Effect of Different Salinization Methods of Silica Filler on Rubber Reinforcement

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Abstract: *The main objective of this work was to investigate the effects of three different methods of surface modification using bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) on silica filler to improve silane linkages between rubber matrix and filler. The filler was treated with silane coupling agent using aqueous, dry, and integral blend methods. Evidence that coupling agent had occurred between fillers and TESPT was identified by Fourier transform infrared spectroscopy (FTIR). The results exhibited the advantages of TESPT as a coupling agent between fillers particles and rubber also revealed that silica has better dispersion in dry method. The effects of different surface modification methods on mechanical properties and morphological characteristics of natural rubber were also investigated.*

Keywords: rubber, silane coupling agent, silica, TESPT

1.   INTRODUCTION

The performance of rubber materials is greatly affected by the dispersion of reinforcing fillers. Almost all rubber materials are produced with the addition of filler particles.[1] The most commonly used inorganic fillers are silica, fibres, ferrite, talc, and calcium carbonate.[2–5] Major problems in the incorporation of the inorganic fillers in the rubber materials are the incompatibility, poor wettability, and weak adhesion between the filler and rubber as well as the non-uniformity of filler dispersion leading to poor physical and mechanical properties. In order to solve these problems, addition of coupling agent is required to ensure the production of final product having high performance.[1,6]

Bifunctional coupling agent such as bis-(3-triethoxysilylpropyl) tetrasulphide (TESPT) is by far the most popular and effective coupling agent for hydrocarbon rubber. The TESPT is an organic silane with ethoxy hydrolysable groups at both ends which enable the silicon groups to bond with inorganic fillers and tetrasulphane groups (S_4 ring) of its centre capable to form crosslink with the rubber molecule chains. Although this type of surface modification is established for enabling different types of fillers such as silica, iron sand, halloysite nanotubes, wood flour, and natural fibre to be used as reinforcement fillers in rubber composites.[7–11] However, the effective processing method to apply TESPT to the inorganic fillers has not been extensively studied.

Therefore, in this work, three different methods namely, aqueous, dry, and integral blending methods were used for surface treatment of TESPT. Evidence of silane coupling agent between fillers and TESPT was verified by Fourier transform infrared spectroscopy (FTIR). Crosslink density assessment and tensile properties of the rubber composites were measured to evaluate the interfacial interaction between the fillers and the rubber matrix.

2.   EXPERIMENTAL DETAILS

2.1   Materials

Natural rubber (Standard Malaysia Rubber [SMR] L grade) and other chemicals including zinc oxide, stearic acid, n-cyclohexyl-2-benzothioazole sulfonamide (CBS), tetramethylthiuram disulphide (TMTD), and n-isopropyl-n'-phenyl-p-phenylenediamine (IPPD) were all purchased from Zarm Scientific & Supplies Sdn. Bhd. (Pulau Pinang, Malaysia). TESPT was purchased from Leap LabChem Co. Ltd. (China). Precipitated silica (Grade Vulkasil S) with density 2.0967 g cm^{-3} and average particle size of 22 nm was supplied by Bayer Co. (M) Sdn. Bhd. (Pulau Pinang, Malaysia).

2.2   Surface Modification of Fillers Particles

2.2.1   Aqueous method

The surface modification of fillers was carried out using an aqueous alcohol solution method. The fillers were subjected to surface treatment with TESPT at 6% by weight (wt%) of the fillers. An aqueous alcohol solution of 95% ethanol was used, and the pH of the solution was adjusted with acetic acid to 4.0–4.5. The TESPT of predetermined quantity was dispersed in the ethanol solution at a ratio

of 1:100 and the mixed solution was stirred for 5 min to assure the hydrolysation of the silane coupling agent. The fillers were then added and stirred for an additional 30 min at room temperature to ensure a uniform distribution of the coupling agent on the surface of the fillers. The mixture was filtered and washed three times with ethanol to remove unreacted coupling agent. The treated fillers were then dried at 80°C in an oven until constant weight was achieved.

2.2.2   Dry method

In dry method, the TESPT silane coupling agent was added at full strength and evenly dispersed in the fillers as it was mixed at high speed mixer. Firstly, the fillers of predetermined quantity were added in a container of rotating mixer. After this, 1 wt % of water was then added to the fillers and the container of rotating mixer was closed to minimise contact with air and let it sit for 8 h at a temperature of 50°C. This promotes even dispersion of the water on the filler surface. Then, the wet fillers were subjected to surface treatment with TESPT at 6 wt % relative to the weight of the fillers. The TESPT was added in the container and the mixture was mixed at 200–250 rpm for 4 h using rotating mixer. Finally, the treated fillers were dried at 80°C in an oven until a constant weight was achieved.

2.2.3   Integral blend methods

In integral blend method the TESPT silane coupling agent was used as a simple additive during mixing and compounding of the rubber and other ingredients in a conventional laboratory two roll mill (XK 160). TESPT at 6 wt % relative to the weight of the particle was added to the rubber compound. The addition of the TESPT was carried out after the fillers were uniformly dispersed in the rubber compound to prevent agglomeration. The mixing and compounding process and sequence of addition of the additives are explained in the next section.

2.3   Preparation of Rubber Composites

The compound formulation used in this study is given in Table 1. Formulations were compounded using a conventional laboratory two roll mill (model XK-160). The compounding began with mastication of rubber on two roll mill for 2–3 min. After mastication, the rubber had become invested on the hot roll, additives (zinc oxide, stearic acid, and IPPD) were then added followed by treated fillers (silica, ferrite, and kenaf) for both aqueous and dry methods or untreated fillers followed by TESPT for integral method. The addition of accelerators (CBS and TMTD) and sulphur were delayed to the last part of the process to prevent premature vulcanisation during compounding. The mixing time was approximately

30 min. The cure time (t90) was then determined using an MDR 2000 Mosarto Moving Die Rheometer (Akron, OH, USA) according to ISO 3417 at 150°C. Compounded rubber samples weighing 35 g were placed in a mould (152 × 123 × 2 mm^3) and were cured in a compression moulder at 150°C under a pressure of approximately 12 Mpa.

Table 1: Formulation of rubber compound.

Material	Loading (phr*)	
	Aqueous, dry, and integral methods	Control sample
Natural rubber (SMR L grade)	100	100
Zinc oxide	5	5
Stearic acid	1	1
IPPD	2	2
Silica	50	50
TESPT (wt%)	6	0
CBS	2	2
TMTD	1	1
Sulphur	1.5	1.5

*Note: *phr = per hundred rubber*

2.4   FTIR

FTIR was recorded using a Perkin Elmer Spectrum instrument (Massachusetts, USA) under an inert air atmosphere, to investigate the inorganic fillers and rubber interaction in the compounds at different treatment methods. The FTIR measurements were performed directly on the final cast rubber composites, and the spectral range was from 900 to 3,500 cm^{-1}. Five separate spectra were acquired at different locations on each sample analysed.

2.5   Morphology

The fracture surfaces of the rubber composites were examined using a field emission scanning electron microscope (FE-SEM model Zeiss SUPRA 35VP, Berlin, Germany). The samples were immersed in liquid nitrogen to frozen and subsequently snapped into pieces to expose the interior of fractured surface. The fracture surface was coated with gold prior to observation at an acceleration voltage of 10 kV.

2.6   Tensile Properties

The tensile tests were performed at room temperature using an Instron testing machine (Model 3366, Massachusetts, USA) according to the ASTM D624 standard test method at a crosshead speed of 500 mm min^{-1}. Dumbbell tensile specimens (gauge length of 50 mm and width of 6.4 mm and thickness of 2 mm) were used for the test. Tensile strength, Young's modulus, and elongation at break were determined. Five specimens for each set of material were tested.

3.   RESULTS AND DISCUSSION

3.1   FTIR

FTIR spectra analysis of rubber filled with untreated and treated silica using different silane treatment methods is shown in Figure 1. For untreated silica filled rubber composites, rubber can be identified by two characterisation peaks around 2,920 and 2,850 cm^{-1} assigned to the C–H stretching vibrations. More peaks are observed at 1,375 and 1,465 cm^{-1} and are assigned to CH_2 stretching, and CH_3 and CH_2 bending, respectively.[12] Silica in the composites can be identified from strong stretching vibrations of the siloxane (Si–O–Si) bond at 1,100 cm^{-1}, and a small peak at 950 cm^{-1} assigned to Si–O stretching, indicating the presence of some silanol (Si–OH) groups.[13] After silica filler rubber composites treated with TESPT, the FTIR spectra show that most of the silanols (Si–OH) reacted to form Si–O–Si bonds. The increment of intensity and shift of peak at 1,100 cm^{-1} are the evidence of interactions. Based on the different processing method it is clear that both aqueous and dry methods show better interaction between silica and rubber than integral method.
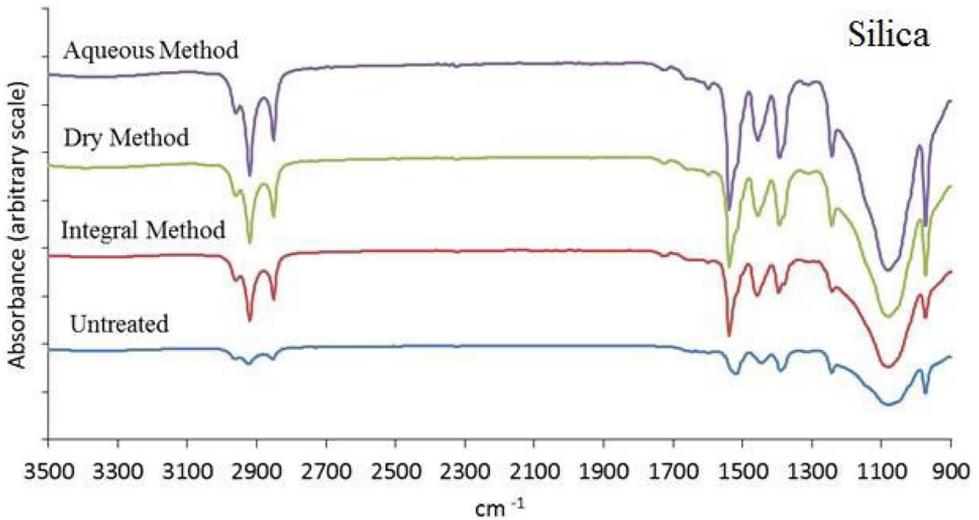
Figure 1:   FTIR spectra of silica filled rubber composites using different TESPT treatment
             methods.

3.2   Morphology

To evaluate the dispersion of fillers and the rubber matrix, the morphologies of the fractured surface of rubber with untreated and treated silica using different silane treatment methods are presented in Figure 2. As shown in Figure 2(a), the fractured surface of untreated silica filled rubber composite exhibits a relatively rough surface with uneven distribution of silica particles. In addition, agglomerate areas of several micrometres can be clearly found in the silica dispersed in the rubber. After the silane treatment of silica, the fractured surface of composites exhibits better dispersion, the agglomerates were effectively broken and uniform distribution by using silane treatment of aqueous and dry methods as shown in Figure 2(b) and 2(c). In Figure 2(d) for the treated silica using integral method, the dispersion of the fillers was improved but some of silica particles agglomerate can be observed. In general, dry method shows the best dispersion for silica filler in the rubber matrix.
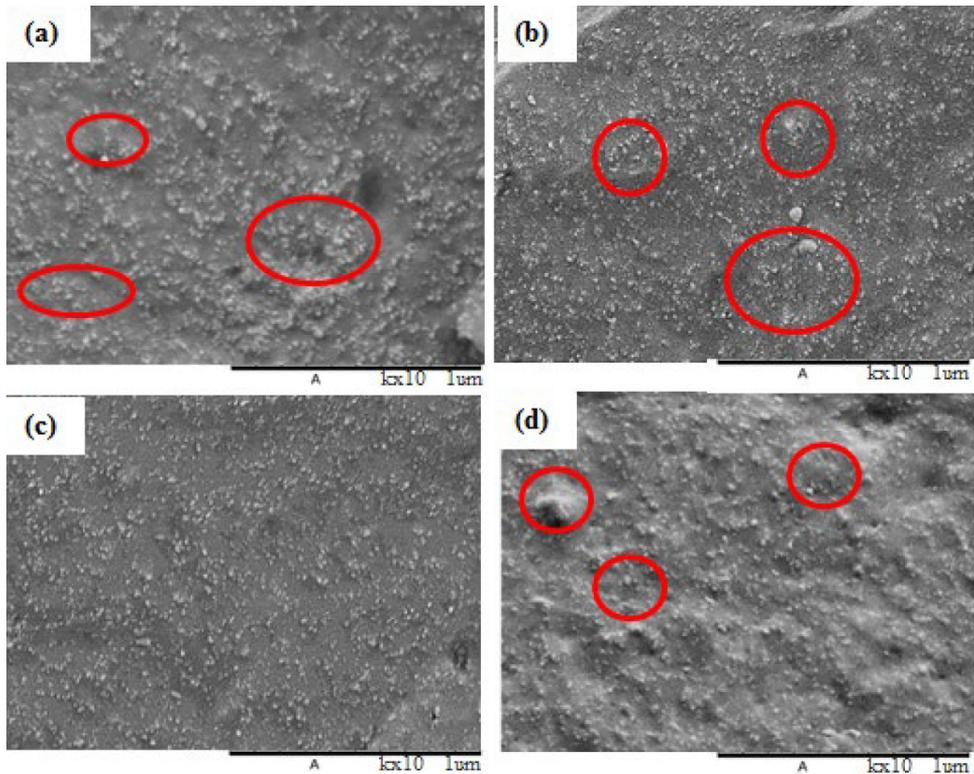
Figure 2:   SEM images of fractured surface: (a) untreated, (b) aqueous, (c) dry, and (d) integral blend methods for silica filled rubber composites.
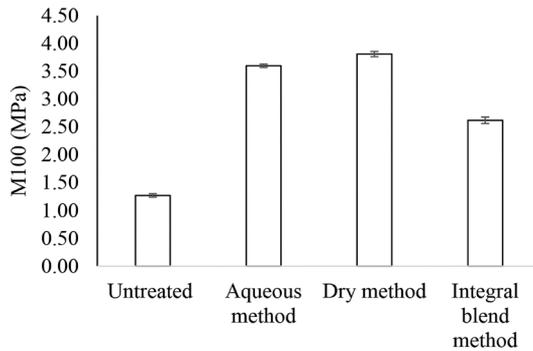
3.3   Tensile Properties

The effect of silica filler on the tensile properties of rubber composites using different TESPT treatment methods are shown in Figure 3. As seen in Figure 3(a), treated silica showed an increment in the tensile strength compared to those of the untreated rubber composites. Two main factors can explain the increment in the tensile strength of the TESPT treated silica compared to untreated rubber composites. First, the silane functional groups can produce strong filler-rubber bonding and thus improve their stress transferring efficiency, leading to increase in tensile strength. In addition, the silanol group grafted onto the surface of fillers can prevent stacking and aggregation of fillers, thus, improve the dispersion state of filler in rubber matrix.[14] Second, the dispersion methods used for silane treated silica in the rubber matrix are the most important factor to be considered. Comparatively, both aqueous and dry methods showed high tensile strength than integral method due to stronger interaction and uniform dispersion of silica.
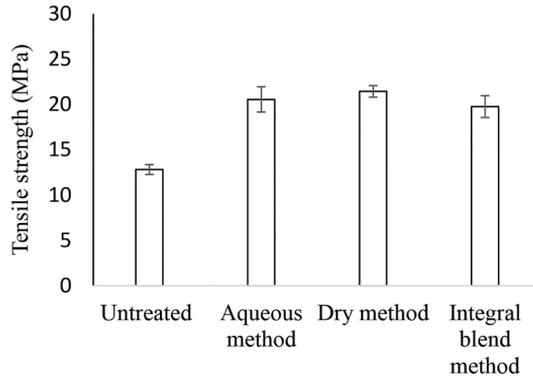
(a)
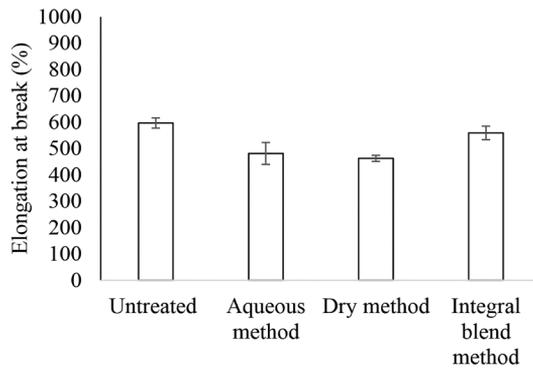
(b)

(c)

Figure 3:   Tensile properties of silica filled rubber composites using different TESPT treatment methods: (a) tensile strength, (b) elongation at break, and (c) modulus M100.

The elongation at break of silica filled rubber composites using different TESPT treatment methods are shown in Figure 3(b). Addition of silica showed decrement in the elongation at break compared to those of the untreated rubber composites. This was because the natural rubber matrix grew stronger and stiffer with inclusion of the treated fillers and resulted in a lower elongation.[15] The most probable explanation for the lower elongation at break for the samples prepared in the presence of TESPT is that TESPT probably settled on the interface between the silica particles and rubber matrix and did not form part of the network. In contrast to tensile strength, both aqueous and dry methods showed lower elongation at break compared to integral method. The higher elongation at break for integral method maybe attributed to poor interaction between fillers and rubber matrix that led to increase in the elongation at break.

The M100 of silica filled rubber composites using different TESPT treatment methods exhibited the same trend as the tensile strength. As shown in Figure 3(c), treated fillers filled rubber composites showed an increment in the modulus M100 compared to those of the untreated rubber composites. The improvement in tensile modulus, associated with the addition of a coupling agent, has been reported in the past.[16] The presence of silane coupling agent reduces the chain mobility and increase rigidity of the treated rubber composites. Thus, exhibit high modulus M100 of the composites.[17] Moreover, the dry method has the highest M100 followed by aqueous and integral methods.

4.   CONCLUSION

In this work, silica filler was successfully modified with TESPT using aqueous, dry, and integral blend methods. FTIR spectra showed that the silanols (Si–OH) reacted to form Si–O–Si bonds. The intensity peak of FTIR spectra revealed that aqueous and dry methods had better interaction between silica and rubber than integral blend method. FTIR results were supported with SEM of the fractured surface where the filler distribution was improved with less agglomeration within the rubber matrix. It was also found that dry method had the highest tensile strength and M100 compared with aqueous and integral blend methods. However, the elongation at break was found to be the lowest compared to other methods, which could be explained due to reduce the chain mobility and increase rigidity of the treated rubber composites.

5.   ACKNOWLEDGEMENTS

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