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Improving properties of modified silica by admicellar polymerization technique for inner rubber tube products

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Abstract

Modified silica using admicellar polymerization technique (APT) has shown to effectively reinforce natural rubber products. The study has shown that reinforcing natural rubber with APT-modified silica at the 40 phr yields excellent mechanical and ozone aging resistant properties. For the 40 parts per hundred of rubber (phr) sample, the cure time was found to be 138.23 ± 1.06 s. The tensile strength, the 300% modulus and the tear strength were 21.55 ± 0.40 Megapascal (MPa), 4.62 ± 0.17 MPa and 73.67 ± 1.58 MPa, respectively. The elongation at break was measured to be 579.96 ± 6.70%. The hardness was 55.33 ± 1.15 shore A. These surpass the standard values for motorcycle and bicycle rubber inner tube products, according to the Thai Industrial Standard (TIS) 683-2530 and TIS 652-2529. Scanning electron microscopy studies revealed that their outstanding mechanical properties were related to the better adhesion between the silica particles and the rubber matrix, resulting from the thermal admicellar polymerization process. The minimal cracks observed after the ozone aging resistance test also suggest high durability.

Keywords: Admicellar polymerization, Inner rubber tube, Silica

1. Introduction

The needs of rubber products have been continuously increased, especially in the tyre industry. Many researchers have developed reinforcement formula to satisfy customers and meet necessary industrial requirements. Recent research focus is to improve various properties of tyres by adding fillers. In general, the automobile and motocycle tyre industry uses carbon black as a reinforcing filler to improve strength of the product. However, carbon black-filled tyres have some drawbacks, such as low flexibility and the color of the product is only restricted to black. The development of other types of fillers that allow products to have lighter colors might open up new markets for the tyre industry.

Silica is often used as reinforcing materials because of its excellent mechanical properties [1-5]. Reinforcing rubber with silica has shown to improve the flexibility, as compared to those with carbon black [2,6,7]. Using silica as a reinforcing material also enable more colors to be added to the products [2]. Yet, silica's surface is composed of silanol functional groups, causing its surface to be hydrophilic. In contrast, rubber surface is hydrophobic. Thus, silica particles cannot be well-bonded with rubber, hindering their reinforcement property that could be useful to improve strength of rubber products. Surface modification is, therefore, important to improve adhesion between silica particles and the rubber matrix. Coupling agents such as amino silane could be used to improved adhesion between silica particles and the rubber matrix [1]. Alternatively, the modification of silica surface can be done through a process called admicellar polymerization technique (APT). This forms a polymeric thin film on the surface of silica that allow better adhesion between the reinforcing particles and matrix [8-11].

Previous studies have shown that the admicellar polymerization induced polyisoprene film can also reduce the acidic nature of silica to improve vulcanization and curing time [12-17]. Gamma radiation-induced admicellar polymerization of isoprene on surface of silica has also shown to provide excellent film formation on silica that help improving adhesion with the rubber matrix [18,19]. Among various modified and unmodified silica-rubber products, APT-modified silica has shown to effectively improve mechanical properties of natural rubber products [1].

For industrial applications, thermal-induced APT is more suitable. This is because it is easily scalable to ramp up production, while providing products with outstanding mechanical properties. A recent study has demonstrated that thermal-induced APT tyres using silica concentration of 30 phr possess good mechanical properties and meet all required properties for automotive and motorcycle tyres [2]. Thermal-induced APT with other phr ratio should also be explored to obtain the optimal silica content that best improve the mechanical properties as well as the adhesive between silica and rubber. This work aims to search for optimal content of the modified silica through thermal APT on the mechanical properties of reinforced natural rubbers, especially for the inner tube products. Their mechanical properties, curing time, resistance against ozone are reported and compared to those reinforced with the carbon black and unmodified silica. The microstructural differences between unmodified and thermal APT-modified silica are also reported and discussed.

2. Materials and methods

2.1 Materials

To prepare APT-modified silica, silica (Hi-Sil®255, Tokuyama Siam Silica Co. Ltd., Thailand), cetyltrimethyl ammonium bromide (CTAB 98%, Fluka, Germany), potassium persulfate (Sigma Aldrich, USA), ethanol (Fisher Scientific, USA) and isoprene monomer (Fluka, Germany) were used in the admicellar polymerization process. Ingredients used for compounding rubbers included natural rubber (STR10-CV50, Bangkok Rubber Co., Ltd., Thailand), carbon black N660 (Behn Meyer Specialty Chemical, Malasia), silica (Hi-Sil®255, Tokuyama Siam Silica Co. Ltd., Thailand), zinc oxide (Global Chemical, Thailand), stearic acid (Pacific Oleo Chemicals, Malasia), polyethylene glycol 4000 (Dongnam Chemical, Korea), Mercapto benzothiazyl disulfide (MBTS, Puyang Willing Chemicals, China), anti-scorching agent (PVI, Toray Fine Chemicals, Japan), anti-ozone wax (okerin 5258, Dupont, USA), calcium carbonate (CP-P 206, Tre Chemicals, Netherland), antioxidant powder (bemox-L, Tre Chemicals, Netherland), sulphur (Utids Enterprise, Thailand).

2.2 Modified silica process

First, the surfactant and sodium hydroxide (pH 8) was dissolved in 8 L of distilled water. Silica (400 g) was then added into the solution. The mixture was stirred for 2 h. Subsequently, 500.99 ml of ethanol, 10.8 g of potassium persulfate, and 40 ml of isoprene were added. Finally, the mixture was stirred for another 2 h and heated at 70 ℃ for 2 h to allow the polymerization to occur. The excess surfactant on the surface of silica samples were rinsed with distilled water. The samples were then dried in an oven at 40 ℃ for 3 days before the next procedure.

Admicellar polymerization consists of a four-step process: admicelle formation on the surface, monomer adsolubilization, polymerization of the monomer dissolved in admicelles, and surfactant removal to expose the surface of polymer film. Figure 1 shows schematic representation of the APT process.

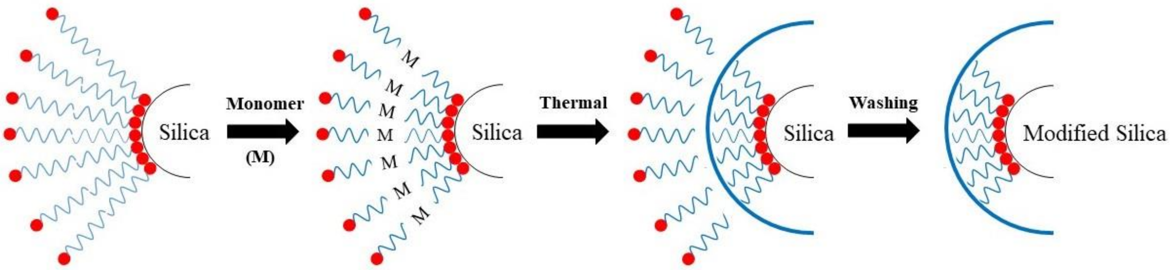

Figure 1 Schematic representation of thermal-induced admicellar polymerization for the modification of silica surface.

2.3 Compounding, vulcanization and rubber mastication

Natural rubber (STR10-CV50, 300 g) was prepared in the two-roll mill (Yi Tzung Co., Ltd, Taiwan) to lessen its viscosity for 10 min. The mixture of the rubber compound was then added according to the ingredients as shown in Table 1. Stearic acid, Bemox-L and the fillers including carbon black, silica and APT- modified silica were then added and continuosly masticated the rubber for 24 min. Processing aids including PEG4000, Okerrin, $CaCO_3$ and PVI were also added. The activator, zinc oxide, was filled and was carefully grinnded The accelerators, MBTS, were subsequently added. The grinding was continuously maintained for another 7 min. Subsequently, a vulcanizing agent, sulfur, was added. To ensure that all ingredients were well mixed, the rubber compound was thoroughly pounded. After the grinding, a moving die rheometer (MDR Model M-3000A, Gotech Testing Machines inc., Taiwan) was employed to assess the cure time. The compressed rubber compound was obtained using a compression molding (G30H15GX, Wabach Genesis Press, USA) at the pressure of 160 kg/cm^2 and the curing temperature of 160 °C for carbon black, and 145 °C cure for silica and modifiled silica, respectively. Finally, the as-prepared vulcanized rubber compound was rested for 24 h.

Table1 Rubber compound formulation.

Ingredients (phr)	Natural Rubber	Stearic Acid	Bemox-L	Carbon black	Silica	Modified silica	Okerrin	$CaCO_3$	PVI	PEG4000	ZnO_2	MBTS	Sulphur
Carbon Black	100	2	1	20-50	-	-	1	25	0.25	1.5	5	0.75	1.8
Silica	100	2	1	-	20-50	-	1	25	0.25	1.5	5	0.75	1.8
Modified silica	100	2	1	-	-	20-50	1	25	0.25	1.5	5	0.75	1.8

2.4 Characterization and Properties testing

A vernier caliper (Mittutoyo model HFW960, Japan) was used to determine sample thickness. A cutting board and machine from PVI (PS-01 Flexo Meter, USA) was used to prepare the sample. A mooney viscometer (MV model M-3000, Gotech Testing Machines inc., Taiwan) was used to determine moonny rubber viscosity. The universal testing machine (AI-7000S from Gotech Testing Machines inc., Taiwan) was used in this work. A durometer shore A (Taclock Co. Ltd., Japan) was used to determine rubber hardness. Surface morphology was studied by a scanning electron microscope (FEI model Helios Nanolab G3 CX SEM) using an accelerating voltage of 5 kV. Prior SEM characterization, the samples were sputtered coated with Au. The ozone aging resistance of the rubber samples was measured using the ozone aging tester (EG-2001 from Toyoseiki, Japan). Each report data is averaged from 3 measurements.

3. Results and discussion

3.1 Mechanical properties of reinforced rubbers using various types of reinforcement

To grasp better understanding about the effect of different types of fillers on various properties of reinforced rubber, carbon black, unmodified silica and APT-modified silica at the content of 30 phr were prepared and tested according to the TIS 683-2530 and TIS 652-2529 standards. The overall testing results are shown in Figure 2.

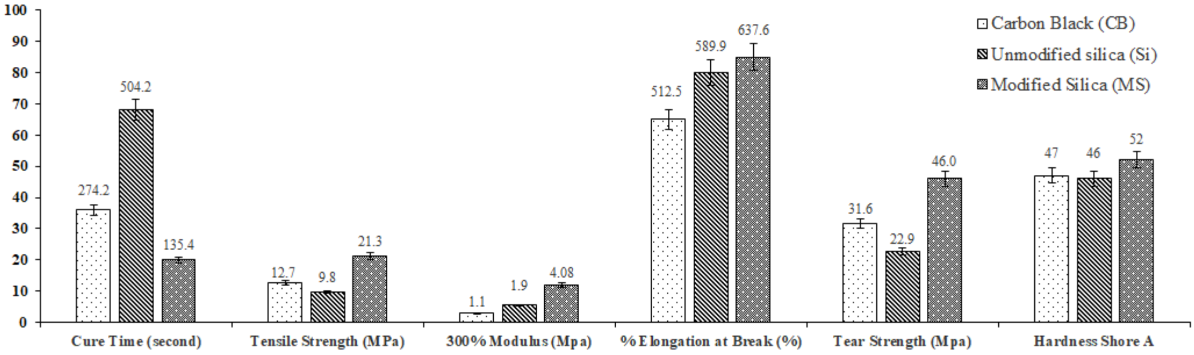

Figure 2 The overview of natural rubber reinforced with various types of reinforcement.

The reinforced natural rubber with APT-modified silica were found to have the fastest cure times, compared to carbon black- and unmodified silica-reinforced rubbers. The APT-modified silica-reinforced natural rubber also possess the best mechanical properties among the tested samples. This might due to the polyisoprene film formation during the APT process that help decreased the acidic nature of silica, which led to superior vulcanization, shorter cure time, and higher tensile strengths. The results demonstrated that surface APT-modified silica-reinforced natural rubber has larger modulus than those reinforced with carbon black and unmodified silica.

3.2 Mechanical properties of natural rubber reinforced with different modified silica ratio (MSR)

To explore the effect of thermal APT-modified silica contents on various properties of reinforced rubber, the samples were prepared using modified silica content of 20-50 phr. Figure 3 revealed that the cure time was increased with increasing modified silica content. The tensile strength was found initially increased with increasing modified silica content. However, when modified silica ratio was greater than 40 phr, the tensile strength deceased. This might be due to the agglomeration of reinforcing silica particle at higher ratio. The 40 phr sample was found to yield the highest tensile strength of 21.55 ± 0.40 MPa, while ccure time of 138.23 ± 1.06 s was still reasonable.

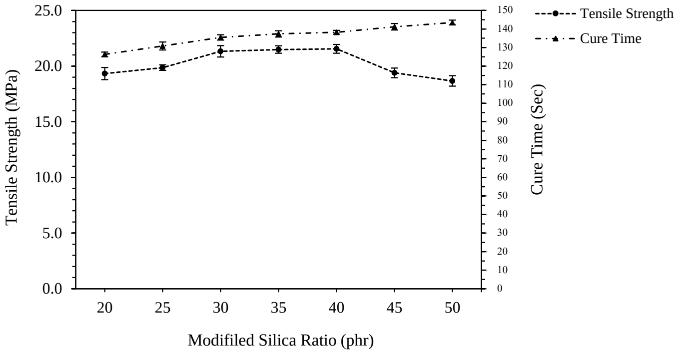

Figure 3 Tensile strength and cure time of modified silica-reinforced natural rubbers reinforced.

Figure 4 shows the tear strength and 300% modulus of modified silica-reinforced natural rubbers. It was found that both the tear strength and 300% modulus increased with increasing content of modified silica upto 40 phr. The 300% modulus and tear strength were found to be 4.62 ± 0.17 MPa and 73.67 ± 1.58 MPa, respectively. As the modified silica ratio is higher than 40 phr, the 300% modulus and tear strength were found to decrease. This is consistent with the decreasing tensile strength when modified silica content was higher than 40 phr, as shown in Figure 3. The results suggest weaker composite at too high modified silica content, which may be due to the agglomeration of modified silica particles.

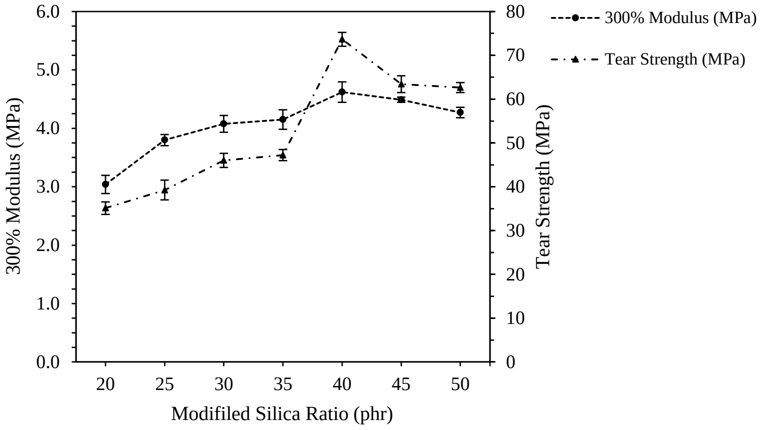

Figure 4 Tear strength and 300% modulus of modified silica-reinforced natural rubbers.

Figure 5 shows the hardness and elongation at break of APT - modified silica-reinforced natural rubbers. The elongation at break was found to decrease as the MSR increased because the adhesive properties needed less MSR. On the other hand, the hardness was found to increase as the MSR increased. At the modified silica ratio of 40 phr, the elongation at break and the hardness were measured to be 579.96 ± 6.70% and 55.33 ± 1.15 shore A, respectively.

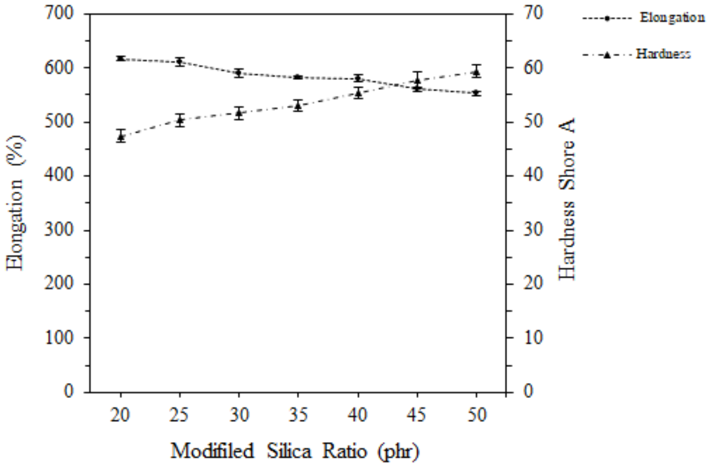

Figure 5 Hardness and elongation at break of modified silica-reinforced natural rubbers.

3.3 Scanning electron microscopy (SEM)

To qualitatively examine the bond between the natural rubber, the modified and unmodified silica particles, SEM were employed to characterize the structural morphologies of the samples. The MSR of 40 phr was used in these comparisons. Figure 6 shows SEM micrographs of reinforced rubber before and after tensile tests. Figure 6 (A) shows a void between the unmodified silica particles and the natural rubber matrix, indicating weak adhesion between the two interfaces. The different polarities between the two surfaces might be responsible for the weak bonding. The unmodified silica surface has been widely regarded as hydrophilic, while that of rubber surface is hydrophobic, respectively. In contrast, the thermal APT-modified silica reinforced rubber showed no cavity in the structure (Figure 6 (B)). The surface of silica was found covered with polyisoprene film, which indicated that the natural rubber strongly attached to the modified silica particles.

After the tensile tested, the SEM micrographs of the tested samples were also taken in orders to analyze and compare the fracture surfaces. Figure 6 (C) clearly displays the detachment of silica particles from the rubber matrix, whereas no separation of the modified silica particle from the rubber matrix was observed in the thermal APT-modified silica sample (Figure 6 (D)). These results clearly demonstrated the significant improvement in the adhesion between the natural rubber and modified silica resulting from the APT treatment.

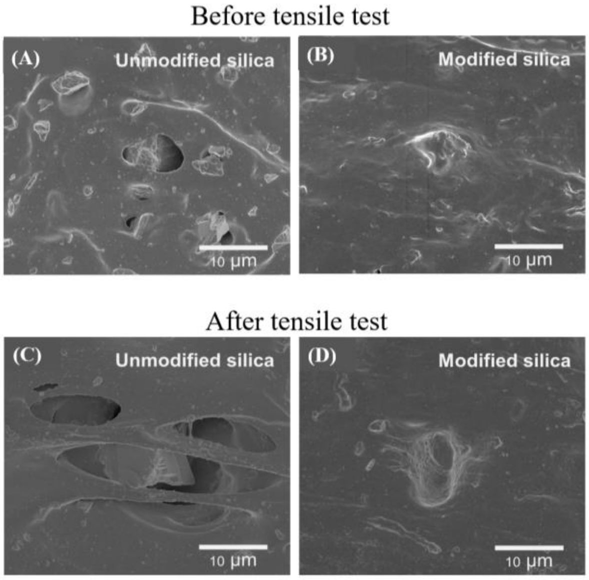

Figure 6 SEM micrographs of natural rubber reinforced with (A) unmodified silica before the tensile test, (B) modified silica by APT before tensile test, (C) unmodified silica after tensile test, (D) modified silica by APT after tensile test.

3.4 Ozone aging resistance (SEM)

The ozone aging resistance test is an investigation to realize the durability of thermal APT-modified silica reinforced natural rubber. Reinforced rubber with 4 different MSR content including 20, 30, 40 and 50 phr were subjected to ozone aging tester in accordance with ISO 1431-1: 2012. The samples were prepared by compression molding using the compression of 160 kg/cm^2, at the temperature of 145 °C for 4 min. The ozone aging test was conducted under ozone concentration of 25 pphm at the temperature of 40 °C. The samples were subjected to 20% elongation for a period of 72 h. The specimens were then compared under optical microscope using the magnification of 9X to determine the deterioration of the rubber as shown in Figure 7.

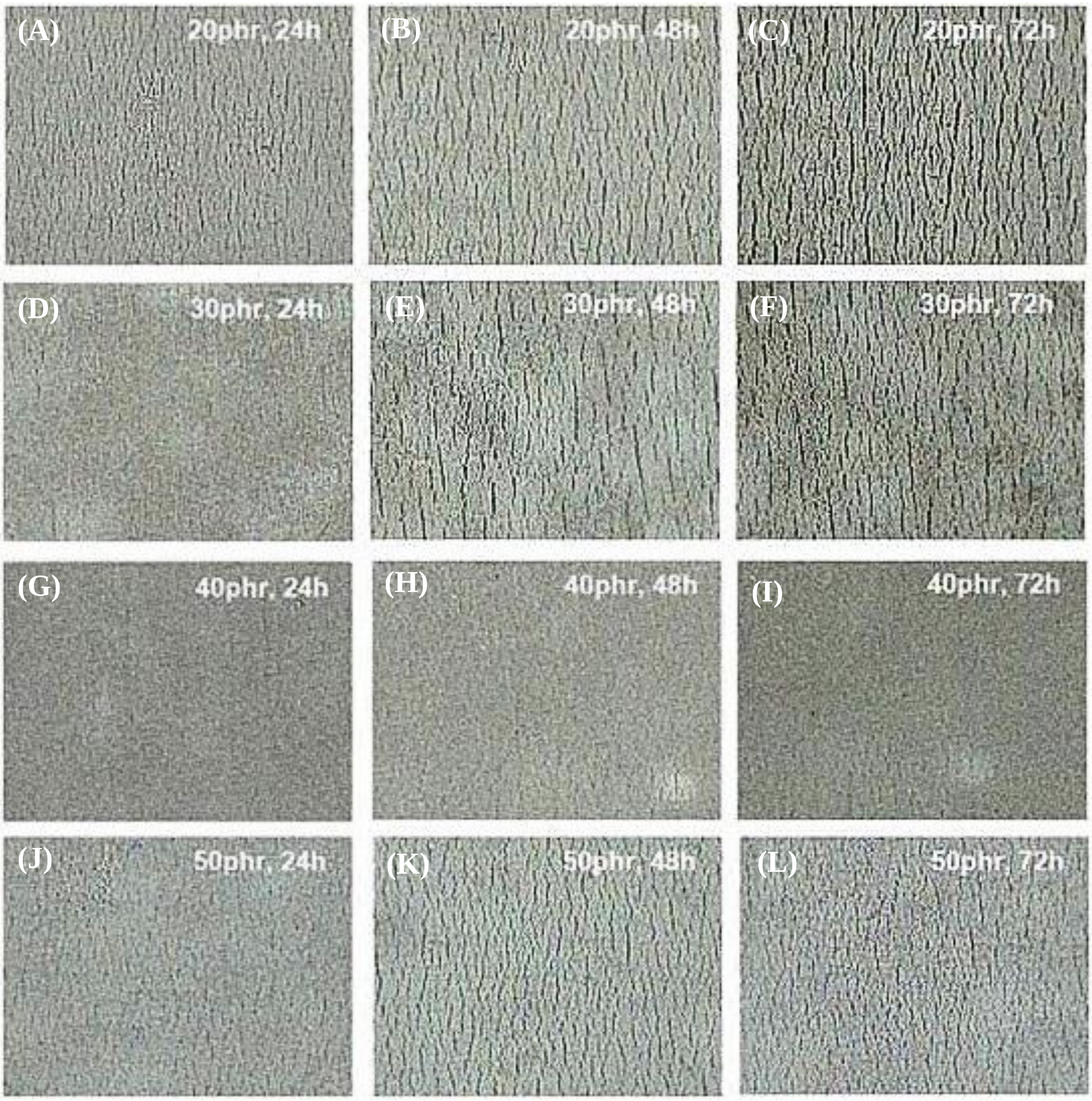

Figure 7 The optical micrographs of modified silica-reinforced natural rubber (A) 20 phr 24 h, (B) 20 phr 48 h, (C) 20 phr 72 h, (D) 30 phr 24 h, (E) 30 phr 48 h, (F) 30 phr 72 h, (G) 40 phr 24 h, (H) 40 phr 48 h, (I) 40 phr 72 h, (J) 50 phr 24 h, (K) 50 phr 48 h, (L) 50 phr 72 h.

Figure 7 (A, D, G and J) shows the surface morphologies of modified silica reinforced natural rubber with various MSR (20, 30, 40 and 50 phr, respectively) after exposuring to ozone for 24 h. It was found that surface cracks existed in all specimens, which indicated rapid deterioration under ozone in these samples. Largest cracks were observed in the 20 phr sample, while minimal cracks were found in the 40 phr sample. Similar trends were also observed in the specimens subjected to ozone test for 48 h and 72 h as shown in Figure 7 (B, E, H and K) and Figure 7 (C, F, I and L), respectively.

4. Conclusions

A filler prepared by modified silica with polymerization technique was applied. Later, Mechanical properties of as-prepared thermal APT-modified silica reinforced rubbers were analyzed and compared to those reinforced with carbon black and unmodified silica. Consequently, the result showed that the thermal APT-modified silica reinforced rubber exhibited superior properties in every aspect. Further study has shown that reinforcing natural rubber with APT-modified silica at the 40 phr content yields the best mechanical and ozone aging resistant properties. For 40 phr sample, the cure time was 138.23 ± 1.06 s. The tensile strength, the 300% modulus and the tear strength were 21.55 ± 0.40 MPa, 4.62 ± 0.17 MPa and 73.67 ± 1.58 MPa, respectively. The elongation at break was measured to be 579.96 ± 6.70%. The hardness was 55.33 ± 1.15 shore A. This modified silica content is believed to be optimal for formulating the chemical formula for inner tube products.

5. Acknowledgements

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