International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:4, No:5, 2010

Polyisoprene-coated Silica/Natural rubber Composite

Chatwarin Poochai, Puttichai Pae-on, Thirawudh Pongpayoon*

***Abstract*—**The commercial white tyres are usually used for forklifts in food and medicine industries. Conventionally, silica is used as reinforcement in the tyres. However, the adhesion between silica particles and rubber is remarkably poor. To improve the problem of adhesion and hence enhance wear resistance, modification of silica surface is one of the solutions.

In this work, the natural rubber compound blending with polyisoprene-coated silica prepared by admicellar polymerization technique was studied to compare with the natural rubber compound of unmodified silica. The surface characterization of modified silica was also examined by SEM, FTIR, and TGA. The results show that polyisoprene-coated silica/natural rubber compound gave better overall mechanical properties, especially wear resistance with the improvement of the adhesion between silica and natural rubber matrix that can be seen in the SEM micrograph.

***Keywords*—**White Tyre, Admicellar Polymerization, Modified Silica, Wear resistance

I. Introduction

SILICA is usually used to produce white tyres because of its white color property and low cost. Silica can also provide additional property benefits and compounding flexibility. However, unmodified silica lacks the ability to make strong interaction between silica and rubber. Additionally, the aggregation of unmodified silica occurs due to strong filler-filler interaction. Silanol and siloxane functional groups on silica are also the effect on the poor dispersion of silica in natural rubber matrix. For these reasons, the compatibility between silica and natural rubber is needed to improvement. Therefore the modification of the silica surface is of considerable interest.

The previous publication reported several techniques for modification of silica surface. Ansarifar A. et al [1], Poh B.T. et al [2], and Urushihara Y. et al [3] used silane coupling agent to modify silica surface. They showed that the modified silica perfectly dispersed in natural rubber matrix and the mechanical properties of natural rubber compound were improved. Other methods such as, grafting and in *situ* polymerization are also available for silica modification. Silica modified by the in *situ* polymerization of organic monomer significantly was studied to represent the improvement of rebound resilience and produce greater overall rubber compound performance than that modified by more expensive silane coupling agents [4].

* Corresponding author. Tel.: +6629132500; fax: +66 25870024.
E-mail addresses: tpongprayoon@yahoo.com, thp@kmutnb.ac.th (T.Pongprayoon).

Admicellar polymerization is an innovative technique applied to improve the materials surface by coating with desired polymer nanoscale. The admicellar polymerization consists of four main steps: admicelle formation, monomer adsolubilization, in *situ* polymerization, and surfactant removal. Fig. 1 illustrates the process of the silica surface modification by admicellar polymerization technique. Benefit of this method is simple with minimal chemical usage as coated ultrathin film and the method is also environmental friendly as it can be carried out in aqueous solution [4, 5].

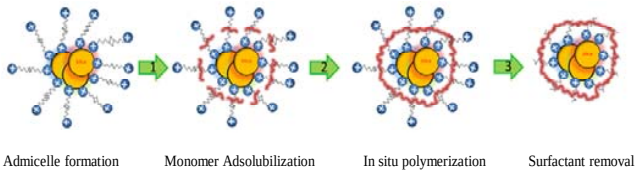

Fig. 1 Steps of admicellar polymerization process.

The objective of this research studied specifically to improve the abrasive wear and other mechanical properties of natural rubber compound using the admicellar-modified silica as reinforcement material. Polyisoprene was applied to coat on silica surface in order to improve the compatibility between the silica surface and the natural rubber.

II. EXPERIMENTAL

2.1 Materials

Silica Hi-Sil®233 (Siam Silica Co., Ltd., Thailand), Cetyltrimethylammonium Bromide ($[CH_3(CH_2)_{15}N(CH_3)_3]Br$ or CTAB (98%, Fluka Switzerland), Potassium Persulfate ($K_2S_2O_8$, Fluka, Switzerland), Isoprene (Aldrich, USA) Ethanol (Fisher Scientific, USA) and Tetrahydrofuran (Fisher Scientific, USA). All materials were used as received.

2.2 Admicellar polymerization modified silica

The mixture solution consisting of CTAB, ethanol, $K_2S_2O_8$, and water was prepared. Then, silica was added into the mixture and continuous stirring for a long period time. The isoprene monomer was added and stirred for a long period time again. Next the mixture was stirred and heated at 70 °C for 2 hours to induce the polymerization. Finally, the modified silica was wash with water to completely remove the CTAB at the upper layer.

2.3 Characterization of modified silica

The modified silica was examined by several techniques such as, Scanning Electron Microscope (SEM) for studying its morphologies, Fourier transform infrared spectroscopy (FT-IR) for characterizing the functional groups of coated film and Thermal Gravimetric Analysis (TGA) for measuring the thermal stability.

2.4 Preparation of natural rubber compound

The natural rubber compounds were prepared by the formulation as shown in Table 1. The samples were designated as S and MS codes. The letter "S" refers to unmodified silica and "MS" refers to modified silica. All ingredients used were the commercial chemical using in the rubber manufacturing. Rubber and ingredients were mixed by internal mixer machine (Lab Tech Engineering Company LTD.) After discharging, the compound was mixed on a two roll-mill or external mixer machine ((Lab Tech Engineering Company LTD.).

TABLE I NATURAL COMPOUND FORMULATION [6]

Ingredients	Ratio (phr)	
	S	MS
Natural Rubber	100	100
Silica	35	-
Treated Silica	-	35
Zinc Oxide	5	5
Stearic Acid	2	2
PEG	2	2
CBS	1	1
TMTD	0.1	0.1
Sulphur	2	2

TABLE II MECHANICAL PROPERTIES MEASUREMENT

Mechanical properties	**Methodology**	**Tools**
Cure Time (TC90, min)	ASTMD 2084	Rheometer Tester
Tensile Strength (MPa), %Elongation, 300% Modulus (MPa)	ASTMD-412	Tensile Tester
Tear Strength (MPa)	ASTMD-624	Tensile Tester
Specific gravity	ASTMD 792	-
Shore Hardness Test (Shore A)	ASTMD-2240	-
Abrasion	DIN 53516	Abrasion Tester

Then, a small compound piece was cut to determine cure time by rheometer. Then, the curatives were finally compression molded by compression mold machine (DAH TYAN Industrial Co., LTD.) at temperature for long period time as well as obtained cure time to vulcanize the natural rubber.

2.5 Mechanical properties measuring

The properties of the natural rubber compound were measured with several techniques based on ASTM given in Table 2. Cure time was measured using a rheometer (EEKON Co., LTD.), according to ASTM 2084. The tensile strength, %elongation, and 300%modulus, and tear strength were measured by Tensile Tester (Instron Co., LTD.), according to ASTM-412 and ASTMD-624, respectively. Moreover, the specific gravity and the hardness (shore A) were determined, according to ASTMD 792 and ASTM-2240, respectively. Wear resistant or abrasion loss was also measured by abrasion tester (FRANK Co., LTD.), according to DIN 53516.

III. RESULTS & DISSCUSION

3.1 Characterization of modified silica

3.1.1 Scanning Electron Microscope (SEM)

Surface morphology measured by SEM was applied to confirm that the silica surface was coated. Fig. 2 shows relatively smooth surface of the unmodified silica (A) and rough surface of the modified silica (B). The roughness on the surface of the modified silica particles was the result from the polyisoprene film formation by admicellar polymerization technique.

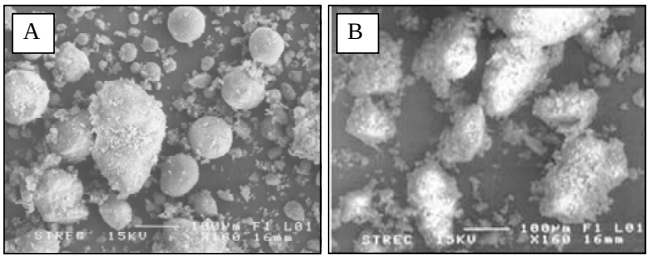

Fig. 2 SEM images of the unmodified silica particles (A) and the modified silica particles (B)

3.1.2 Fourier transforms infrared spectroscopy (FT-IR)

FT-IR was used to identify polyisoprene coated on the modified silica. The chemical functional groups of the modified silica were characterized by comparing with the functional groups of the prepared polyisoprene and unmodified silica. Fig. 3 represents the results to show the characteristic peaks of the measured samples. The two characteristic peaks at approximately 1600 and 2700-2900 cm^{-1} represent the C=C stretching vibration and C-H stretching modes of $-CH_3$ group in aliphatic compound, respectively, for polyisoprene (Fig 3A). As for the unmodified silica (Fig 3B), a broad band between 3000 and 3600 cm^{-1} is assigned to the O-H stretching vibration of the silanol groups (Si-OH), while a strong band centered at about 1100-1200 cm^{-1} corresponds to the Si-O-Si antisymmetric stretching vibration of the siloxane groups. The result was obvious that the FT-IR spectra of the admicellar-modified silica (Fig 3C) show two

characteristic peaks of both polyisoprene and silica. This confirms that the modified silica was coated with polyisoprene film.

3.1.3 Thermal Gravimetric Analysis (TGA)

The TGA results are shown in Fig. 4. Firstly, CTAB had the highest degradation rate at 275 °C. Secondly, polyisoprene was slowly degraded in range between 275 and 500 °C. Thirdly, untreated silica lost less than 10% of its original weight which mostly due to moisture and other impurities. Lastly, the modified silica had similar degradation pattern to that of the polyisoprene. The results can be seen to confirm that the silica was successfully coated with polyisoprene film.

3.2 The properties of natural rubber compound

Fig. 5 illustrates all properties of natural rubber compound, such as, cure time, tensile strength, %elongation, 300% modulus, tear strength, specific gravity, hardness, and abrasion, as following.

3.2.1 Cure Time

The result shows that the cure time of the unmodified silica was longer than the cure time of the modified silica because of the surface of unmodified silica containing polar functional group of silanol and siloxane. These can be trapped with accelerators and zinc complex. Therefore, the vulcanization reaction is retarded [7]. As the polyisoprene film coated on the modified silica surface, it made less chemically reactive silica surface that had the effect to reduce the amount of the trapped accelerators and zinc complex.

3.2.2 Tensile Strength and 300% Modulus

The results of both tensile strength and 300% modulus of the modified silica/rubber compound show the improvement of both tensile and modulus properties due to the increasing of rubber-filler interaction of polyisoprene coated silica and natural rubber matrix.

Better rubber-filler interaction could lead to better filler dispersion in the rubber matrix improving the macro scale properties of rubber compound. However, unmodified silica has high self interaction due to silanol and siloxane groups leading to agglomerate in the natural rubber matrix during mixing to make the poor strength properties of the natural rubber compound. Therefore, the natural rubber compound mixed with admicellar-modified silica was stronger than which mixed with the unmodified silica.

3.2.3 %Elongation

The elongation at break of the rubber compound mixed with the modified silica tended to decrease because of the increasing of dispersion and crosslink density between the modified silica and natural rubber bond during vulcanization.

3.2.4 Tear Strength, Specific gravity and Hardness (Shore A)

The tear strength, specific gravity, and the hardness properties of the rubber compound mixed with the modified silica tended to lower than the rubber compound mixed with the unmodified silica. Therefore, these properties can not be developed by the admicellar–modified silica.

3.2.5 Abrasion Resistance

The results of abrasion resistance of the natural rubber mixed with modified silica and unmodified silica show that the abrasion resistance of the rubber compound mixed with the modified silica tended to increase (lower rubber weight loss). It has been reported that abrasion resistance is controlled mainly by the modulus and the friction coefficient of the vulcanization. Higher modulus and lower friction coefficient give the vulcanizates with better abrasion resistance. In addition, a vulcanizates with good filler dispersion is claimed to have a better wear property than that with poor filler dispersion. Therefore, poor silica dispersion or strong silica-silica interaction is thought to be another reason for dramatic reduction in abrasion resistance [8].

3.3 Morphology of silica and natural rubber matrix

Morphology of the rubber compound mixed with silica was examined by SEM. Fig. 5 can conclude that the adhesion between the unmodified silica and rubber matrix was less than the adhesion between the modified silica and rubber matrix because the unmodified silica had free space between its particle and the rubber matrix, comparing with the modified silica compound that had no any void and the silica was completely covered by rubber matrix. The reasons are that silica contains the hydrophilic groups (silanol [R_3SiOH] and siloxane [$SiOR_2$] groups) on its surface but natural rubber contains hydrophobic groups (cis-1,4-polyisoprene), whereas the surface of the modified silica was coated by polyisoprene that has high compatibility with natural rubber. Therefore, the modified silica particle can be closed by natural rubber matrix.

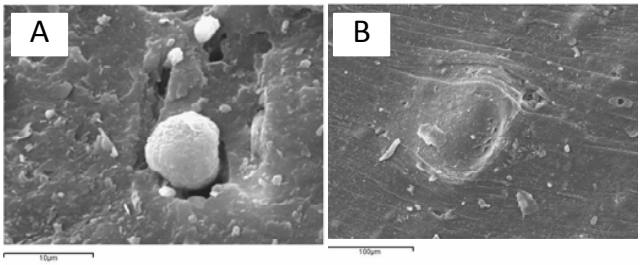

Fig. 5 SEM images of adhesion between silica and natural rubber
A) Unmodified silica and B) Modified silica

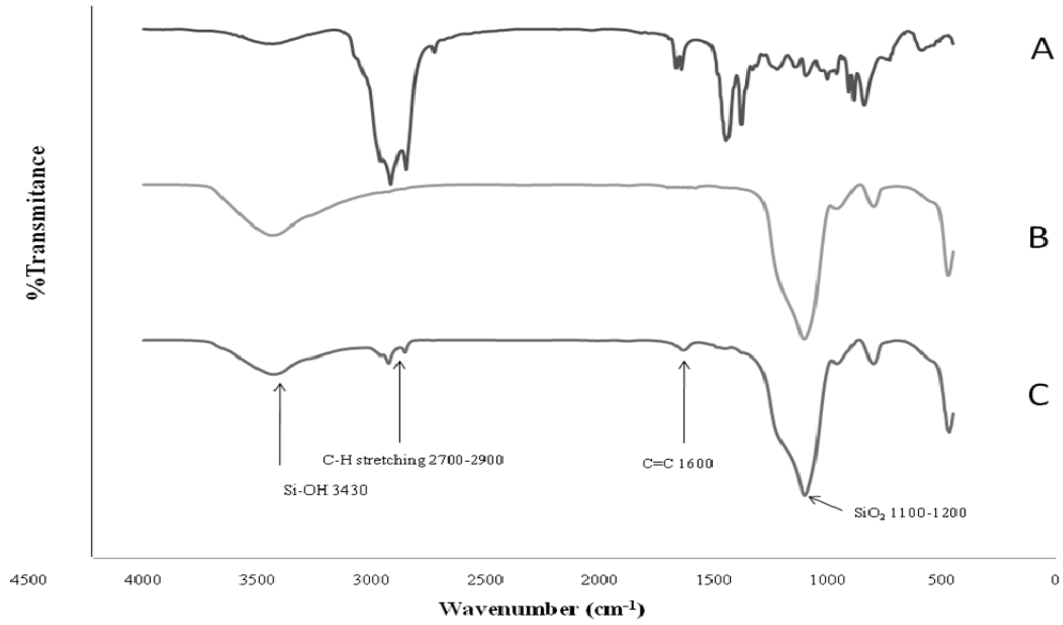

Fig. 3 FT-IR spectra of: A) polyisoprene, B) unmodified silica, and C) Admicellar-modified silica

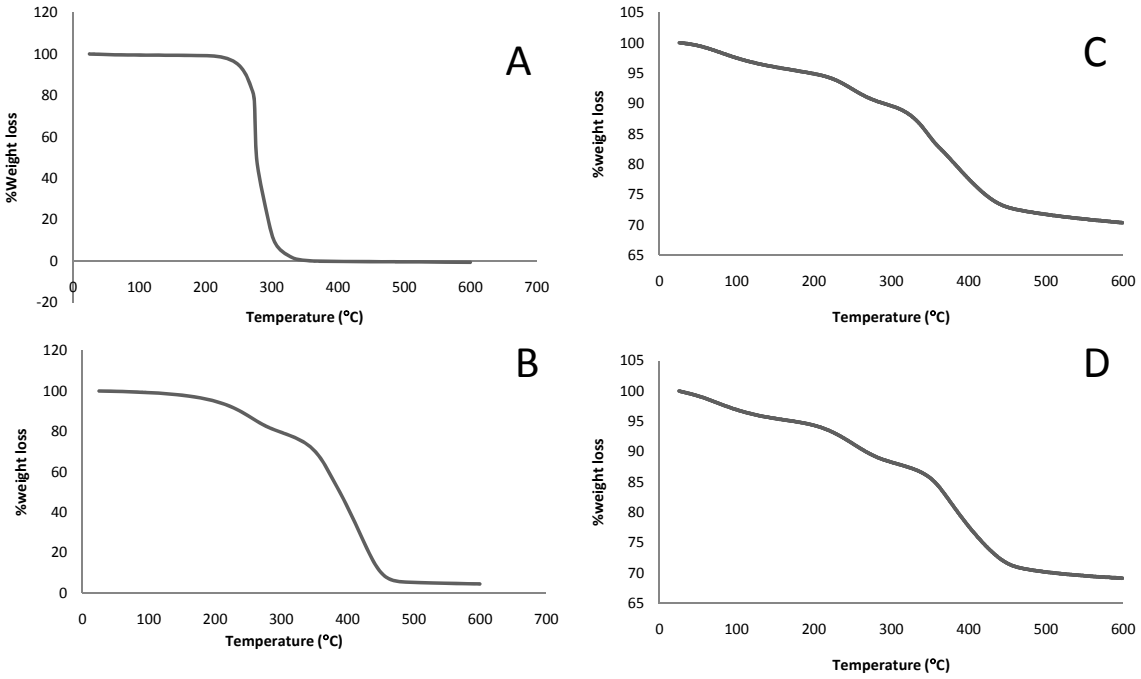

Fig. 4 TGA thermograms of: CTAB (A), polyisoprene (B), unmodified silica, and admicellar-modified silica (D)

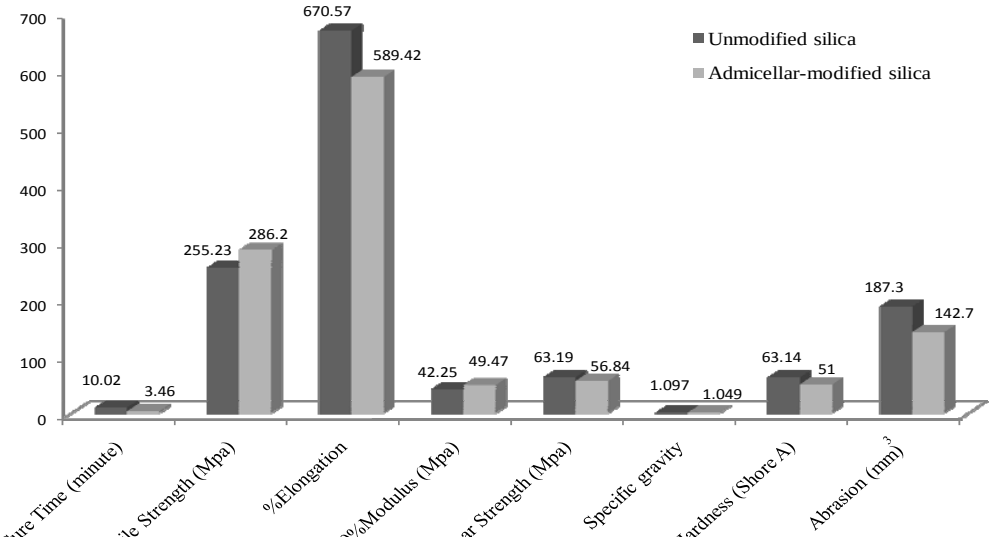

Fig. 5 The all properties of natural rubber compound mixed with unmodified silica and modified silica

IV. CONCLUSION

It can be concluded that the natural rubber compound mixed with the modified silica by polyisoprene coating as a reinforcement material gave better cure time and other the mechanical properties such as tensile strength, modulus and abrasion resistance than the rubber compound mixed with unmodified silica. However, elongation, tear strength, specific gravity and hardness, these properties, they can not be developed by the modified silica.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial supports from The Thailand Research Fund (TRF). We also thank Banpan Research Laboratory Co.,Ltd with the kind support for preparing the rubber compounds and testing all their properties.

REFERENCES

[1] Ansarifar A., Azhar A., Ibrahim N., Shiah S.F., and Lawton J.M.D, "The use of a silanised silica filler to reinforce and crosslink natural rubber," *International Journal of Adhesion & Adhesives* 25 (2005) 77-86.

[2] POH B.T. and NG C.C. Effect of silane coupling agents on the mooney scorch time of silica-filled natural rubber compound. Eur. Polym. J. Vol.34, 7, pp. 975-979,1998.

[3] Urushihara Y., Li L., Matsui J., and Nishino T. In *situ* observation of filler displacement during tensile deformation of nanosilica-filled natural rubber using field-emission scanning electron microscope. Composites: Part A 40 (2009) 232-234.

[4] Nontasorn P., Chavadej S., Rangsunvigit P., O'Havior J.H., Chaisirimahamorakot S., and Na-Ranong N. Admicellar polymerization modified silica via a continuous stirred-tank reactor system: Comparative properties of rubber compounding. Chemical Engineering Journal 108 (2005) 213-218.

[5] Yooprasert M., Pongprayoon T., Suwanmala P. Hemvichian K. and Tumcharern G. Radiation-induced admicellar polymerization of isoprene on silica: Effects of surfactant's chian length. Chemical Engineering Journal 156 (2010) 193-199.

[6] Rattanasom N., Prasertsri S., and Ruangritnumchai T. Comparison of the mechanical properties at similar natural rubber filled with various reinforce-fillers. Polymer Testing 28 (2009) 8-12.

[7] Sae-oui P., Sirisinha C., Thepsuwan U., and Hatthapanit K. " Comparison of reinforcing efficiency between Si-69 and Si-264 in a conventional vulcanization system" Polymer Testing 23 (2004) 871-879.

[8] Rattanasom N. Saowapark T., and Deeprasertkul C. Reinforcement of natural rubber with silica/carbon black hybrid filler. Polymer Testing 26 (2007) 369-377.