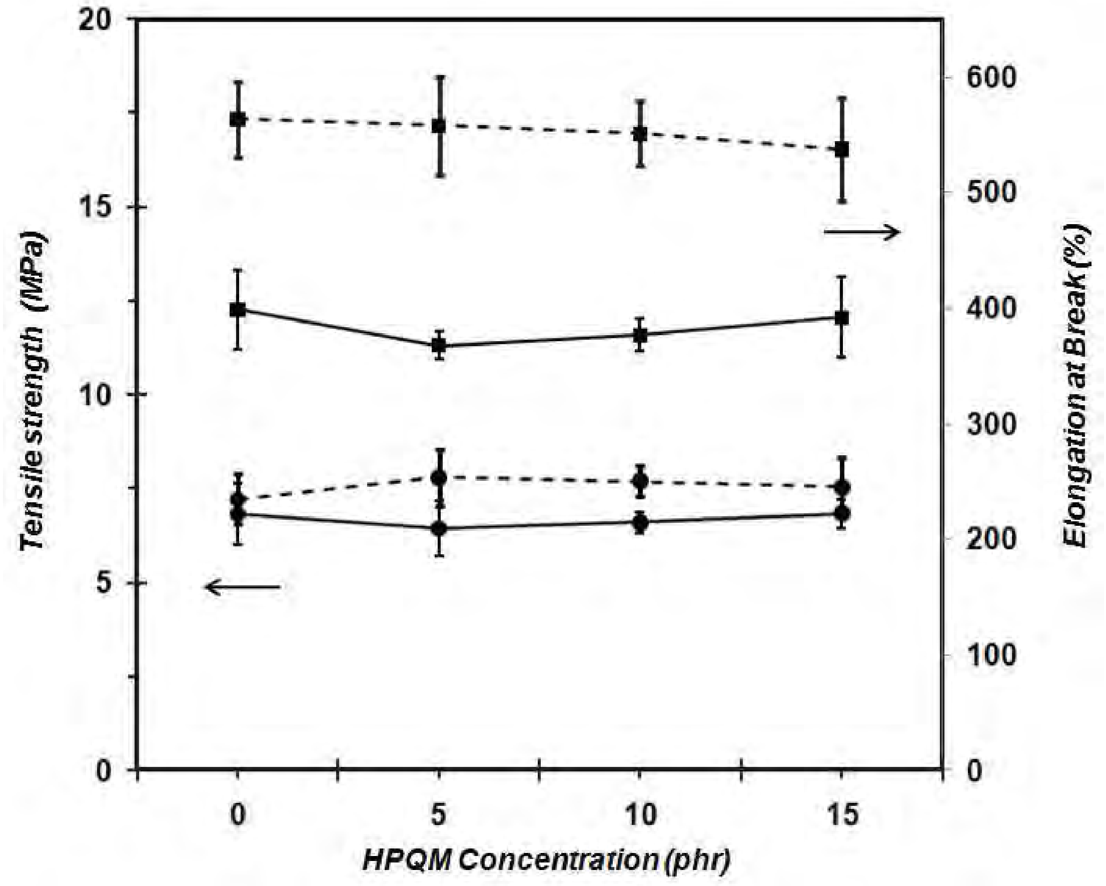


Figure 1 Tensile strength and elongation at break for silicone rubber vulcanizates filled with HPQM before (solid line) and after (dashed line) UV aging of 21 days

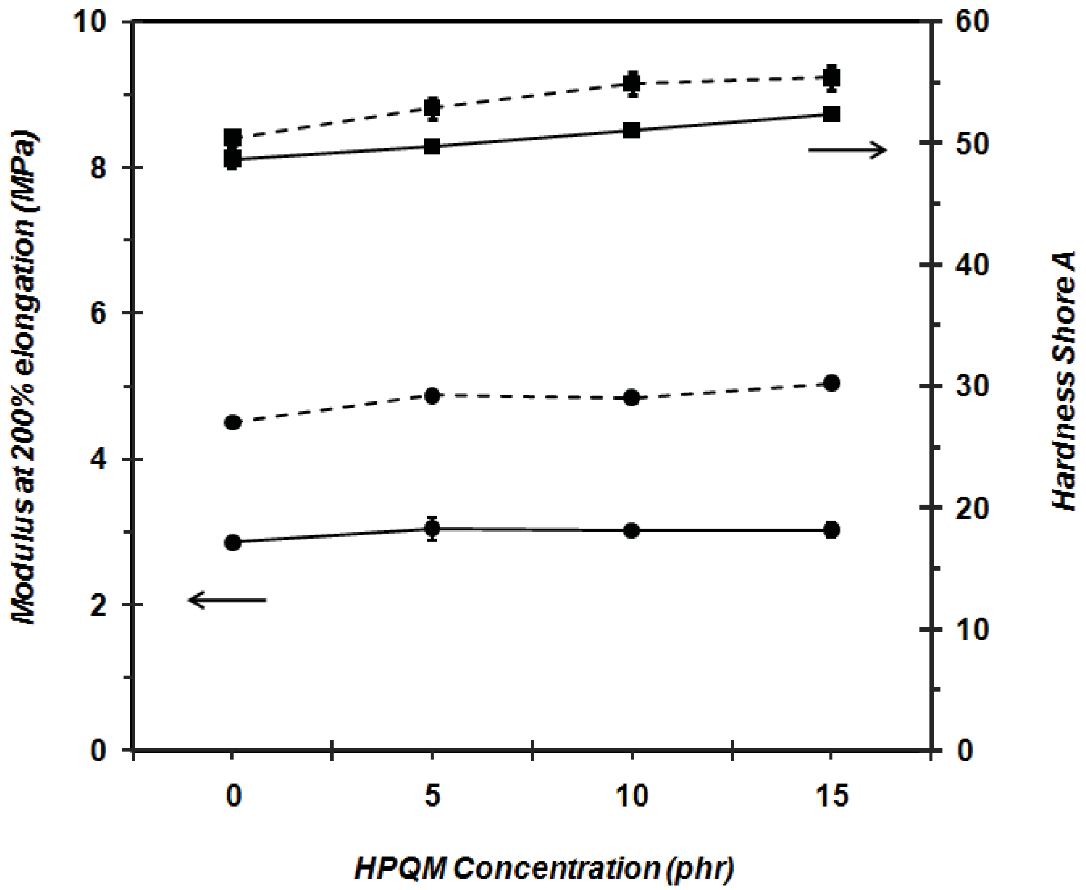
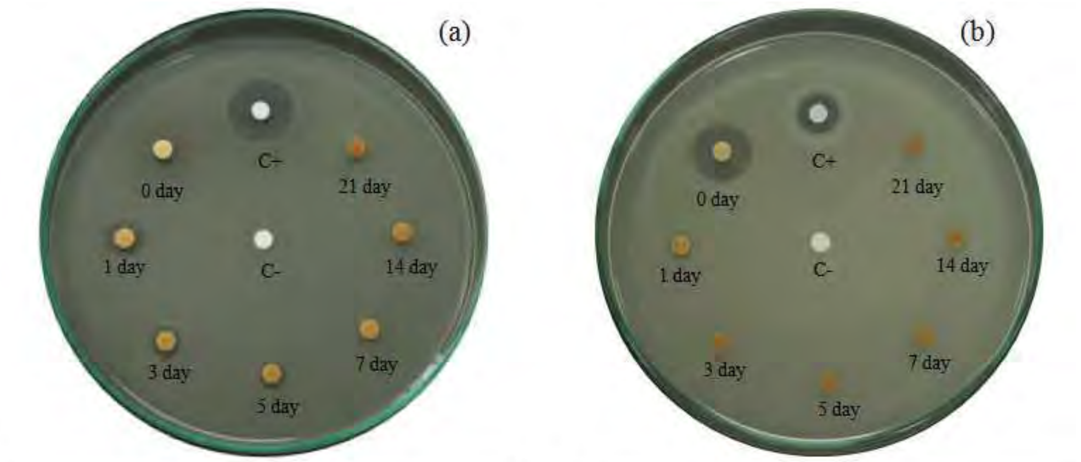


Figure 2 Tensile modulus at 200% elongation and hardness for silicone rubber vulcanizates filled with HPQM before (solid line) and after (dashed line) UV aging of 21 days



UV aging (day)	0	1	3	5	7	14	21
Clear Zone radius (mm)	9.15	4.45	2.55	1.60	1.25	0	0

UV aging (day)	0	1	3	5	7	14	21
Clear Zone radius (mm)	7.75	1.25	0	0	0	0	0

Figure 3 Effect of UV aging time on clear zone for silicone rubber vulcanizates with HPQM of 15 phr for various UV aging times for (a) *E.coli*, and (b) *S. aureus*

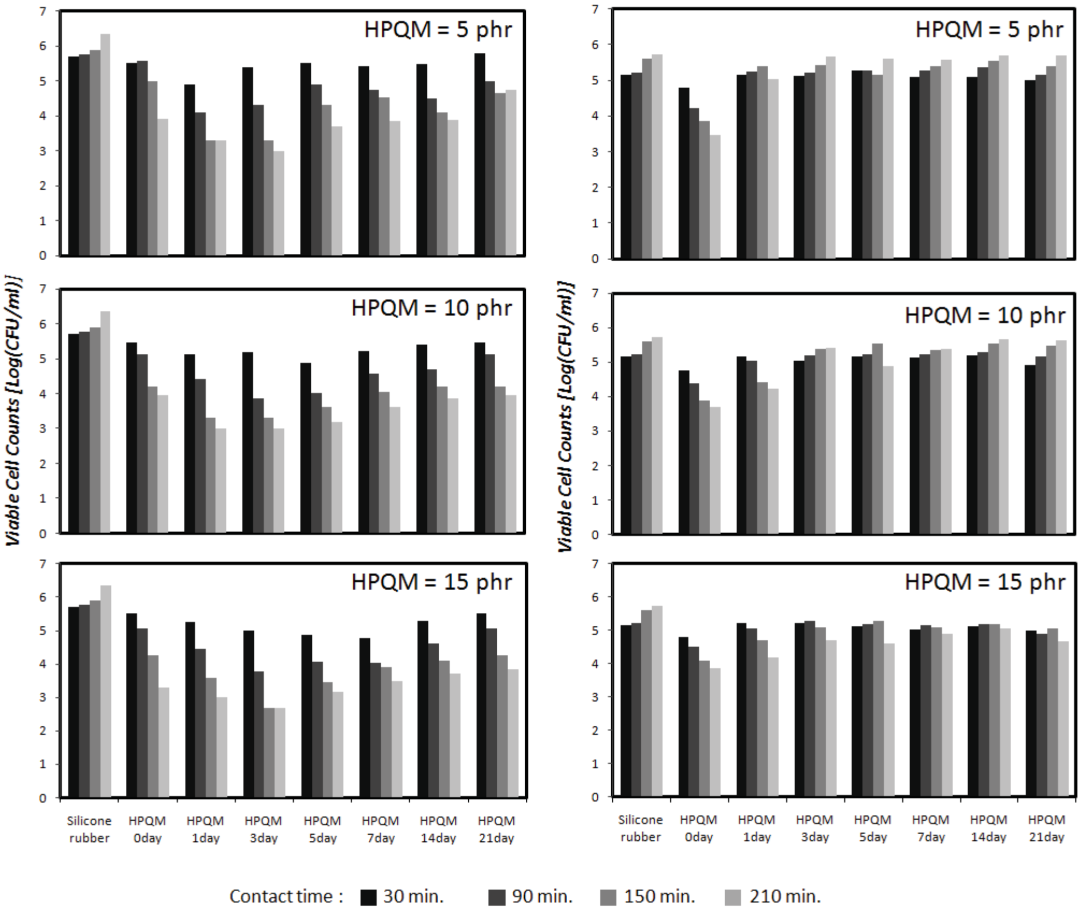


Figure 4 Viable cell count for *E. coli* (left) *and S. aureus* (right) colonies for HPQM loading at 5, 10 and 15 phr

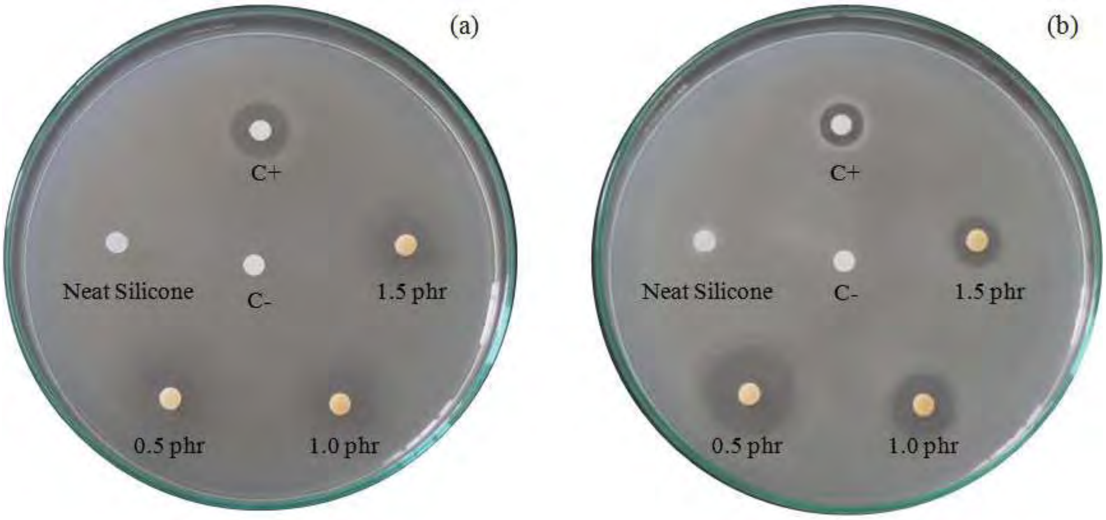


Figure 5 Effect of peroxide loading on clear zone for silicone rubber vulcanizates with HPQM of 10 phr for various UV aging times for (a) *E.coli*, and (b) *S. aureus*

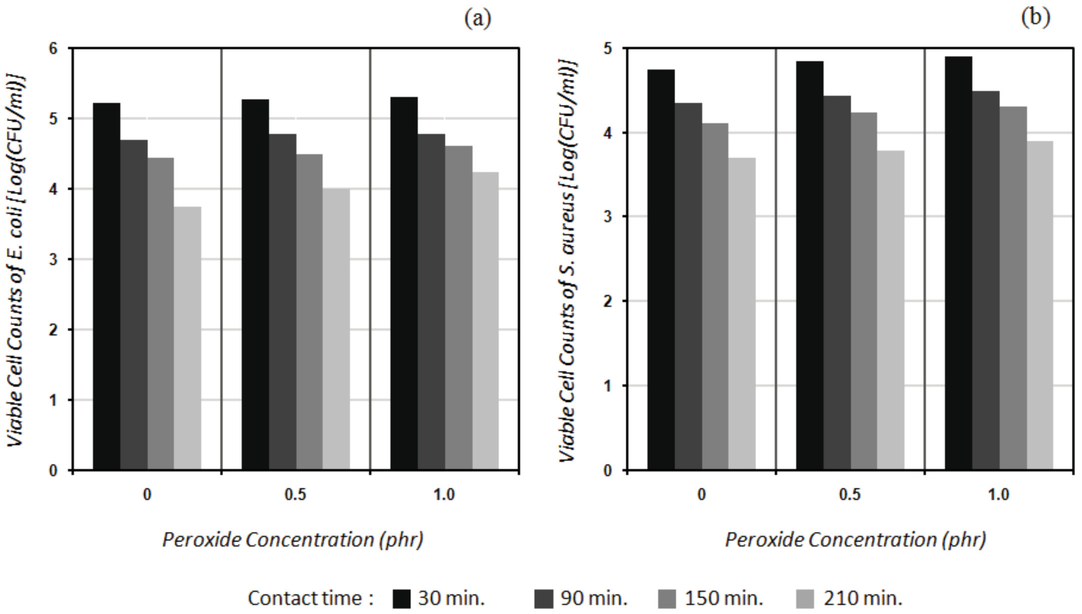


Figure 6 Viable cell count for *E. coli* (a) and *S. aureus* (b) colonies as a function of peroxide loading at 0.5, 1.0 and 1.5 phr

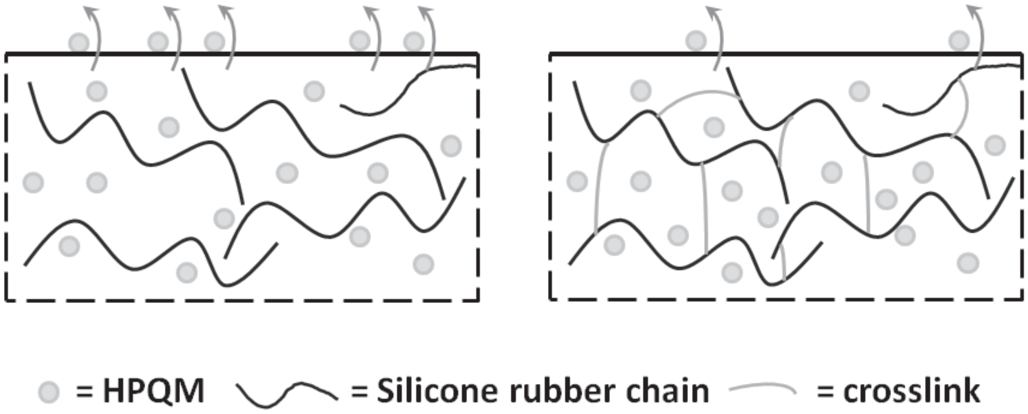
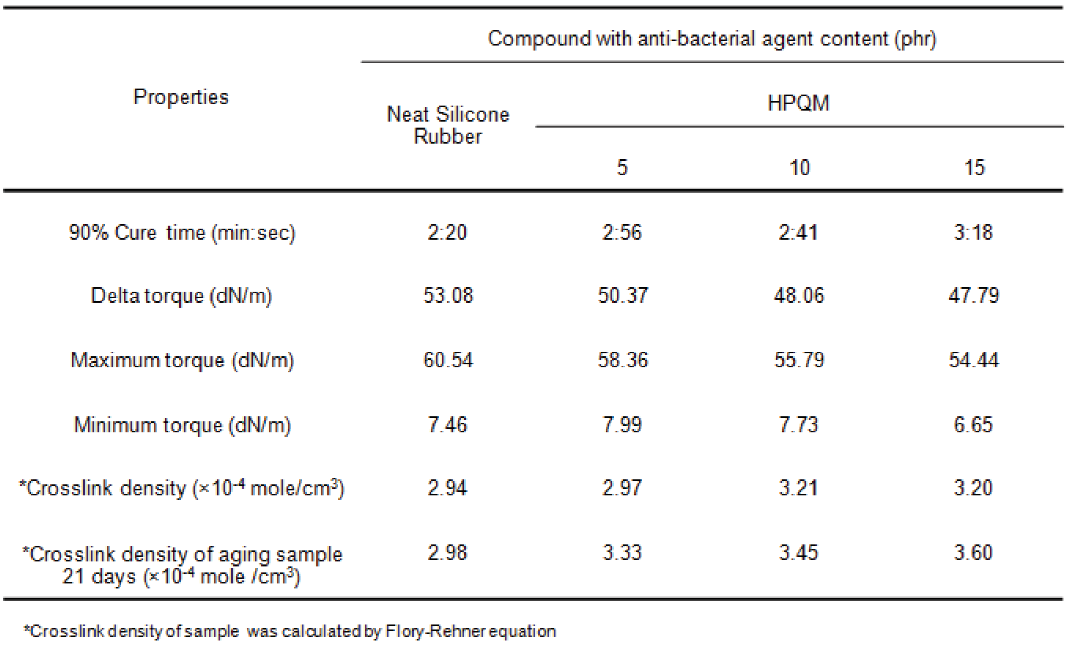


Figure 7 Releasing model of HPQM particles from silicone rubber various peroxide contents

Table 1 Cure time, delta torque, maximum torque, minimum torque and crosslink density for silicone rubber vulcanizates with various HPQM loadings



Properties	Compound with anti-bacterial agent content (phr)			
	Neat Silicone Rubber	HPQM		
		5	10	15
90% Cure time (min:sec)	2:20	2:56	2:41	3:18
Delta torque (dN/m)	53.08	50.37	48.06	47.79
Maximum torque (dN/m)	60.54	58.36	55.79	54.44
Minimum torque (dN/m)	7.46	7.99	7.73	6.65
*Crosslink density (×10^{-4} mole/cm^3)	2.94	2.97	3.21	3.20
*Crosslink density of aging sample 21 days (×10^{-4} mole /cm^3)	2.98	3.33	3.45	3.60

*Crosslink density of sample was calculated by Flory-Rehner equation

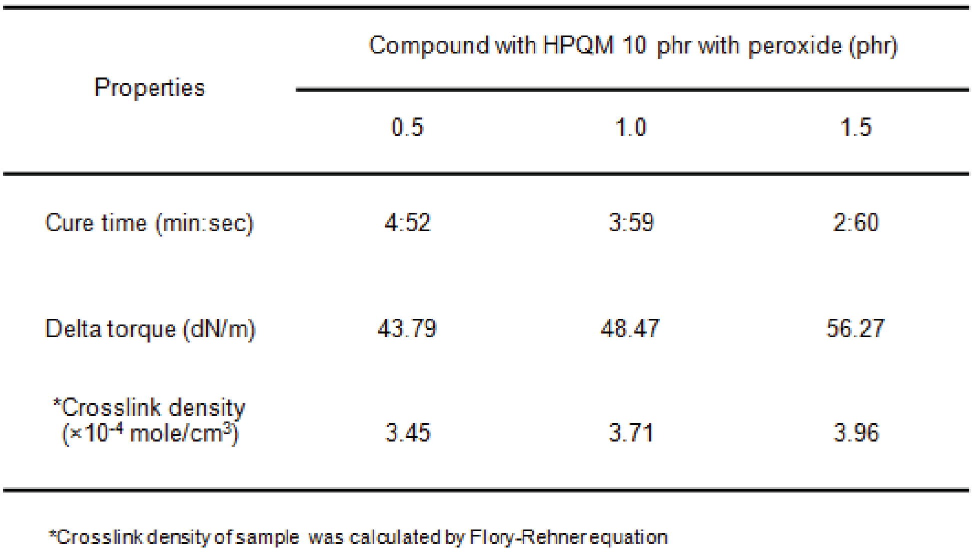
Table 2 Lightness changes for silicone rubber vulcanizates with HPQM loadings and UV aging times

Compound		Lightness (L*)						
		Non aging	UV Aging (day)					
			1	3	5	7	14	21
Neat Silicone Rubber		46.66	46. 94	47.54	47.86	48.17	48.23	48.80
Silicone Rubber with HPQM	content (phr) 5	54.25	53.32	51.14	50.70	48.39	47.90	45.42
	10	65.61	57.47	54.21	53.03	49.88	48.72	45.37
	15	66.73	57.62	53.00	49.95	47.82	47.65	43.10

Table 3 Contact angle values for silicone rubbers filled with HPQM at 15 phr with and without UV aging

	Compound	Contact angle value (°)	Wettability form
Non aging	Neat Silicone Rubber	111.8 ± 2.8	
	Silicone Rubber with HPQM	67.2 ± 5.3	
Aging 21 days	Neat Silicone Rubber	111.9 ± 2.3	
	Silicone Rubber with HPQM	96.9 ± 4.1	

Table 4 Cure time, delta torque and crosslink density for silicone rubber vulcanizates with different peroxide loadings



Properties	Compound with HPQM 10 phr with peroxide (phr)		
	0.5	1.0	1.5
Cure time (min:sec)	4:52	3:59	2:60
Delta torque (dN/m)	43.79	48.47	56.27
*Crosslink density ($\times 10^{-4}$ mole/cm^3)	3.45	3.71	3.96

*Crosslink density of sample was calculated by Flory-Rehner equation

Enhancement of Rubber–Carbon Black Interaction by Amine-Based Modifiers and Their Effect on Viscoelastic and Mechanical Properties

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ABSTRACT: Improvement in rubber–filler interaction is desirable for rubber technologists due to its influence on numerous properties of rubber compounds and vulcanizates. In practice, there are coupling agents commercially available for the improvement of silica–rubber interaction. Surprisingly, only a limited number of works have been focused on interaction enhancement between carbon black (CB) and rubber. Thus, in the research presented in this article, attempts to improve interaction between ethylene–propylene rubber (EPM) and carbon black (CB) have been made by the use of either *p*-phenylene diamine (*p*-PDA) or *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS) as an interaction modifier. Bound rubber content (BRC), used as an indicator for rubber–filler interaction and viscoelastic behavior of CB masterbatches and CB-filled EPM compounds were investigated and correlated. Results from the measurement of BRC in the CB masterbatches revealed that *p*-PDA was more effective in the enhancement of rubber–CB interaction than TBBS. Such improved interaction led to a decrease in magnitude of CB percolation (Payne effect). In respect of viscoelastic behavior, the interaction modifiers affected G' only in the small strain region (<1% strain) by slightly raising the value of G'. However, as strain was increased ($\geq$1%), G' for all compounds was coincident implying a disruption of weak interaction between CB and rubber. In the case of EPM vulcanizates, *p*-PDA yielded greater enhancement in mechanical properties than TBBS. The results of BRC, viscoelastic behavior, and mechanical properties were apparently in good agreement. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 126: E315–E321, 2012

Key words: rubber–filler interaction; carbon black; bound rubber; viscoelastic behavior; EPM

INTRODUCTION

Dynamic mechanical properties of rubber are known to be important in numerous engineering products including tires and vibration isolators. To achieve good dynamic properties with low hysteresis, a high-elastic contribution is required and viscoelastic effects had to be minimized.[1] Practically, the reinforcing fillers particularly carbon black (CB) and precipitated silica (PSi) are incorporated into rubber to enhance mechanical properties of the vulcanizates. However, with poor rubber–filler interaction, molecular slippage of the rubber molecules can take place at the filler surfaces leading to a viscous contribution and thus to heat build-up (HBU).[2] Fortunately, in PSi–filled systems, enhancement of rubber–PSi interaction is practically achieved by the use of a silane coupling agent (SCA). Typically, the SCA is composed of two functionally active end groups, i.e., the readily hydrolysable alkoxy group for reacting chemically with the silanol groups on silica surfaces and the organo-functional group for being compatible with rubbers. By this means, the strong chemical linkages between silica and rubber are developed, resulting in a decrease in molecular slippage at the silica surfaces. For CB, its surface reactivity comes mainly from the oxygen-contained functional groups including ketone, aldehyde, and hydroxyl, which provide interaction between CB and the rubber matrix.[3] In general, the interaction between CB and rubber takes place through Van der Waals forces, which are weaker than the covalent bonds found in silane-treated silica systems. Molecular slippage of rubber molecules at CB surfaces can therefore easily take place, especially at high strains. The energy dissipation process occurring from such slippage leads to the development of heat under cyclic deformation,

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which is undesirable. This is usually termed heat build-up (HBU). Attempts to improve interaction between CB and rubber have been carried out using various approaches such as modification of CB surface[4] or rubber matrix[5] and synthesis of coupling agent.[6,7] Some published work has reported that CB dispersion can be enhanced by grafting polymers onto CB surfaces via polycondensation reaction to produce functionalized CB.[8–13] In addition, it has been shown that the CB surface oxidation by oxygen plasma or oxidizing agents to generate the oxygen-containing functional groups on CB surfaces promotes their reactivity.[14] However, these techniques are not yet practical due to the complication in treatment conditions and therefore the solid-state modification of CB surfaces or *in situ* method has gained interest recently. For example, CB modification based on the radicals generated from the rubber matrix as a result of mechanical force has been reported.[15–17] In addition, some amine-based reagents, including *p*-aminobenzenesulfonyl azide and dinitrosodiamine, have been found to provide CB–rubber interaction enhancement via a coupling reaction.[6,18] Thus, the aim of the research described in this article is to improve interaction between ethylene–propylene rubber and carbon black by the use of maleic anhydride grafted liquid polybutadiene (Ricon 130MA8) in association with either *p*-phenylene diamine (*p*-PDA) or *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS). It is anticipated that the rubber–carbon black interaction to be developed in the present work is the result of interactions among amine groups of *p*-PDA or TBBS, active functional group on carbon black surfaces (e.g., lactone, aldehyde, and carboxyl groups), maleic anhydride (MA) groups of Ricon130MA8 and an EPM matrix. Bound rubber content (BRC, as an indication of rubber–filler interaction) and viscoelastic behavior of rubber compounds were investigated and correlated.

EXPERIMENTAL

Materials

All mixing ingredients were used as-received. Ethylene–propylene rubber (EPM, Keltan 520 with 60% ethylene content) was supplied by DSM elastomers Asia, The East Asiatic (Thailand), Thailand. The N330 carbon black was manufactured from Thai Carbon Products, Thailand. Functionalized liquid polybutadiene (Ricon 130MA8) was purchased from Chemical Innovation, Thailand. As claimed by the manufacturer, there is 8% maleic anhydride adducted, 20–35% 1, 2 vinyl content and 3,100 g/mol number-average molecular weight. The *N-tert*-butyl-2-benzothiazole sulfenamide (Santocure-TBBS) was purchased from Reliance Technochem (Flexsys), Thailand. The *p*-phenylene diamine (*p*-PDA) was purchased from Sigma-Aldrich, India. Dicumyl peroxide 40% dispersed in kaolin (Luperox DC40KE) was received from Akema, India. Chemical structures of Ricon130MA8, *p*-PDA, and TBBS are shown in Figure 1.

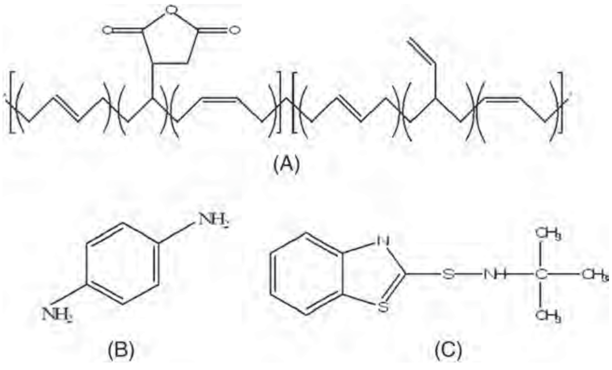

Figure 1 Chemical structures of: (a) Ricon130MA8, (b) *p*-PDA, and (c) TBBS.

Compound preparation

The preparation procedure of EPM compounds was carried out using a two-stage mixing process and compound formulations are illustrated in Table I. Mixing was performed using a laboratory-scale internal mixer (Brabender Plasticorder, Germany) at a rotor speed, set temperature and fill factor of 40 rpm, 140°C and 0.7, respectively. In the first stage, 100 phr CB was mixed with pre-masticated EPM for 4 min followed by the addition of 50 phr Ricon 130MA8. The mixing was continued for 5 min and then various constituents, ranging from 0 to 0.20 phr, of either *p*-PDA or TBBS were added and mixed further until 15 min of mixing time had elapsed. The mix was discharged from the mixing chamber and denoted as "*CB masterbatch (CB-M/B).*" In the second stage of mixing, the CB-M/B was diluted with raw EPM to achieve final CB loading of 45 phr. The mixing was performed at a mixing temperature of 60°C for 2 min. Finally, Luperox DC40KE was added into the compound 3 min prior to being discharged. The mix was then sheeted on a two-roll mill (Collin W100T, Germany) and denoted as "*EPM compound.*" It had to be noted that during the experiment, a wide range of *p*-PDA loadings were used, but the maximum loading of *p*-PDA to be used in this work was 0.2 phr. The EPM compounds with higher *p*-PDA loadings above 0.2 phr were carried out, but found to have encountered cure suppression phenomenon, which was caused by the excessive amine group acting as a radical scavenger during the peroxide vulcanization process.[19]

Testing of rubber compounds

The determination of BRC was based on the dissolution technique. The preweighed rubber compounds

TABLE I
Compound Formulations

Materials	Loading (phr)
Carbon black masterbatches (CB-M/B)	
EPM (Keltan 520)	100
CB N330	100
Ricon 130MA8	50
p-PDA	0–0.20
TBBS	0–0.20
EPM compounds	
EPM (Keltan 520)	55
CB-M/B	112.5
Luperox DC40KE	5

were immersed in toluene, an appropriate solvent for EPM, to dissolve the unbound rubber. The dissolution was carried out at the temperature of 85°C for 1 day. The insoluble part was then filtered and dried overnight at 70°C prior to weighing. Thereafter, the rubber content in the insoluble part was measured using a thermogravimetric analyzer (TGA, Mettler SDTA851) over a temperature range of 40–600°C at a heating rate of 20°C/min. The value of BRC was calculated using eq. (1).[20]

$$\mathrm{BRC}(\%) = \frac{W_d - F}{R} \times 100 \qquad (1)$$

where W_d was the weight of the dried gel.

F was the weight of the filler in the gel (same as weight of the filler in the original sample) and R was the weight of the polymer in the original sample.

Viscoelastic behavior of compounds was monitored by the use of an oscillatory rheometer, namely, Rubber Process Analyzer (RPA2000, Alpha Technology). Strain and frequency sweep tests were conducted by varying strain from 0.5 to 1000% at a test frequency of 10 rad/s and by varying frequency from 0.1 to 100 rad/s at a given strain of 1% (within the linear viscoelastic region), respectively. The dynamic storage moduli (G') as functions of strain and angular frequency at 100°C were then recorded. The difference in storage moduli at low and high strains ($\Delta G'$), termed the "Payne effect," is used to represent the degree of filler–filler interaction.[21]

Cure characteristics were determined using a moving die rheometer (TechPro RheoTech MD+) at 160°C. The torque difference (M_H–M_L) was used to represent the crosslink density of the vulcanizates.[22]

Mechanical properties of rubber vulcanizates measured in this work include hardness and tensile properties, and dynamic loss. The tensile test was conducted using a universal testing machine (Instron model 5566, USA). Tensile strength, elongation at break, and modulus at 100% strain (M_{100}) were determined as per ASTM D412. The hardness was determined according to ASTM D2240 using a Wallace Shore A durometer (Wallace Cogenix, UK).

RESULTS AND DISCUSSION

Bound rubber content

Typically, the degree of interaction between filler and rubber could be quantified by a measure of BRC.[20,23] Higher BRC implies the greater interaction between rubber (i.e., EPM in this case) and CB. Figure 2 reveals that, with increasing *p*-PDA based modifier, BRC of the CB-M/B tends to increase continuously. The results imply that the development of rubber–CB interaction could be enhanced by the addition of *p*-PDA. Probably, the amine groups of *p*-PDA could act as connections between maleic anhydride (MA) group of Ricon130MA8 and the functional groups (e.g., lactone, carboxylic, or hydroxyl groups) on the carbon black surface. Since the number of active groups on a CB surface is reported to be relatively small (e.g., 1–2% active oxygen in furnace blacks),[24] the magnitude of a BRC increment is not very high. Unlike *p*-PDA, TBBS does not appear to significantly alter BRC. The greater rubber–filler enhancement efficiency of *p*-PDA might be caused by the relatively low magnitude of steric hindrance leading to the relatively high opportunity for amine groups to react with active sites on CB surfaces (e.g., lactone, aldehyde, and carboxyl groups) and MA groups of Ricon 130MA8.

Figure 3 represents the BRC results of the EPM compounds prepared by diluting the modified CB-M/B with virgin EPM. It is evident that, at any given modifier loading, BRC of the EPM compounds is slightly higher than that of the CB-M/B. Such additional interaction found in the EPM compounds might be attributed to the free radicals generated during the mixing process. Also, the interaction developed from such radicals in a large EPM matrix might govern the total magnitude of bound rubber formation in the EPM compounds. It is evident that

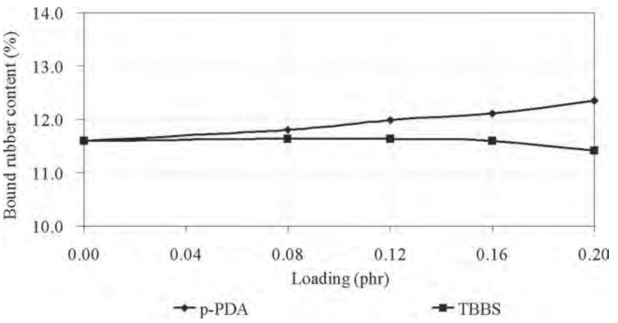

Figure 2 Bound rubber content (BRC) of carbon black masterbatches (CB-M/B) modified with various loadings of *p*-PDA and TBBS.

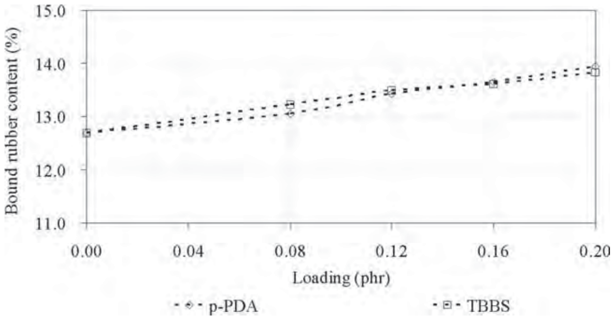

Figure 3 Bound rubber content (BRC) of EPM compounds modified with various loadings of *p*-PDA and TBBS.

the BRC of the EPM compounds increases progressively with increasing loading of the modifiers, regardless of modifier type.

Viscoelastic behavior

Figures 4(a) and 4(b) show viscoelastic behavior of the CB-M/B modified with various loadings of *p*-PDA and TBBS, respectively. It is evident that there is no torque rise with time indicating no sign of crosslink development by the incorporation of *p*-PDA or TBBS into the CB-M/B. In other words, the increase in BRC by the use of interaction modifier as reported previously appears not to be caused by the scorch phenomenon of the CB-M/B. However, it could be that the thermal degradation gives rise to the misleading torque results observed. To clarify this point, the modification process temperature was reduced from 140 to 60°C, so that the thermal degradation effect could be minimized. According to the Arrhenius concept, the systems with no thermal degradation should demonstrate relatively high bulk viscosity due to the minimal magnitude of thermal degradation. As shown in Figure 5, the system prepared at the high temperature of 140°C still revealed higher torque than that at 60°C, supporting the development of rubber–filler interaction at high temperature.

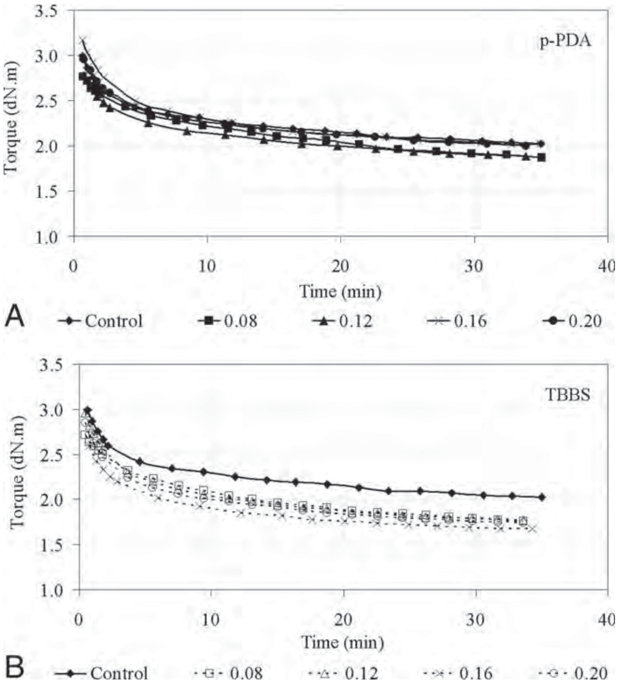

Figure 4 Viscoelastic behavior of carbon black masterbatches (CB-M/B) modified with various loadings of: (a) *p*-PDA and (b) TBBS.

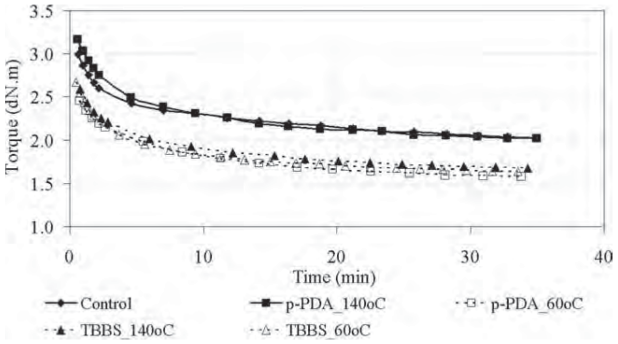

Figure 5 Viscoelastic behavior of carbon black masterbatches (CB-M/B) modified with 0.16 phr of *p*-PDA and TBBS prepared at 140 and 60°C.

Figure 6 exhibits the results of strain-dependent modulus ($\Delta G'$) which is an indication of the Payne effect of the CB-M/B modified with different modifiers. As reported elsewhere, the decrease in magnitude of $\Delta G'$ is used as an implication of reduction in filler–filler interaction and thus CB percolation. Such $\Delta G'$ reduction would then lead to an improvement in filler dispersion degree.[21,25] Thus, as evidenced from Figure 6, both modifiers gave decreasing in $\Delta G'$ of the CB-M/B implying the enhancement in the degree of filler dispersion. The magnitude of $\Delta G'$ tended to decrease with increasing modifier loading and approached the minimum at 0.12 and 0.16 phr of *p*-PDA and TBBS, respectively. The results imply

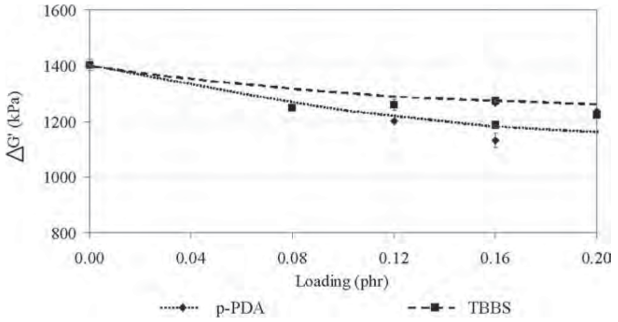

Figure 6 Magnitude of the Payne effect of carbon black masterbatches (CB-M/B) influenced by either *p*-PDA or TBBS.

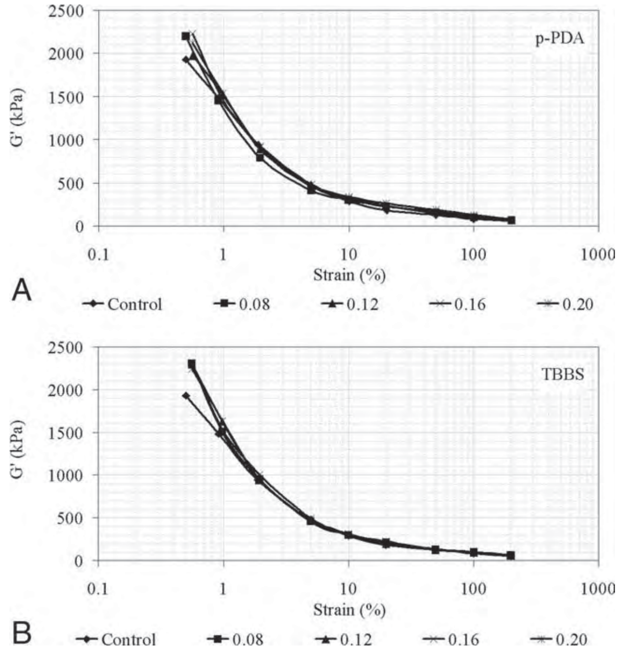

Figure 7 Strain sweep test results of the EPM compounds with various loadings of (a) *p*-PDA or (b) TBBS as interaction modifier.

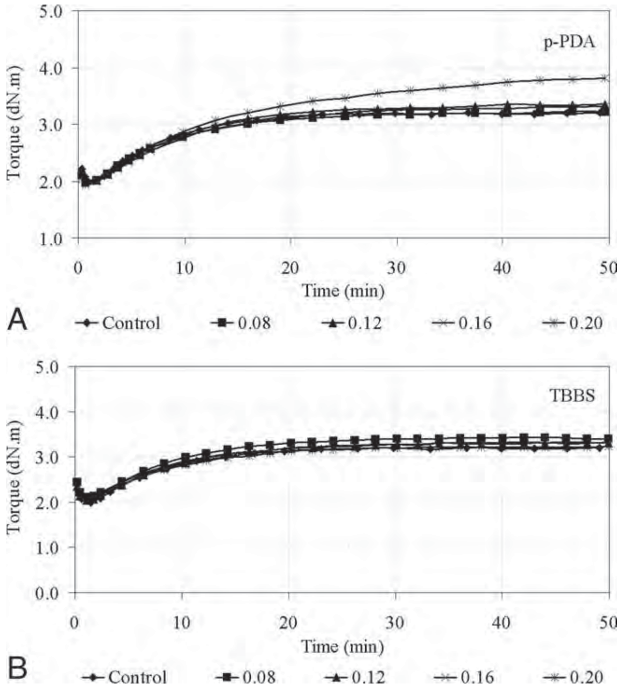

Figure 8 Cure behavior of EPM compounds modified with various loadings of: (a) *p*-PDA and (b) TBBS.

that the presence of *p*-PDA or TBBS in the carbon black-filled EPM could enhance the degree of CB dispersion to some extent. However, in the case of the EPM compounds where the modified CB-M/B was diluted by raw EPM, it is evident from Figure 7 that only a slight increase in G′ was observed, specifically in the small strain region (<1%). Beyond this point, G' for all compounds is coincident. The drop in G' at high strain is probably caused by the disruption of filler network and/or filler–rubber interaction.[26,27] The similarity in G' results of the EPM compounds regardless of modifier type is in good agreement with the BRC results as shown previously in Figure 3.

Figure 8 illustrates cure behavior of the EPM compounds with various contents of *p*-PDA or TBBS as interaction modifiers. It appears that no significant change in cure behavior was observed in the presence of *p*-PDA and TBBS. An exception was found in the cure curve of the compound having 0.2 phr of *p*-PDA as a modifier, in which the torque rise is greater than the others. In fact, at high loading of *p*-PDA, larger amounts of amine groups are available to react with MA group in Ricon130MA8. It is widely accepted that the MA group is a very reactive group which could react rapidly with peroxide[28,29] and thus the presence of MA in rubber molecule could retard the peroxide vulcanization. At 0.2 phr of *p*-PDA, it is thought that all of the MA groups in Ricon130MA8 might fully be reacted with amine groups. More free radicals from peroxide were therefore available for crosslink reaction particularly in the Ricon130MA8 phase leading to greater state-of-cure. At low loadings of *p*-PDA, some MA groups were still available in the Ricon130MA8 resulting in a relatively low degree of crosslink density in the Ricon130MA8 phase. The cure curve characteristics were thus mainly controlled by the crosslink of the EPM phase. No significant change in cure curve characteristics was therefore observed. A similar explanation is also applied to the TBBS. As TBBS has only one groups of amine per molecule, it is believed that 0.2 phr of TBBS was not enough to fully remove the MA groups in Ricon130MA8 phase. No significant difference in cure curve was therefore observed.

To support the proposed explanation of cure behavior affected by interaction modifiers, the cure characteristics of the following systems were

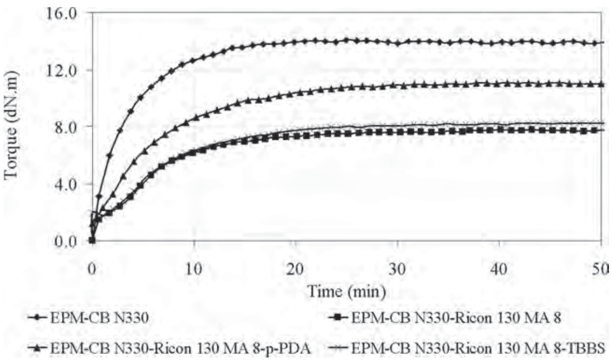

Figure 9 Cure behavior affected by interaction modifiers.

TABLE II
Comparison of Mechanical Properties of EPM Vulcanizates with Various Loadings of *p*-PDA or TBBS as Interaction Modifiers

	Loading (phr)	TS (MPa)	EB (%)	M_{100} (MPa)	Hardness (Sh A)
Control	0.00	3.73 ± 0.64	342.5 ± 12.9	1.64 ± 0.01	62.1 ± 1.0
p-PDA	0.08	5.36 ± 0.27	411.9 ± 15.5	1.61 ± 0.02	61.6 ± 0.4
	0.12	4.99 ± 0.05	372.3 ± 8.8	1.71 ± 0.02	62.8 ± 0.5
	0.16	6.31 ± 0.14	429.1 ± 11.7	1.63 ± 0.01	63.1 ± 0.7
	0.20	7.17 ± 0.09	429.0 ± 10.9	1.73 ± 0.01	65.2 ± 0.7
TBBS	0.08	4.99 ± 0.47	380.7 ± 12.7	1.61 ± 0.01	63.6 ± 0.9
	0.12	5.00 ± 0.44	380.5 ± 19.7	1.57 ± 0.01	62.3 ± 0.5
	0.16	5.04 ± 0.15	393.6 ± 9.7	1.57 ± 0.02	62.3 ± 0.7
	0.20	4.88 ± 0.20	403.9 ± 10.0	1.48 ± 0.03	62.7 ± 1.3

measured: System (I) containing EPM with unmodified CB; System (II) having EPM with CB and Ricon130MA8; System (III) containing EPM with CB, Ricon130MA8 and *p*-PDA; System (IV) having EPM with CB, Ricon130MA8, and TBBS. As illustrated in Figure 9, the System (I) as a control system exhibited the highest state-of-cure. By the presence of Ricon130MA8, the state-of-cure observed in System (II) reduced drastically, implying the cure retardation phenomenon of EPM matrix by the Ricon130MA8. The incorporation of *p*-PDA could reduce the magnitude of the cure retardation phenomenon (see System III). Unlike *p*-PDA, the TBBS does not appear to have given any significant change in magnitude of cure retardation. All results agreed very well with the cure behavior as discussed previously in Figure 8.

Mechanical properties of EPM vulcanizate

Table II depicts the mechanical properties of the EPM vulcanizates modified with various types and loadings of interaction modifiers. It is evident that all mechanical properties, especially tensile strength and elongation at break, increased significantly with increasing *p*-PDA content. Since the addition of *p*-PDA up to 0.16 phr caused no significant change in crosslink density (as evidenced from the cure curve characteristics), it could be summarized that the enhancement in mechanical properties found in the system with *p*-PDA was mainly the result of improvements in rubber–filler interaction and degree of filler dispersion rather than the increased crosslink density. However, the greatest improvement in the mechanical properties found at 0.2 phr of *p*-PDA may have arose from the combined effects of the enhanced filler dispersion, the improved rubber–filler interaction and the increased crosslink density, particularly the co-crosslink between Ricon130MA8 and EPM phases. Unlike *p*-PDA, the presence of TBBS gave a significant improvement in elongation at break in association with a slight enhancement in tensile strength. As TBBS had no significant effect on crosslink density, the improvement in tensile strength might be attributed to the improved filler dispersion and the enhancement of rubber–filler interaction. Surprisingly, the modulus of the vulcanizate was found to reduce with increasing TBBS content. The reduction of modulus is thought to be the consequence of improved filler dispersion which dominates the small improvement of rubber–filler interaction found when TBBS is used as a modifier.

CONCLUSION

The attempt to develop interaction between ethylene-propylene rubber (EPM) and carbon black (CB) as reinforcing filler was conducted by the use of either *p*-PDA or TBBS as interaction modifiers.

Results of the CB-M/B suggest that BRC as an indication of rubber–CB interaction was increased with increasing loading of the interaction modifiers, especially *p*-PDA. Magnitude of the Payne effect decreased with the increased loading of *p*-PDA which was in line with the BRC data. The enhancements in mechanical properties particularly tensile strength and elongation at break of EPM vulcanizates modified with *p*-PDA were observed. Compared with *p*-PDA, TBBS has a lesser effect on the mechanical properties of the vulcanizates. Such enhancements were mainly governed by the improved interaction between CB and the EPM matrix.

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Cure Behavior and Antimicrobial Performance of Sulfur-Cured NR Vulcanizates Containing 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate or Silver Substituted Zeolite

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Cure Behavior and Antimicrobial Performance of Sulfur-Cured NR Vulcanizates Containing 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate or Silver Substituted Zeolite

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Abstract

This work used 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) or silver substituted zeolite (SSZ) as an antibacterial agent for improving the antibacterial performance of natural rubber (NR) compounds vulcanized by conventional vulcanization (CV), semi-efficient vulcanization (Semi-EV) and efficient vulcanization (EV) systems. The cure behavior and anti-bacterial performance for the NR vulcanizates were studied by varying loadings of HPQM or SSZ, contact times and vulcanization systems. The antibacterial performance for the rubber compounds was examined by Halo test and Plate-Count-Agar (PCA) methods against *Escherichia coli* (*E.coli*, ATCC 25922) and *Staphylococcus aureus* (*S.aureus*, ATCC 25923) as the testing bacteria. It was found that the cure time and crosslink density were dependent on the vulcanization recipe used, but were not affected by the addition of HPQM or SSZ agent. Diphenylguanidine (DPG) at 1.0 phr in the NR vulcanizates by the EV system had the ability to kill the *E. coli* and *S. aureus* bacteria. The NR vulcanizate by CV system showed the most pronounced anti-bacterial performance, as compared with the other two vulcanization systems, via migration and diffusion processes of HPQM or SSZ agent onto the NR surfaces, this being identified by the relatively high reduction of contact angle values. It was found in this work that HPQM showed the most preference for NR compounds with the CV system with the contact time of 120 min or longer to achieve bacteria killing efficacy of 99.0-99.9%, the efficacy being more effective for *E.coli* bacteria.

Key words: Natural rubber, Curing system, Anti-bacterial performance, Crosslinking.

Introduction

Natural rubber (NR) is a linear polymer of an unsaturated isoprene, and primarily obtained from the *Hevea brasiliensis* tree, and is used extensively in many applications and products, such as, rubber bands, tires, conveyor belts, football bladders, and rubber tubes. In house-ware applications, natural rubber is used for making children's toys, gloves, stationary and kitchen equipment. Since the natural rubber consists of protein, amino acid, carbohydrate and fat [1] some bacteria are able to grow in it. Most species of bacteria can be classified into two categories, gram positive and gram negative bacteria, based on their responses to a laboratory technique, and the most common harmful bacterial diseases are respiratory infections [2-3]. In this respect, the bacterial contaminations are of main concern in natural rubber products, especially when used in contact with humans. The addition of antimicrobial agents into the rubber products is one of the preferred methods to prevent the natural rubber products from microbial contaminations.

Antibacterial agents that are widely used include heavy metals, metal oxide, nano-materials and organic substances. Silver metal is one of the widely used antibacterial metals for quite some time. The antibacterial performance of silver is dependent on the silver ion (Ag^+), which usually interacts with the available sulfur, oxygen or nitrogen in bio-molecules to inactivate the bacteria [4-5]. Another form of silver that exhibits an excellent antibacterial activity is silver substituted zeolite (SSZ) [6]. The antibacterial mechanism of SSZ occurs when contacting with moisture or liquid to initiate ion exchange and producing silver ion attached to the bacteria [7-8]. The antibacterial efficiency also depends on the categories and structures of bacteria. Another widely used anti-bacterial agent is 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) which is an organic substance containing multi-functional groups to prevent the growth of bacteria by inhibiting cell wall or DNA synthesis in the rubber products [9].

Based on available evidences for natural rubber research [10-14], most studies aim to improve the properties of natural rubber compounds by focusing on physical, mechanical, thermal and stability properties in various forms of natural rubbers, such as homopolymers, blends and thermoplastic elastomers, coated rubber substrates, but very rarely give concern to the anti-bacterial properties. The natural rubber products can be value-added if they have abilities to prevent the bacterial growth. Recent works [8, 15-23] have indicated that silver ions and HPQM have been given attentions and used for preventing the bacteria growth in rubbers and their blends. Bakar *et al*. [15] studied the effect of silver nanoparticles added with natural rubber latex prepared by latex-salt mixing and casting on a microscope glass substrate, and found a formation of silver nanoparticles in the natural rubber film at the interface area of the rubber particles. They also found that protein was necessary for stabilization of the silver nano-particles in the natural rubber. Lever *et al*. [8, 23] studied the antibacterial activity of natural rubber added with Ag^+ based zeolite (Zeomic) against *S. aureus* and *K. pneumoniae.* It was found that the natural rubber added with Zeomic could not kill *S. aureus* whereas *K. pneumonia* decreased when adding Zeomic agent. Kaali *et al*. [16] reported the anti-bacterial properties of polyurethane and silicone rubber products with addition of Ag^+ based zeolite against *S. aureus* and *P. aeruginosa* bacteria, which was found to improve with increasing the loading of Ag^+ based zeolite. The addition of silver particles and HPQM could also give the antibacterial effect in plastics, such as polypropylene [17], polycarbolatone [18] polyethylene [19-20], polyamide [21], and poly(lactic acid) [22].

It has been widely known that the properties of natural rubber compounds are very much dependent on their curing characteristics since it has been widely known that the rubbers can be vulcanized in different ways [24]. These are mainly referred to type and degree of crosslinkings in the rubber products (i.e., products with sulfur or non-sulfur cure, and with different crosslink densities). Based on the existing literatures [8, 15-23], none of the published evidence has studied the effect of curing characteristics on the anti-bacterial activities of natural rubber compounds. Therefore, a relationship between curing characteristics and antibacterial properties of natural rubber filled with selected anti-bacterial agents was established for the first time in this work. The HPQM and SSZ with various loadings added into the natural rubber compounds with different vulcanization systems were prepared and their antibacterial performance was examined. Halo and Plate-Count-Agar (PCA) methods were selected as qualitative and quantitative measurements against *E. coli* and *S. aureus* bacteria. The surface analysis on the rubber compounds before and after anti-bacterial agent loading was investigated by contact angle technique in order to substantiate the antibacterial activity results.

Experimental

Materials and chemicals

Natural Rubber (Standard Thai Rubber, STR-5L, supplied by PI Industry Co., Ltd., Bangkok, Thailand) was used as polymeric matrix, and zinc oxide (ZnO) (supplied by Thai Lysaght Co., Ltd., Bangkok, Thailand) and stearic acid (supplied by Imperial Industry Co., Ltd., Thailand) were used as activators. Mercaptoben zothaiazole (MBT), supplied by Zeon Advanced Polymix Co., Ltd., (Bangkok, Thailand) and diphenyl guanidine (DPG), supplied by Siam Chemi Co., Ltd., (Bangkok, Thailand) were used as accelerators. Sulfur, supplied by Zeon Advanced Polymix Co., Ltd., (Bangkok, Thailand) was used as main curing agent. Silver substituted zeolite (designated as SSZ and supplied by Yamamoto Trading Co., Ltd., Bangkok, Thailand) and 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (designated as HPQM and supplied by Koventure Co., Ltd, Bangkok, Thailand) were used as anti-bacterial agents, the chemical structure of HPQM being given in **Scheme 1**. The testing bacteria used in this work were *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923). *E.coli* is one of the major causes for severe anemia, kidney failure, while *S.aureus* causes nosocomial infections, pyoarthritis, endocarditis and other disorders.

Preparation of natural rubber test-pieces

The natural rubber (NR) compounds were vulcanized in three different systems; namely: conventional vulcanization (CV), semi-efficient vulcanization (Semi-EV) and efficient vulcanization (EV) whose chemical formulations and quantities are given in **Table 1**. The NR test-pieces were prepared through mastication, compounding and vulcanization processes. The natural rubber was first masticated on a laboratory two roll mill (Yong Fong Machinary Co., Ltd., Thailand) for 5 min, before compounded with zinc oxide, stearic acid, MBT, DPG and sulfur for another 25 min. Then the rubber was compounded with an anti-bacterial agent and continued mixing on the two-roll mill for another 5 min. The total times for masticating and compounding the rubber with the required chemicals were 35 min and this was the same for all vulcanization systems. In vulcanization process, the rubber compounds were then compression-molded using a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at pressure of 180 kg/cm^2 with a cure temperature of 160^{o}c to produce vulcanized natural rubber. The cure time used for completion of the vulcanization process used the time for 90% cure which was determined by an Oscillating Disk Rheometer (ODR).

Cure characteristics and crosslink density

The mixing torque difference and cure time 90% (t_c90) of the natural rubber compounds for each vulcanization system were determined using an ODR (Model ODR GT 7070-S2, GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 160^{o}C. This temperature was the same as used for vulcanizing the rubber compounds as stated earlier. The determinations of the crosslink density for the vulcanized natural rubbers were carried out through the Flory-Rehner model whose calculations are expressed as Eqn. 1. [25]

$$-ln(1-V_r)-V_r-\chi V_r^2=2V_s\eta_{swell}(V_r^{1/3}-\frac{2V_r}{f}) \qquad \text{(Eqn. 1)}$$

where v is the moles of crosslinks per unit volume of polymer, v_2 is the volume fraction of polymer in the swollen sample, V_1 is the molar volume of the solvent and v_0 is the volume fraction of polymer at the time of crosslinking. The v_0 term is used to correct for material that is extracted by the solvent. χ is the rubber-solvent interaction parameter (0.3795 in this case).

Antibacterial performance

The anti-microbial performance for the natural rubber compounds was studied by both qualitative and quantitative aspects, these being referred to as Halo test and Plate-Count-Agar (PCA) methods, respectively. The Halo test was used as qualitative assessment of anti-bacterial activity and initiated by mixing the nutrient agar and the nutrient broth in ratio 1:1 and incubated testing bacterial solution (OD_{600} = 0.1) onto sterilized Petri dishes. The vulcanized rubber samples, which were cut into disc form of 6 mm in diameter, with and without antibacterial agents, were gently placed over solidified agar. The Petri dishes were then incubated at 37^{o}C for 24 hr before investigating and measuring the inhibition dimensions.

Plate-Count-Agar (PCA) method is regarded as quantitative assessment of bacterial reduction and this work followed the ASTM E 2149 (2001) standard test. Nutrient broth was used as a growing medium of *E. coli* and *S. aureus* bacteria in overnight inoculums. After that it was diluted by peptone solution and cultivated bacteria 5 ml shaken on a reciprocal shaker at the speed of 100 rpm at 37^{o}C for contacted time of 30, 60, 120, 180 and 240 min, respectively. Dilution factor of n4 and n5 were considered, depending on the preferred number of initial bacteria colony which usually ranges from 30 to 300 colonies (where n is a dilution factor). 100 µl of bacterial solution were placed over the agar into sterilized Petri dishes. The inoculated plates were cultivated at 37°C for 24 h before counting the active or survival bacteria and the evaluation of the anti-bacterial efficacies in terms of Colonies forming unit per milliter (*cfu/ml*) was expressed as Eqn. 2. [26]

$$cfu/ml = \frac{A}{(10^{-n} \times B)} \qquad \text{(Eqn. 2)}$$

where A is number of counting bacteria, n is dilution times, and B is volume of solution bacteria(100 μl).

Surface characterization by contact angle measurement

In this work, the contact angles of deionized water on surfaces of vulcanized NR test-pieces were measured by a drop method using a Contact Angle Goniometer (Model 100-00 from Ramé-hart Instrument Co. Ltd., New Jersey, USA). The contact angles were referred to as wettability on the surfaces of vulcanized NR with and without incorporation of HPQM or SSZ agent. The results were given by microscopic images, and the contact angle values were averaged for advancing stages of drops for 5 times/100 μL droplets at least five independent determinations.

Results and Discussion

Cure behavior

Figure 1 shows the cure times at 90% cure (t_c90) for three natural rubber (NR) vulcanization systems (CV, Semi-EV and EV) with various loadings of HPQM or SSZ. It should be noted that the differences in cure times between the three vulcanization systems should not be compared directly since these three systems had different amounts of curing agents (sulfur, DPG and MBT), but only the effect of HPQM or SSZ addition on the changes in cure times was of interest. In general, it was found that the addition of HPQM or SSZ had a small effect on the cure time, the changes being less than one minute and within the experimental errors (+/-5.0%). Therefore, it could be said that the vulcanization reactions were not interfered with the addition of HPQM or SSZ. To substantiate this claim, the results of ODR torque difference and Flory-Rehner crosslink density for same experimental systems are given in **Figure 2**. The variations in the torque difference and crosslink density results were caused by the different amounts of the major vulcanizing agents used. It was found again here that the addition of HPQM or SSZ did not change the torque difference and crosslink density results, the small differences being within the experimental deviations of +/-5.0%. However, it was interesting to mention that the torque differences and crosslink densities for CV and Semi-EV systems were very much higher than those for EV system. This was expected since the amount of sulfur added in the CV vulcanization system was higher. The decreasing sequences of crosslink density and torque difference were the same as those of sulfur content in these three vulcanization systems (see **Table 1**).

Anti-bacterial performance

Qualitative evaluation by Halo test

Figure 3 and **Table 2** shows inhibition zone results from the Halo test for the three NR vulcanization systems filled with HPQM or SSZ against *E. coli* and *S. aureus* bacteria. The inhibition zone results from neat NR, a filter paper doped with $CuSO_4$ (as positive control sample) and a blank filter paper (as negative control sample) were also considered for comparison purposes. It was found that NR alone could not kill the *E. coli* and *S. aureus* bacteria, but the NR with HPQM or SSZ exhibited the killing performance at the loadings of 3 and 5 phr for *E. coli* only. Based on the quantitative clear zone radius, the NR vulcanizate with 5 phr HPQM or SSZ was more effective than that with 3phr. The occurrence of inhibition zone for the NR vulcanizates with HPQM or SSZ agent clearly indicated that these two anti-bacterial agents were diffusible in the NR matrix. The addition of HPQM or SSZ agent did not give any inhibition zone for *S. aureus*. For the effect of vulcanization system, it was found that the CV vulcanization system exhibited the greatest inhibition zones followed by the semi EV and the EV systems. The reason for this was related to the amount structure of the crosslinks formed for each vulcanization system. It has been widely accepted [24, 27-28] that the majority of crosslink type in the CV system for natural rubber is polysulfidic crosslink while the EV system mostly contains mono- and di-sulfidic crosslinks. For any given crosslink densities, the vulcanizates with highly polysulfidic crosslinks would have greater free volumes within the crosslink structures, allowing any small molecules (such as, particles, gas, and fluids) to penetrate more easily than those with high amounts of mono- or di-sulfidic crosslinks. If this was the case, the relatively higher diffusion of HPQM or SSZ agent within the NR vulcanizates with the CV system was reasonable and thus, greater effectiveness in killing the bacteria as compared with those with the semi-EV and EV systems. However, it should be noted that the Halo test is only a qualitative evaluation which is relatively simple and quick for evaluating diffusion abilities of anti-bacterial agent to kill the bacteria on solidified agar. The Halo test usually needs to be confirmed by other testing methods which allow survival bacteria to be counted quantitatively [29-30].

The diffusion of HPQM or SSZ agent could be confirmed physically by the determination of chemistry change on the NR surface whether or not there were HPQM or SSZ agent on the NR surface, this being carried out though a contact angle test. The maximum loading of HPQM or SSZ at 5 phr was used and the results were compared with the NR vulcanizates without adding the HPQM or SSZ. **Table 3** shows the contact angle values of neat NR, and NR with either HPQM or SSZ for three different vulcanization systems. It can be observed that the initial contact angle values of neat NR vulcanizates for three vulcanization systems were different (CV=115.94^{o}±3.90, Semi-EV=128.50^{o}±4.48 and EV=121.05^{o}±2.22), this being due to differences in the amount of vulcanizing chemicals with each vulcanization system as already given in **Table 1**. In order to observe the chemistry changes on the rubber surface, the contact angle values of the same vulcanization must be considered. It was observed that adding either HPQM or SSZ decreased the contact angle values of the NR vulcanizates, suggesting greater hydrophilicity of the NR. The changes in the contact angle of the NR compounds with HPQM were more pronounced than those with SSZ., the most obvious decrease in contact angle value being observed for the CV system with 5 phr HPQM (about 82.86^{o}±2.93). This was because of the easiest migration of the HPQM onto the NR surfaces to contact and eventually kill the bacteria. These contact angle results were found to correspond well to the greatest inhibition zone (diffusability) of the CV system as earlier presented in **Table 2**.

Quantitative evaluation by PCA test

Since there were some published evidences [30-31] claiming that some vulcanizing recipes had abilities to kill the *E. coli* and *S. aureus* bacteria it would be essential in this present work to determine whether or not the chemicals used in the vulcanization recipes in this work had abilities to kill the bacteria. **Figure 4** shows percentage survivals of *E. coli* and *S. aureus* bacteria over 0-240 min contact times from the PCA method for NR compounds vulcanized by CV, semi EV and EV systems ***without*** adding HPQM or SSZ agent. It can be seen that there were no changes in bacteria survivals for CV and Semi-EV systems, suggesting that there were no occurrence of bacteria killings in the CV and Semi-EV systems. However, it was obvious that the bacteria (especially *E. coli*) progressively decreased with contact time for EV system, indicating a bacteria killing in the EV vulcanization system. In order to clarify this, all the chemicals (except for HPQM and SSZ) were used in "neat form" (without adding them into the rubber compounds) and were considered individually for their anti-bacterial performance. The results of bacteria survival (in cfu/ml) for each chemical are given in **Figure** 5 and the control flask (shaken without rubber sample) was also considered for comparison purposes. It was shown that ZnO, Stearic acid, MBT and sulfur samples gave bacteria survivals, suggesting that they were not effective chemicals for killing the bacteria. But, DPG killed the *E. coli* and *S. aureus* very effectively. Therefore, the results and conclusion in **Figure** 5 became the answer or reason for the decrease in bacteria survivals in **Figure 4**.

Figures 6 and **7** show the percentage survivals for *E. coli* as a function of contact time for NR compounds vulcanized by three different vulcanization systems added with HPQM or SSZ, respectively. It was found that the percentage survivals of *E. coli* for NR vulcanizates with CV and Semi-EV systems were very similar. That was, the *E. coli* survivals decreased with increasing HPQM or SSZ agent from 1 to 5 phr. the *E.coli* survivals in most cases were greater than 99%. This suggested that HPQM and SSZ had effective abilities in killing the *E. coli.* The effective contact time for reducing the *E. coli* survivals was greater than 120 min. For the NR vulcanizate with EV system, it was found that the effect of addition of HPQM or SSZ was insignificant; the *E. coli* survival for the NR vulcanizate with HPQM agent was the same as that without HPQM. The reduction of *E. coli* survival for the vulcanizate without HPQM was caused by the anti-bacterial property of the high DPG loading in the EV system as already proved with the experimental data and discussed in **Figure 5**. However, the effect of HPQM became more significant and sufficiently pronounced to suppress the effect of DPG in the vulcanizate when adding high dosage of the HPQM (3- 5 phr) under the contact times of greater than 180 min. Similar behavior was also observed for the NR vulcanizates with SSZ agent.

Figures 8 and 9 show the percentage survivals for *S. aureus* with varying contact times for three different NR vulcanization systems added with HPQM and SSZ, respectively. The results were very similar to those for the *E. coli* bacteria as given in **Figures 6 and 7**, with additional observation in that the effect of HPQM or SSZ loading appeared to be more sensitive to the *E. coli* as compared with to the *S. aureus*. This was because that the *E. coli* in general have higher growth rate as compared to the *S. aureus*. Besides, in PCA method which was performed in peptone solution, the bacteria had made contacts very thoroughly with HPQM or SSZ. The newly grown *E. coli* during the shaking in peptone was probably weak, and was easily killed by the HPQM or SSZ as compared to *the S. aureus* which have lower growth rate. This claim was in good agreement with Zhang *et al*. [32] and Silapasorn *et al.* [33]. Finally, it was found that the minimum and recommended loading for HPQM or SSZ for effective killings of the *S. aureus* was about 5 phr, but the *S. aureus* survivals in most cases were still lower than 99%.

Conclusions

HPQM or SSZ anti-bacterial agent was loaded at different amounts into natural rubber compounds vulcanized by three different systems, and their cure characteristics and antibacterial performance were monitored. The results suggested that the addition of HPQM or SSZ had a small effect on the cure time change and did not change the torque difference and crosslink density results. Neat NR vulcanizates could not kill the *E. coli* and *S. aureus* bacteria, but relatively high dosage of diphenylguanidine (DPG) at 1.0 phr in the EV system could result in bacteria reduction. HPQM or SSZ agent had abilities to diffuse through the NR compound, the diffusion process being more pronounced for HPQM and with the NR vulcanizates by CV system, this claim being substantiated by the relatively high reduction of contact angle values. The NR vulcanizates by CV system exhibited better anti-bacterial performance than those with Semi-EV and EV systems. Based on the results in this work, HPQM showed a most preference for NR compounds with CV system with the contact time of 120 min or longer, while SSZ was most suitable for the NR compounds with EV system at the contact time of 180 min or longer in order to achieve bacteria killing efficacy of 99.0-99.9%. These two anti-bacterial agents (HPQM and SSZ) were quite effective for *E. coli* bacteria.

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Captions for Tables

Table No.	Caption
Table 1	Chemical compositions for natural rubber compounds
Table 2	Inhibition zone by the halo test against *E. coli* and *S. aureus* for CV, Semi-EV and EV vulcanization systems
Table 3	Contact angle values for NR vulcanizates with CV, Semi-EV and EV systems with HPQM or SSZ at 5 phr

Captions for Schemes

Scheme No.	Caption
Scheme 1	The chemical structure of 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM)

Captions for Figures

Fig. No.	**Caption**
Fig. 1	Cure time at 90% (t_c90) for natural rubber vulcanizates with CV, Semi-EV and EV systems containing various loadings of HPQM or SSZ agent
Fig. 2	Torque difference (a) and crosslink density (b) for NR vulcanizates with CV, Semi-EV and EV systems with varying loadings of HPQM or SSZ agent
Fig. 3	Effect of type and loading of *E. coli* agent on physical inhibition zone in the Halo test: (a) and (d) CV system, (b) and (e) Semi-EV system, and (c) and (f) EV system
Fig. 4	Percentage bacteria survival of NR vulcanizates with various vulcanization systems against (a) *E. coli* agent and (b) *S. aureus*
Fig. 5	Percentage bacteria survival of main chemicals in NR vulcanizing recipe against (a) *E. coli* agent and (b) *S. aureus*
Fig. 6	Percentage bacteria survival for *E. coli* colonies of NR compounds added with HPQM (a) CV system, (b) Semi-EV and (c) EV system
Fig. 7	Percentage bacteria survival for *E. coli* colonies of NR compounds added with SSZ (a) CV system, (b) Semi-EV and (c) EV system
Fig. 8	Percentage bacteria survival for *S. aureus* colonies of NR compounds added with HPQM (a) CV system, (b) Semi-EV and (c) EV system
Fig. 9	Percentage bacteria survival for *S. aureus* colonies of NR compounds added with SSZ (a) CV system, (b) Semi-EV and (c) EV system

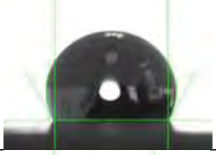
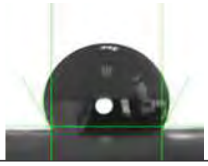
Table 1. Chemical compositions of natural rubber compounds

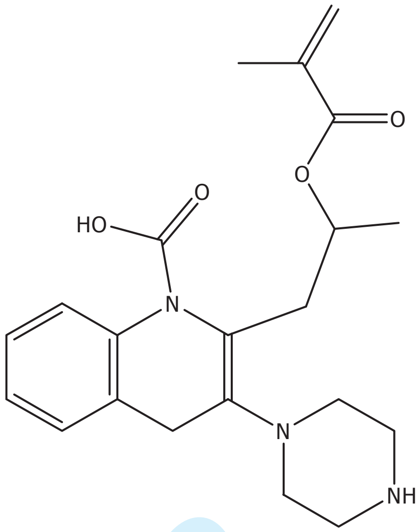
Components	**Vulcanizing systems (phr)**		
	CV	**Semi-EV**	**EV**
Natural Rubber (STR 5L)	100 part		
Zinc oxide (ZnO)	5		
Stearic acid	2		
Mercaptobenzothiazole (MBT)	0.5	1.5	2.5
Diphenylguanidine (DPG)	0.2	0.6	1.0
Sulphur	3.0	1.2	0.2
2–hydroxypropyl–3–piperazinyl–quinoline carboxylic acid methacrylate (HPQM) or silver substituted zeolite (SSZ)	Varying 0 / 1 / 3 / 5		

Table 2. Inhibition zone by the halo test against *E.coli* and *S.aureus* for CV, Semi-EV and EV vulcanization systems

NR compound	**Antibacterial content** (phr)	**Inhibition zone of *E.coli*** (mm)			**Inhibition zone of *S.aureus*** (mm)		
		Vulcanization system			**Vulcanization system**		
		CV	**Semi-EV**	**EV**	**CV**	**Semi-EV**	**EV**
Neat NR	0	0	0	0	0	0	0
NR + HPQM	1	0	0	0	0	0	0
	3	2.8	2.7	2.0	0	0	0
	5	3.7	3.0	2.8	0	0	0
NR + SSZ	1	0	0	0	0	0	0
	3	2.7	2.0	1.5	0	0	0
	5	3.5	2.5	1.9	0	0	0

Table 3. Contact angle values for NR vulcanizates with CV, Semi-EV and EV systems with HPQM or SSZ at 5 phr

Vulcanization system	NR compound	Contact angle value (Degree)	Wettability form
CV	Neat NR	115.9 ± 3.9	
	NR + HPQM	82.9 ± 2.9	
	NR + SSZ	114.4 ± 3.1	
Semi-EV	Neat NR	128.5 ± 4.5	
	NR + HPQM	119.7 ± 1.4	
	NR + SSZ	125.4 ± 3.6	
EV	Neat NR	121.1 ± 2.2	
	NR + HPQM	118.4 ± 1.7	
	NR + SSZ	117.3 ± 1.8	



Scheme 1. The chemical structure of 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM)

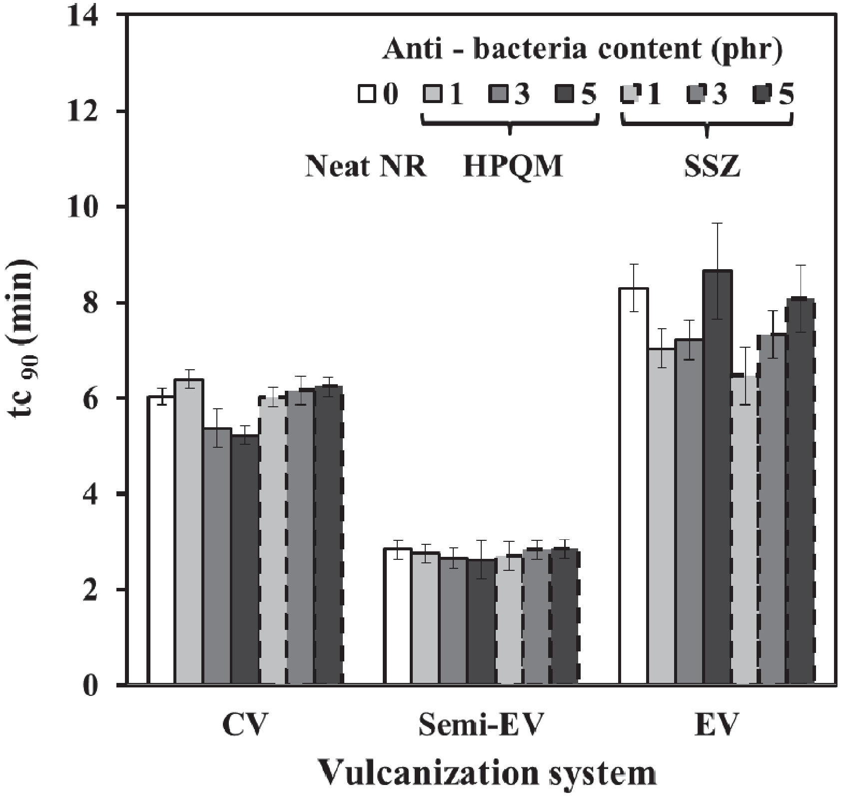


Figure 1. Cure time at 90% (tc_{90}) for natural rubber vulcanizates with CV, Semi-EV and EV systems containing various loading of HPQM or SSZ agent

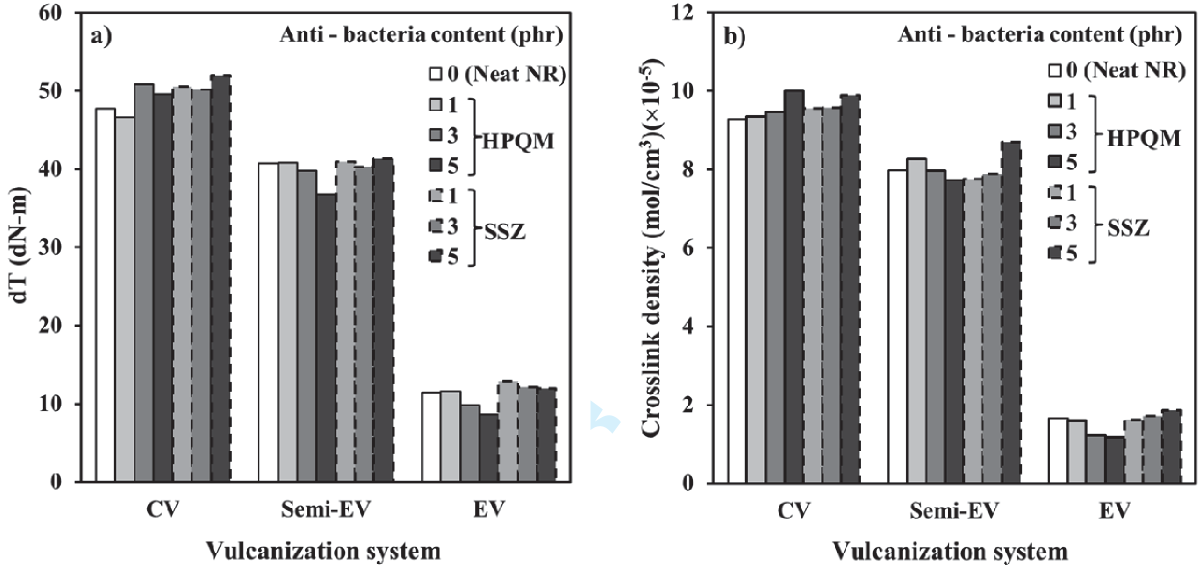


Figure 2. Torque difference (a) and crosslink density (b) for NR vulcazates with CV, Semi-EV and EV systems with varying loadings of HPQM or SSZ agent

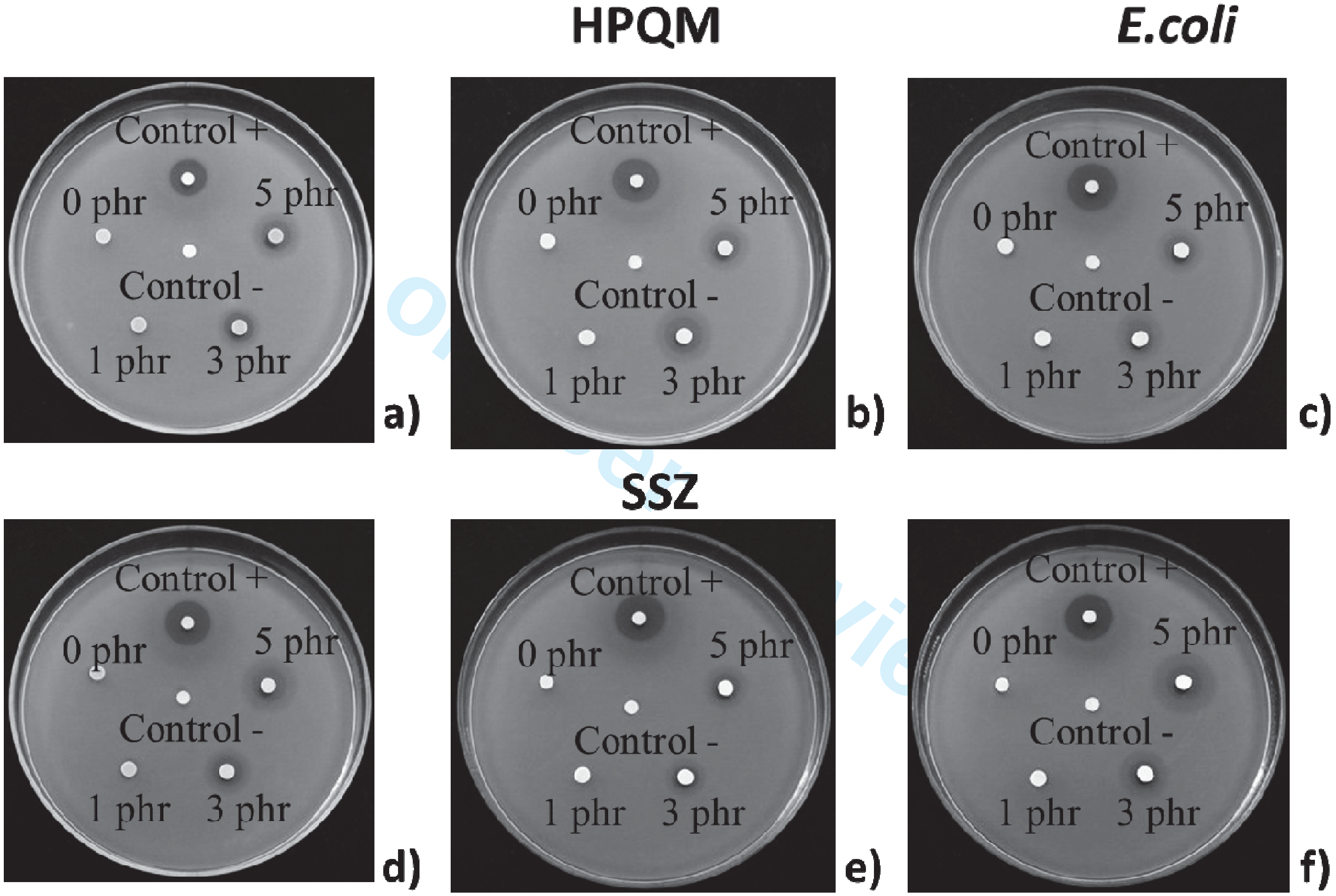


Figure 3. Effect of type and loading of *E.coli* agent on physical inhibition zone in the Halo test a) and d) CV system, b) and e) Semi-EV system, and c) and f) EV system

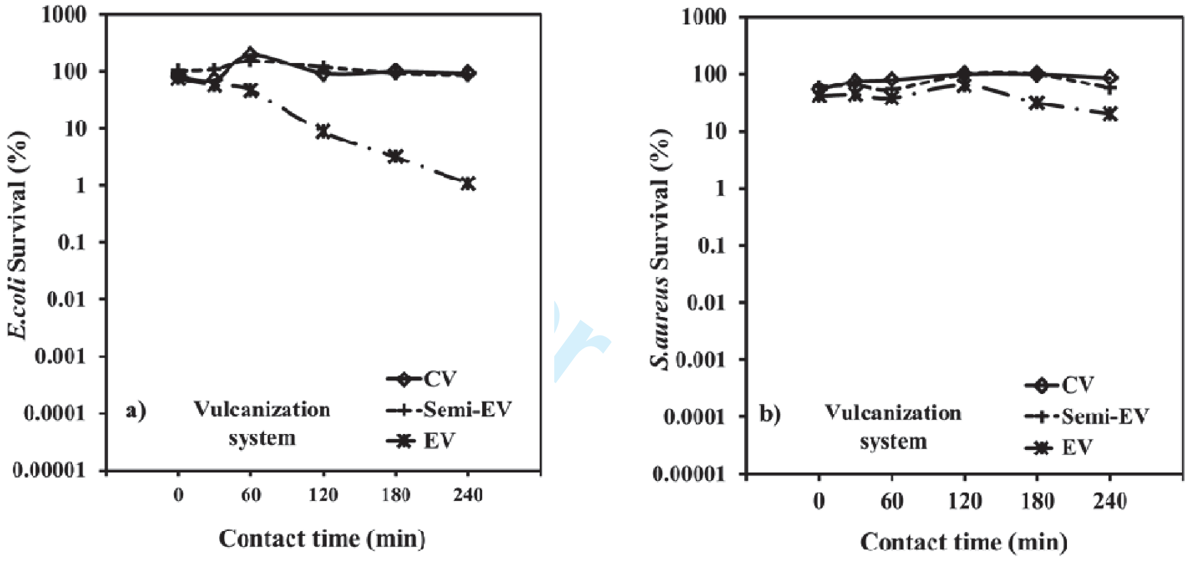


Figure 4. Percentage bacteria survival of NR vulcanizates with various vulcanization systems against *E.coli* agent a) and *S.aureus* b)

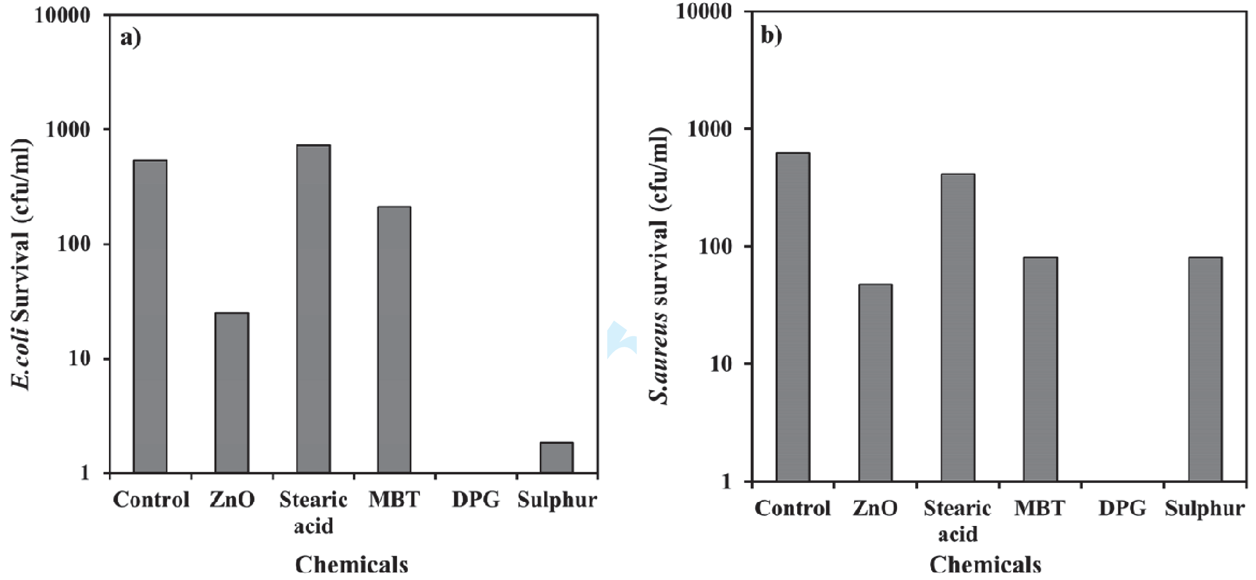


Figure 5. Percentage bacteria survival of main chemicals in NR vulcanizing recipe against *E.coli* agent a) and *S.aureus* b)

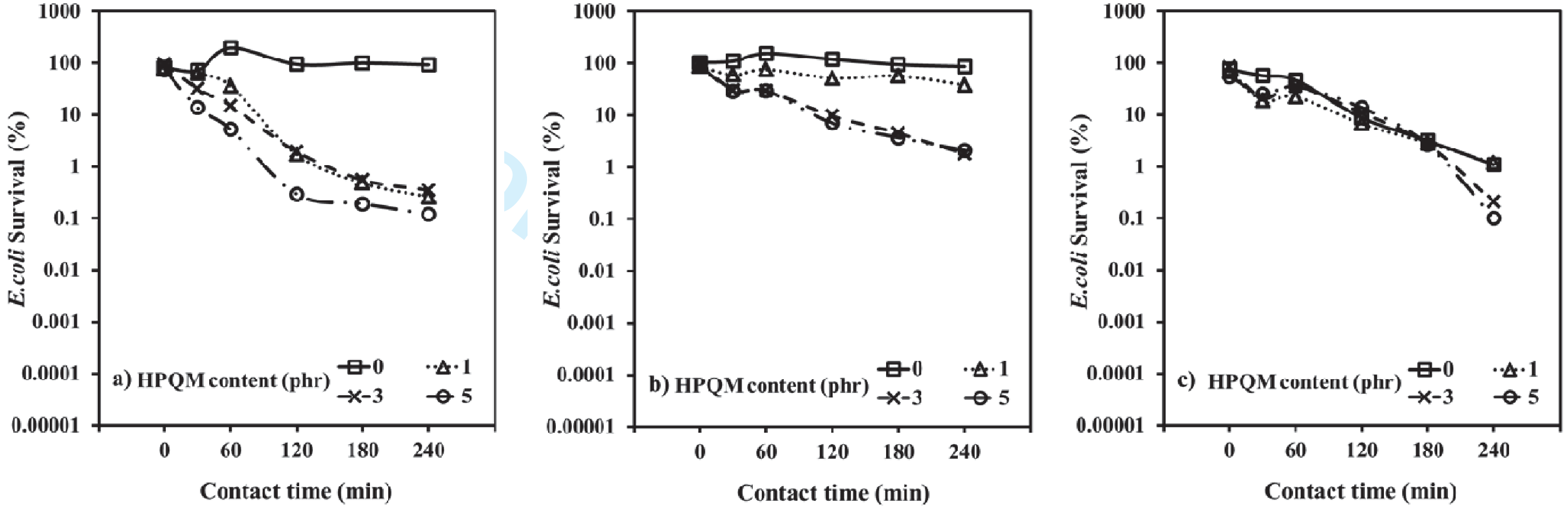


Figure 6. Percentage bacteria survival for *E.coli* colonies of NR compounds added with HPQM for CV system a), Semi-EV b), and EV system c)

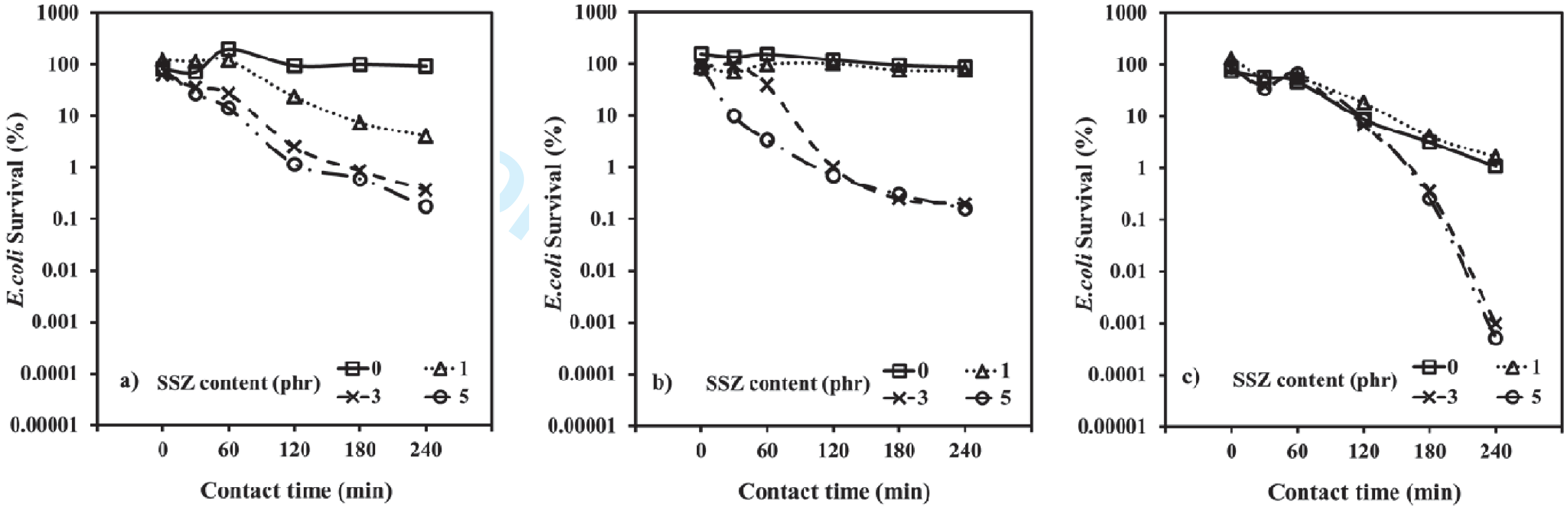


Figure 7. Percentage bacteria survival for *E.coli* colonies of NR compounds added with SSZ for CV system a), Semi-EV b), and EV system c)

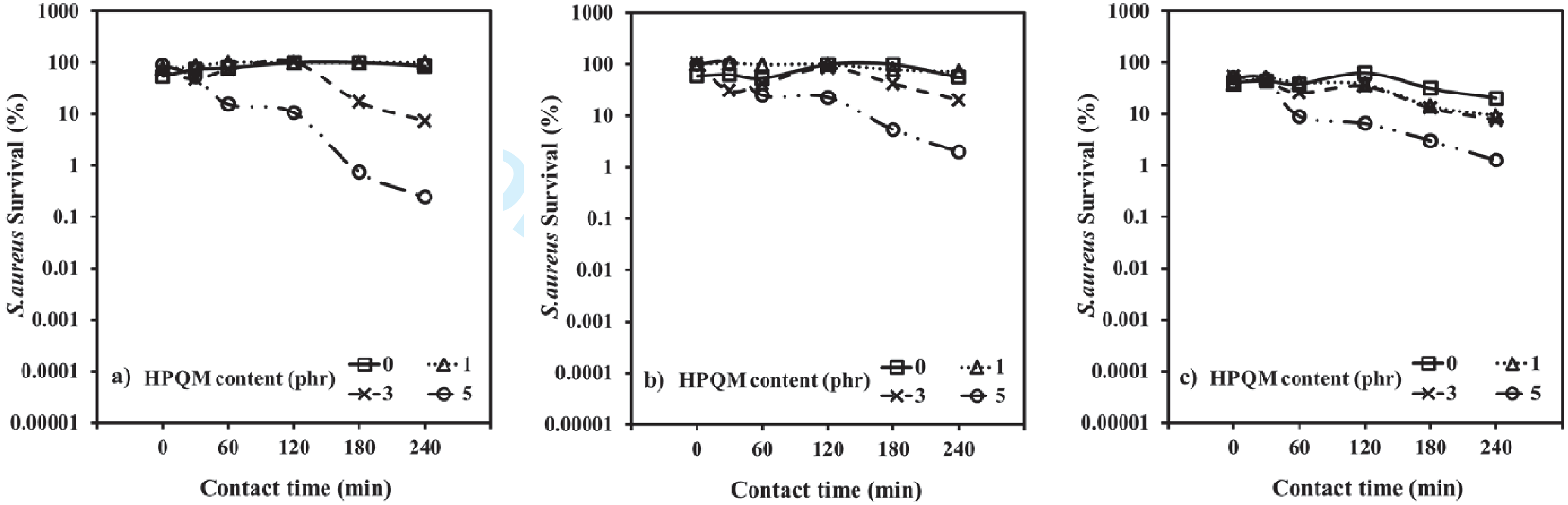


Figure 8. Percentage bacteria survival for *S.aureus* colonies of NR compounds added with HPQM for CV system a), Semi-EV b), and EV system c)

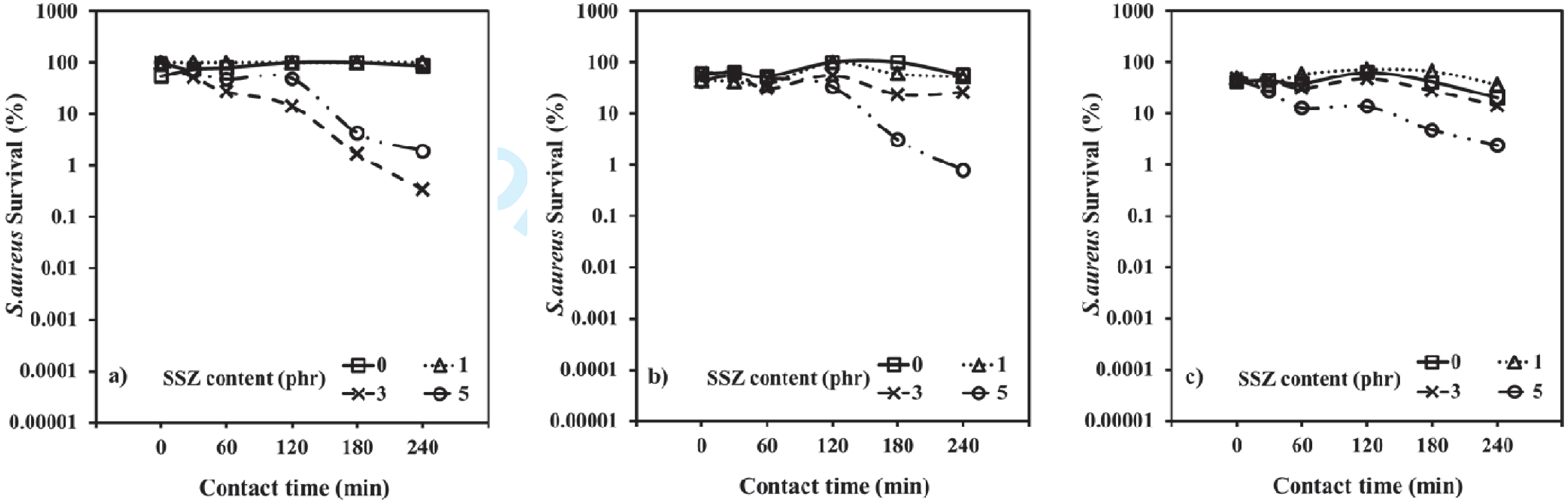


Figure 9. Percentage bacteria survival for *S.aureus* colonies of NR compounds added with SSZ for CV system a), Semi-EV b), and EV system c)

Anti-microbial Performance and Cure & Mechanical Properties for Peroxide-Cured Silicone Rubber Compounds

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Anti-microbial Performance and Cure & Mechanical Properties for Peroxide-Cured Silicone Rubber Compounds

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Abstract

In this work, nano-silver colloids, Ag-based zeolite compound Ag-based zeolite (Zeomic) or 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQCAM) was used as anti-microbial agents and/or mechanical property improvers in peroxide cured silicone rubber vulcanizates. The silicone rubber vulcanizates were prepared using a two-roll mill, followed by a hydraulic press to vulcanize the rubber compounds and their cure characteristics, mechanical properties and anti-bacterial performance were assessed. The anti-microbial performance for the silicone rubber compounds was examined through Plate-Count-Agar and Drop-Plate-Agar methods, and Halo test. The results suggested that the additions of all anti-microbial agents slightly increased the cure time, except for Ag-based zeolite. The additions of all anti-microbial agents also affected the mechanical properties of the rubber vulcanizates. Ag-based zeolite appeared to give the silicone rubber compound with most improved mechanical properties whereas 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQCAM) exhibited the most effective anti-microbial agent, considered by the occurrence of inhibition zone and 99% reductions of the *Staphylococcus aureus* and *Escherichia coli*. The changes in silicone rubber surfaces with addition of anti-bacterial agents were found by progressive decreases in water contact angles. This was observed only for HPQCAM agent, which was associated with diffusion and releasing mechanisms of the HPQCAM to kill the bacteria. The lightness for the silicone vulcanizates appeared to decrease with nano-silver content, but to increase with increasing Ag-based zeolite or HPQCAM agent.

Key words: Silicone rubber, Vulcanization, Antimicrobial performance, Mechanical properties

Introduction

Bacteria are commonly found in the ground, water and in other living organisms and they can cause diseases and become harmful to the environment, animals and humans. Remarkable examples of such concerns include bad consequences of food poisoning due to certain strains of *Escherichia coli (E. coli)* being found within the bathroom and kitchen. Most species of bacteria can be grouped into two categories based on their responses to a laboratory technique, these being referred to as gram-positive and gram-negative bacteria [1-3].

Nano-sized inorganic particles, of either simple or composite nature, display unique physical and chemical properties, and can be used for development of novel nano-devices which become useful in numerous physical, biological, biomedical, and pharmaceutical applications [4-9]. A number of recent achievements offer the possibilities of generating new nano-structured materials with designed surface and structural properties [10-13]. Silver is a non-toxic, non tolerant disinfectant that can reduce many bacterial infections [14]. Nano silver particles are generally smaller than 100 nm and contain 20–15,000 silver atoms and have been supplied in the form of chemical compounds because of technical difficulties dealing with the elemental form. As the size of the silver particles reduces to the nano-scale regime, their anti-bacterial efficacy increases enhances because of their larger total surface area per unit volume [15]. Although silver ions and silver-based compounds are toxic to microorganisms showing strong biocidal effects on as many as 12 species of bacteria including *E. coli* [16], the effects of nano-silver particles on microorganisms and anti-microbial mechanism have not been fully understood. Recently, the effects of nano-silver on anti-bacterial performance in polymeric materials have been paid attention to by scientists and technologists for value-added purposes of the polymer products. Generally, nano-silver has exhibited different effects depending on the molecular structures of the polymers used

[17-19]. Positive effect of nano-silver powders on polypropylene (PP) was observed [17] whereas negative effect was noted when using PC/ABS and TPE systems [18]. More recent and comprehensive studies were carried out by Pongnop et al. [19] who investigated the anti-bacterial performance against *E. coli* by blending and coating nano-silver onto thermoplastics having different molecular structures and found that medium-density polyethylene (MDPE), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) in neat form could not inhibit the *E. coli* growth. But after introducing the nano-silver particles, the PVC exhibited the highest % *E. coli* reduction. Another form of nano-silver is known as Zeomic which is inorganic silver based zeolites compound by chemical synthesis. Studies by Kawahara et al [20] and Kaali et al [21] suggested that addition of Ag-based zeolite in polymeric materials not only improved the anti-microbial performance, but also affected the physical, thermal and/or chemical properties of the polymers. The mechanism of Ag-based zeolite in the anti-microbial effect involves moisture or liquid contact with Ag-based zeolite to initiate silver ions in order to attack the bacteria [22]. Another anti-bacterial agent is 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQCAM) which has a trade name of BIOCLEANACT™ and could perform anti-microbial activities in polymeric materials [23].

Silicone rubber is the most widely used among biocompatible rubbers [24] as well as blending with other polymers [25]. The applications of silicone rubber include medical house-ware applications (children's toys, computer keyboards, phone keypad, ear plugs, ear phones and watch) that are likely to contact with human body. In such applications, the microbial contaminations are of main concern. The addition of anti-microbial agents into the rubber products is one of the widely referred methods to prevent the silicone rubber products from microbial contaminations [18,26] and also to affect the mechanical and thermal properties of the silicone rubber compounds [27]. Kaali et al.[18] observed studied the anti-microbial effect against MRSA and *P. aeruginosa* of Zeomic agent in polyurethane (PU) and silicone rubber (SR), prepared by injection molding, and solution casting techniques, respectively. Yang and Park [26] assessed the mechanical and anti-bacterial properties of silicone rubber contained 1-ethyl-6-fluoro-7-{4-[2-hydroxy-3-(2-methylacryloyloxy) propyl]piperazin -1-yl}-4-oxo-1,4-dihyroquinoline-3-carboxylic acid (MQ) and its polymer (PMQ), and found that the tensile strength of the silicone rubber decreased with increasing MQ and PQM contents with satisfactory anti-bacterial activity against *E. coli* and *S. aureus*. Betts et al [27] carried out silver and silver platinum coating on polyurethane and silicone by a combination of magnetron sputtering and neutral atom beam plasma sources. The results showed that the anti-bacterial activity of silver on the polyurethane and silicone substrates was dependent on the release of silver ions and the use of platinum enhanced the release of silver ions from the silver coating.

Recent literatures have indicated that silicone rubbers are used in many applications such as tanning industry, plastics, automobiles, mold and die industries, electronic and medical devices [24]. Most recent efforts focus on improving the mechanical properties of the silicone rubbers, but knowledge and understanding of its anti-bacterial properties are very limited and extremely required. This present work aimed to explore the curing and mechanical properties, and anti-bacterial properties of silicone rubber filled with a wider range of anti-bacterial agents, which included nano-silver colloids, Ag-based zeolite compound (Zeomic) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQCAM or BIOCLEANACT™), under a variety of testing conditions. The effects of dosages of anti-bacterial agents and contact time were of our main interests. The differences in the mechanical and anti-bacterial property results were discussed and explained in connection with morphological results and changes in surface characteristics.

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 Zeomic, supplied by Yamamoto Trading Co., Ltd., Thailand) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (designated as BIOCLEANACT™, supplied by Micro Science Tech Co., Ltd, South Korea) were used as the anti-bacterial agents. The pH values, measured by Sevenmulti pH meter (supplied by Mettler Toledo, Co., Ltd., Scswerzenbach, Swisserland), for nano-silver colloids and HPQCAM were 5 and 12, respectively. *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) were used as testing bacteria.

Sample preparation

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. 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 an anti-bacterial 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.

Cure characteristics and crosslink density

The cure characteristics of the silicone rubber compounds were assessed through delta torque (differences in maximum and minimum torques), cure time and crosslink density using an Oscillating Disk Rheometer (Model ODR GT 7070-S2, GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 165°C. The crosslink density determination for the vulcanized silicone rubber compounds was carried out with Flory-Rehner method given as **Equation 1** [28-29]. In this work, toluene was used as solvent for the swelling test.

$$v = \frac{-[\ln(1-v_2)+v_2+\chi v_2^2}{2V_1(v_0^{2/3}v_2^{1/3}-v_2/2)} \qquad \text{(Eqn. 1)}$$

where v is the moles of crosslinks per unit volume of polymer, v_2 is the volume fraction of polymer in the swollen sample, V_1 is the molar volume of the solvent and v_0 is the volume fraction of polymer at the time of crosslinking. The v_0 term is used to correct for material that is extracted by the solvent. χ is the rubber-solvent interaction parameter (0.499 in this case).

Mechanical properties

The tensile properties (tensile modulus at 200% elongation, tensile strength and elongation at break) of the silicone rubber vulcanizates followed ASTM D 412-92(1998) with dumbbell-shaped sample and tested by a universal testing machine (Auto-graph AG-I, Shimadzu, Tokyo, Japan). A hardness durometer (Shore A) Model 475, PTC instruments,(MA, USA) was used for hardness evaluation in accordance with ASTM D 2240-03 (2003). All reported data were averaged from at least five independent experiments.

Anti-bacterial performance

The anti-microbial performance for the silicone rubber compounds was examined qualitatively and quantitatively through Halo testing method, and Plate-Count-Agar (PCA) and Drop-Plate methods, respectively.

- The Halo test was initiated by mixing the nutrient agar and the nutrient broth in ratio 1:1 and incubated testing bacterial solution (OD_{600} = 0.1) onto sterilized Petri dishes. The rubber samples (6mm in diameter), with and without anti-bacterial agents, were gently placed over solidified agar. The Petri dishes were then incubated at 37^{o}C for 24 hr for a zone of inhibition.
- Plate-Count-Agar (PCA) and Drop-Plate (DP) methods followed ASTM E 2149 (2001). The PCA method is suitable for quantitative assessment of bacterial reduction. Nutrient Broth was used as a growing medium of *E. coli* and *S. aureus* bacteria in overnight inoculums. After that it was diluted by peptone solution and cultivate bacteria 5 ml shaken on a reciprocal shaker at the speed of 100 rpm at 37^{o}C for contacted time of 30, 90, 150 and 210 min, respectively. Dilution factor of n4 and n5 were considered, depending on the preferred number of initial bacteria colony ranging from 30 to 300 colonies (when n is a dilution factor). 100 µl of bacterial solution was placed over the agar into sterilized Petri dishes. The inoculated plates were cultivated at 37^{o}C for 24 h before counting the active bacteria and evaluating the anti-bacterial efficacies using **Equation 2** [23]. In case of DP method, the same procedure used for PCA method was employed, except for the drop size. In DP method, 10 µl of bacterial solution was placed over the agar into sterilized Petri dishes at a preferred number of initial bacteria colony of 3 to 30 colonies. The advantage of the DP method over PCA method was less time-consuming, and effort required to disperse the drops onto an agar plate. In DP method, one Petri dish contained a number of active bacteria growths for different contact times at