Research article

Effect of plasma-polymerised acetylene-coated silica on the compound properties of natural rubber composites

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ABSTRACT

Silica-filled natural rubber (NR) encounters incompatibility problems, owing to the strong particle-particle interaction arising from the hydrogen bonds of hydroxyl groups, which generally leads to the formation of agglomerates. The addition of coupling agents, especially silane coupling agents, reduces the agglomeration. However, this has some disadvantages, such as toxicity, a risk of pre-curing, and the generation of ethanol during mixing. This work aims to focus on the effect of filling the plasma-polymerisation of polyacetylene-coated silica into natural rubber compounds. The deposition of plasma-polymerised acetylene applied to silica particles was firstly carried out using a radio frequency (RF) with an input power of 20 kW for 60 min and further incorporated into NR compounds. On the surface of the coated silica analysis, the formation of a polyacetylene layer on the silica surface was obviously confirmed that it exhibited more stability in water. The following polyacetylene-coated silica (PA-coated silica)-filled NR compound properties were analysed: mixing energy and temperature, Payne effect, complex viscosity, and cure characteristics. The NR compounds mixed with PA-coated silica showed a lower mixing torque, dumping temperature, Payne effect, and viscosity, when compared to NR compounds with unmodified silica and ordinary silane systems. However, the differences were insignificantly noticed in the cure characteristics of the compounds. Polyacetylene-coated silica developed from plasma polymerisation can be used to improve the uniformity of dispersion, as well as the compatibility of silica in a natural-rubber matrix, without changing its cure characteristics, compared to the one with a silane coupling agent.

1. Introduction

The chemical compatibility between a filler and a rubber matrix plays an important role in the dispersion of the filler in the matrix, and also the adhesion between the two phases, which determines the final properties of filled-rubber compounds. The mixing of silica-filled natural-rubber compounds is more difficult and complicated, compared to that of black carbon. This is because silica is an inorganic filler that has a high concentration of very polar hydroxyl groups on the surface. Therefore, a basic difficulty lies in the incompatibility of highly polar silica and non-polar hydrocarbon rubbers.

Various strategies have been applied to improve silica–rubber interactions, including modifying the silica surface using a coupling agent, and applying polar or functionalised rubbers that can enhance the compatibility between the rubber and filler (Cataldo 2002; Choi 2002; George et al., 2002). Silane coupling agents are commonly used to chemically bond a polymer to silica to improve the filler dispersion and to increase the reinforcement level. The processing conditions and mixing step need well-controlled to allow the functional groups on the silane fully reacting with the silanol groups on the silica surface (Luginsland et al., 2002; Ansarifar et al., 2003; Reuvekamp et al., 2009; Kaewsakul et al., 2012). However, the silane system has some disadvantages, such as high cost, toxicity, risk of pre-curing during the mixing stage, and the generation of ethanol during the mixing (Wolff 1996).

In addition, a new technology for silica-surface modification using plasma-polymerisation techniques has been investigated. This technique...
is a process by which gaseous monomer molecules are stimulated with the aid of electrical energy to form an active species, which reacts with the substrate surface and forms as a film on the substrate surface. Akhavan et al. (2013) investigated the hydrocarbon monomers types for depositing a hydrophobic film on the silica surface to reduce its surface energy. Nah et al. (2002) studied the effects of the surface modification of silica by plasma polymerisation with an acetylene monomer, together with a modification using a silane coupling agent, for a comparison of the dispersion and physical properties of styrene-butadiene rubber (SBR).

The surface modification of silica by either plasma polymerisation or silane greatly improved the dispersion of silica particles in SBR vulcanisates. Moreover, the use of plasma-coated silica with an acetylene monomer under vacuum conditions in solution SBR (S-SBR), ethylene propylene diene monomer (EPDM), S-SBR/EPDM, and nitrile butadiene rubber (NBR)/EPDM compounds resulted in a better filler dispersion and a lower Payne effect, compared to untreated silica (Tiwari et al. 2008a).

In the present work, a silica surface was modified by a radio-frequency (RF) plasma-polymerisation coating with an acetylene monomer. The plasma modified silica was characterised using an immersion test, the contact angle, Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The investigated plasma-modified silica affecting the compound properties of filled natural rubber (NR) were compared with composites modified using a silane coupling agent.

2. Materials and methods

2.1. Materials

Acetylene ($C_2H_2$) gas was used as a monomer for plasma polymerisation. The natural rubber (Ribbed smoked sheet 3; RSS3) was locally produced in Nakhon Si Thammarat, Thailand. The NR was compounded using precipitated silica (Ultrasil VN3), bis-triethoxysilylpropyl tetrasulphde (TESPT) (Evonik, Germany), treated distillate aromatic extract (TDAE) oil (H&R, Germany), polymerised-2,4,4-trimethyl-1,2-dihydroquinoline (TMQ), zinc oxide (ZnO), stearic acid, diphenylguanidine (DPG), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), and sulphur (Reliance Technochem, Thailand).

2.2. Plasma-acetylene coating on silica

Figure 1 shows the schematic diagram of the plasma reactor and apparatus and the chamber for plasma polymerisation. The reactor power system consists of a radio-frequency generator (50 kHz) with a 20-kW input power, matching network, stainless cylinder chamber, stainless electrode, vacuum pump, silica-containing plate, and shaker rod. Argon (Ar) and acetylene gases were used as the carrier gas and monomer, respectively.

The plasma polymerisation was carried out by charging 10 g of dried silica into the plate. The reactor was closed and maintained a pressure of 1–10 torr. The Ar and acetylene gases were introduced for 60 min of plasma polymerisation; the plate was shaken every 10 min to refresh the powder surface exposed to the plasma phase. The modified silica was assessed by measuring the changes in its surface energy by immersing it in water (Tiwari et al., 2011).

Another test to confirm the hydrophilic and hydrophobic nature of the silica surface was the contact-angle measurement (DMs-401, Kyowa) of a water drop on the glass plate. The chemical structures of the modified silica were characterised using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), thermogravimetric analysis (TGA, SDT Q600, TA Instruments) with a heating rate of 10 °C/min, and scanning electron microscopy (SEM, Merlin compact, Zeiss) with an energy dispersive X-ray spectrometer (EDX, Oxford, Aztec).
2.3. Preparation of silica-filled NR compounds

The silica-filled compounds formulations are listed in Table 1. Compounds with and without TESPT were also prepared to comparison study. The NR compounds were done by a two-step mixing procedure (Saramolee et al., 2014). The first step was in an internal mixer with a mixing chamber volume of 379 cm³ (Haake Rheomix 3000), at a mixing temperature of 100–140°C, a rotor speed of 60 rpm, and a fill factor of 0.7. The NR was masticated for 2 min prior to silica, oil, and TESPT (if any) were added and mixed for 5 min. ZnO, stearic acid, and then TMQ were subsequently added and mixed for 3 min.

The batch was finally discharged at a total mixing time of 10 min to reach end temperatures approximately in the range of 140–150°C. This allowed the TESPT to properly react with the silica during the internal mixing (Kaewsakul et al., 2012). The CBS, DPG, and sulphur were added on a two-roll mill as a second mixing step to avoid compound scorch. The final compounds were sheeted out and kept overnight before being moulded to the optimum cure state (t90) at 150°C, using a hydraulic press to prepare the test specimen.

2.4. Investigation of the compound properties of the silica-filled NR

The compound viscosities were determined using a rubber process analyzer (D-RPA 3000, MonTech, Germany) in a frequency-sweep test in the range of 0.1–33 Hz at a 14% strain and 80°C. The Payne effect of the cured compounds was studied using a D-RPA at 100°C. The strain was varied in the range of 0.56–100% at the frequency of 0.50 Hz.

The bound-rubber content (RB) is a crucial reinforcement parameter that can indicate the level of the filler–rubber interaction. It was determined by cutting 0.2 g of the uncured compound into small pieces, then placing them in a steel cage, and immersing them in toluene at room temperature. After 72 h, the steel cage with the swollen sample was removed from the toluene, dried at 105°C for 24 h, and immersed again in toluene for 72 h, either with or without an ammonia atmosphere. It was then removed from the toluene and weighed, after drying at 105°C for 24 h. The RB was calculated according to the following equation (Wolff et al., 1993):

\[ RB = \frac{W_{fg} - W_{f} + m_{f} + m_{p}}{W_{f} + m_{f} + m_{p}} \times 100 \]

Table 1. Silica-filled compound formulation.

| Ingredient          | Amount (parts per 100 parts of rubber, phr) |
|---------------------|--------------------------------------------|
| NR (RSS3)           | 100.0                                      |
| Silica              | 30.0                                       |
| PA-coated silica    | -                                          |
| TESPT*              | -                                          |
| TDAE oil            | 5.0                                        |
| Zinc oxide          | 3.0                                        |
| Stearic acid        | 1.0                                        |
| TMQ                 | 1.0                                        |
| DPG**               | 0.6                                        |
| CBS                 | 1.2                                        |
| Sulphur             | 1.5                                        |

*Amount of TESPT (phr) = 0.00053 \times Q \times CTAB,
**Amount of DPG (phr) = 0.00012 \times Q \times CTAB,
where Q is the silica content (phr) and CTAB is the specific surface area of the silica (Ultrasil VN3 = 167 m²/g) (Guy et al., 2009).

![Figure 2](image-url) Optical images of particles placed on the interface of water and air: (a) uncoated silica and (b) PA-coated silica. Contact-angle images of (c) uncoated silicon glass and (d) PA-coated silicon glass.
where $W_{fg}$ is the weight of the filler and gel after drying at 105 °C for 24 h, $W$ is the weight of the polymer compound, and $m_f$ and $m_p$ are the weights of the filler and polymer in the compound, respectively.

The cure characteristics (minimum and maximum torques, and scorch and cure times) were determined using an oscillating disc rheometer (ODR, GOTECH, GT-7070S2) at 150 °C, according to the ASTM D2084 standard test method.

3. Results and discussion

3.1. Characterisation of acetylene-coated silica

The change in surface energy of the silica surface was investigated by immersing it in water. The uncoated silica absorbs water and settles to the bottom immediately. After the plasma-polymerisation coating on the
silica surface, it floats on water, as shown in Figures 2a and b. This is due to the increased hydrophobic nature of the silica surface.

To confirm the hydrophilic and hydrophobic nature of the silica surface, a contact-angle test was carried out by dropping water onto the glass sheets at room temperature. The contact angle was recorded 10 s after the water droplet was applied to the surface of the glass sheets. Figures 2c and d show the images of a water droplet held on the surfaces of uncoated and coated glass sheets, respectively. The contact angle for the glass sheet after coating was found to be significantly increased, from 25.28° to 70.32°, which is attributed to the stable hydrophobic surface of the PA-coated silica.

TGA thermograms of the uncoated and coated silica are shown in Figure 3. The decomposition rate of the uncoated silica was higher than that of the PA-coated one. The large amount of moisture absorbed on the surface of the uncoated silica is responsible for the higher decomposition rate. The PA-coated silica showed two weight-loss steps, indicating the presence of a hydrocarbon film on the modified surface. The PA-coated silica showed a 1–2 wt% loss in comparison with the uncoated silica (Tiwari et al. 2008a). This is attributed to the formation of a polyacetylene film on the surface, after the plasma-polymerisation process.

An elemental analysis of the pure and PA-coated silica was determined by XPS measurement. Figure 4 presents the XPS spectra of uncoated and PA-coated silica. The chemical components of the uncoated silica surface are strong, in terms of O 1s (530.0 eV) and Si 2p (100.0 eV) peaks. After the plasma-polymerisation process, the coated silica showed a significant increase in the C 1s intensity (282.0 eV), as shown in

| Sample          | Element (Mass Conc. %) | C   | O    | Si   |
|-----------------|------------------------|-----|------|------|
| Uncoated silica |                         | 1.88| 54.36| 43.76|
| PA-coated silica|                         | 25.93| 43.06| 31.01|

Table 2. XPS results of uncoated and PA-coated silica.

3.2. Properties of silica-filled rubber compounds

The mixing behaviours of the silica-filled NR compounds can be determined by measuring the mixing torque and mixing temperature. The properties of the PA-coated-silica-incorporated NR are compared with those of the uncoated-silica and silane-silica-filled NR compounds.

Figure 6 shows the variation of the mixing torque and mixing temperature over time for the compounds containing different silica particulates. At the end of mixing, that is, after 10 min, the temperatures of all compounds had reached approximately 150 °C. The same levels of torque and temperature were observed in the first step of mixing during the rubber mastication. After the mastication, a sharp increase in the mixing torque was noticed, upon the addition of silica. The compound filled with uncoated silica showed the highest mixing torque. The introduction of a silane coupling agent and PA-coated silica into the NR compound clearly showed a reduction in the mixing torque and temperature. This can be attributed to the minimisation of the formation of silica agglomerates and the compound viscosity.

Figure 7 shows the complex viscosities of silica-filled NR compounds containing various types of silica. The uncoated silica-filled compound viscosity was higher than that using silane and the PA-coated silica. This indicates that the compounds filled with silane silica and PA-coated silica provided better compatibility with the NR matrix and hence, a reduction in the oxygen percentage.

Figure 5. SEM images and EDX spectra of (a, c) uncoated silica and (b, d) PA-coated silica (50,000x).
of the compound viscosity. Considering treatment techniques, the PA-coated silica provided a reduction in compound viscosity similar to the silane-treated silica. This indicates that the polyacetylene-modified silica improved the filler dispersion.

A lower Payne effect indicates a lower filler–filler interaction in filled-rubber compounds (Payne and Whittaker 1971). Figure 8 shows the Payne effect of silica-filled NR compounds with various types of silica. The Payne effect of the uncoated-silica-filled compound was the highest because of the strong filler–filler interaction arising from the hydrogen bonds between the hydroxyl groups on the silica surface. The use of a silane coupling agent substantially decreased the Payne effect of the silica-filled NR compound, compared to the one filled with uncoated
silica. The compound filled with coated silica decreased the Payne effect to the lowest level. This result indicates a lower filler–filler interaction, in the case of the coated-silica-filled NR compound.

Figure 9 shows the bound-rubber content ($R_b$) of the PA-coated-silica-filled NR compounds and also compares them with the compounds filled with uncoated and silane silica. The compounds were evaluated under two treatment conditions: ambient and ammonia atmospheres. The $R_b$ content obtained under ambient conditions is the total value of both physical and chemical $R_b$. Under the ammonia atmosphere, weak physical interactions, such as hydrogen and van der Waals bonds, are disrupted; thus, only chemical $R_b$ can be analysed (Wolff et al., 1993).

The silane-silica-filled compound showed the highest total and chemical $R_b$ contents. This is attributed to the TESPT silane-enhanced network formation and resulted in a strong filler–rubber interaction (Kaewsakul et al., 2013). In contrast, the PA-coated-silica-filled compounds clearly showed a higher $R_b$ content, compared to the uncoated-silica-filled one. This is attributed to the enhanced filler–rubber interactions caused by the acetylene-plasma polymerisation coated on the silica surface. However, the compound filled with coated silica exhibits a lower $R_b$ content, compared to the one with silane silica.

Figure 10 shows the curing characteristics of silica-filled NR compounds with different types of fillers, in terms of scorch time ($t_{sc}$), cure time ($t_{90}$), minimum torque ($M_L$), and maximum torque ($M_H$). The NR compound filled with uncoated silica shows longer scorch and cure times, compared with the treated silica. These are caused by the presence of polar silanol groups on the silica surface, which can adsorb or interact with the alkaline accelerators and hence, reduce the curing speed. The silane-silica-filled and PA-coated-silica-filled compounds exhibited the same levels of both scorch and optimum cure times. Moreover, the minimum torques of the silane silica and PA-coated silica were not significantly different. This indicates that the PA-coated silica provided cure characteristics similar to the ordinary silane-silica system. The silane-silica system showed a higher maximum torque, compared to the compound with PA-coated silica, owing to the strong chemical interactions between the silica and rubber. However, the maximum torque of the uncoated-silica-filled rubber was the highest. This is attributed to poor filler dispersion.
4. Conclusions

In this study, acetylene plasma polymerisation was successfully used to modify silica surfaces and hence, improved the filler dispersion. To obtain a hydrophobic deposit, the CH formation must be enhanced, with plasma parameters with an input power of 20 kW and an RF frequency of 50 kHz. The operation pressure was maintained in the range of 1–10 torr with a fixed gas-flow rate of 15 sccm and a duration of 60 min. The PA-coated silica showed very high stability in water, which could be related to its high degree of hydrophobicity. Hence, it significantly improved the mixed NR compounds, indicated by a lower mixing energy, Payne effect, and complex viscosity than those of compounds with uncoated silica. The silane-silica-filled and PA-coated-silica-filled compounds showed faster scorch and cure times, compared to the uncoated-silica-filled compound, owing to less interaction with the alkaline accelerators. However, silica surface modifications by either silane or plasma polymerisation did not exhibit a significant change in the $M_1$ and $M_2$ of the NR compounds.

Declarations

Author contribution statement

Prachid Saramolee: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Suchanat Trubmusik, Thirayu Sunthondecha: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mudtorlep Nisoa: Contributed reagents, materials, analysis tools or data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Jobish Johns: Conceived and designed the experiments; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

No additional information is available for this paper.

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Additional information

No additional information is available for this paper.