

Properties of Rice Husk Ash Silica Filled Prevulcanized Deproteinized Natural Rubber Latex Film

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Abstract. Silica extracted from rice husk ash (RHA-Si) was incorporated in deproteinized natural rubber (DPNR) latex compounds up to 20 phr. The cast films were prepared after the prevulcanization at 70°C for 2 hours. The effect of RHA-Si loading on swelling and tensile properties was investigated. Scanning electron microscope (SEM) was used to examine morphology of the prevulcanized films. Dynamic mechanical behaviors of filled prevulcanizates were studied using the dynamic mechanical analyzer (DMA). Two types of tests, namely, temperature sweep and strain sweep test were performed. Swelling test revealed the decrease in crosslink density with increasing RHA-Si loading more than 10 phr. The presence of RHA-Si increased the modulus at 100% strain of the prevulcanized DPNR latex films. Conversely, tensile strength and elongation at break decreased with increasing RHA-Si loading. The poor filler-rubber distribution was evidenced by SEM image. The DMA results exhibited that storage modulus (G') and damping factor ($\tan\delta$) increased with increasing RHA-Si loading. The narrow linear viscoelastic (LVE) region was noticed for prevulcanizates filled with high RHA-Si content. Glass transition temperature (T_g) of highly filled DPNR shifts to low temperature.

Introduction

Silica is the conventional reinforcing-fillers used to enhance the mechanical properties of various rubbers. In recent years, silica from the rice husk has attracted much attention [1] because of their ability to enhance the mechanical properties of rubber vulcanizates comparable to the commercial silica. The use of rice husk ash silica (RHA-Si) as reinforcing-fillers, therefore, can reduce the cost of the production and also add value to the local agricultural residues.

Natural rubber latex (NRL) is the liquid obtained from rubber tree (*Hevea brasiliensis*) including cis-1,4-polyisoprene as a major component. The other ingredients in NRL, such as protein, lipid, carbohydrate, sugar, metal and water, are called non-rubber. Proteins existing in NRL is a cause of immediate-type allergy which has emerged as a serious health issue [2,3]. Low protein rubber is a key aspect in the management of NRL allergy. Urea-deproteinization is the rapid and efficient method to remove the allergenic proteins on the surface of the rubber particles [4].

RHA-Si can be applied as reinforcement for deproteinized natural rubber (DPNR) [5]. It is reported that RHA-Si used as filler can enhance viscoelastic property and cure behavior of DPNR and NR comparable to the commercial silica. Generally, the incorporation of filler to rubber is intended to improve in processability, enhance of certain properties and reduce in cost. However, the effect of

same filler on properties of dry rubber is different from that of latex compound [6]. The present study reports the effect of addition of RHA-Si on properties of prevulcanized DPNR latex films. The effect of RHA-Si loading on swelling and tensile properties was investigated. Morphology and dynamic mechanical behavior of filled films were also evaluated.

Experimental

Materials

Natural rubber (NR) latex with 60% dry rubber content (DRC) was supplied by Thai Rubber Latex, Thailand. All compounding ingredients including aqueous dispersion of 60% sulfur, 50% zinc diethyl dithiocarbamate (ZDEC), 50% zinc dibenzyl dithiocarbamate (ZBDC), 50% zinc oxide (ZnO) and 50% Lovinox CPL were in dispersion form and manufactured from Lucky four, Thailand.

Preparation of deproteinized natural rubber latex

The incubation of NRL was performed with 0.1% urea in the presence of sodium dodecyl surfactant (SDS) at room temperature for 1 hour. Subsequently, the mixture was centrifuged for 90 minutes at speed of 5000 rpm. The cream fraction separated from the liquid residue was redispersed in 1 wt % SDS solution, and was washed twice by centrifugation to prepare DPNR latex.

Preparation of rice husk ash

Rice husk was washed by distilled water and further pretreated with 1 M HCl. After the reaction, the acid was completely removed from the rice husk by washing with distilled water. It was then dried overnight in an oven. The treated rice husk was calcination in an electric furnace by controlling the temperature at 700 °C for 5 hours. Silica was finally obtained in the form of white ash. The chemical composition and structure of RHA-Si were then investigated with X-ray fluorescence (XRF) and X-ray diffractometer (XRD). The results showed that RHA-Si contained a large amount of silica (90%) with amorphous structure [5].

Prevulcanization of deproteinized natural rubber latex

The prepared DPNR latex compounds were mixed with 1.5 phr of sulfur, 0.5 phr of ZDEC, 0.5 phr of ZBDC, 0.5 phr of ZnO and 1.0 phr of LowinoxCPL. RHA-Si utilized as reinforcing-filler was charged as 20% dispersion to the DPNR latex with various loadings of filler from 0 to 20 phr (i.e., at 0, 5, 10, 15 and 20 phr). Prevulcanization was carried out by heating the latex compound in beaker immersed in water bath at temperature of 70°C for 2 hours. The DPNR latex was vulcanized in the fluid state. After the latex was cooled, the films were cast in glass cell with 0.6 mm thickness.

Swelling test

A test specimen weighing about 1.5 grams were cut from DPNR film and immersed in toluene for 5 days at room temperature. After 5 days, the swollen sample was removed from toluene and then wiped with a tissue paper. The swollen weight was measured. Swelling behavior of prevulcanizates was determined from swelling index (SI), calculated by the following relationship:

$$SI (\%) = [(swollen\ weight - initial\ weight) / initial\ weight] \times 100 \quad (1)$$

Tensile properties

The universal tensile tester (Instron model 5566, USA) was used for measuring the tensile properties as per ASTM D412-98 at a crosshead speed of 500 mm/min. Test specimens for tensile were punched out from the molded sheets using ASTM die C.

Morphology

A scanning electron microscope (JEOL JCM-6000) was utilized for evaluating the quality of dispersion and distribution of filler in the rubber matrix. The newly exposed surface prepared by a cryogenic fracturing technique was sputter coated with gold to prevent electron bombardment prior to the examination.

Dynamic mechanical properties

The dynamic mechanical properties of filled DPNR prevulcanizates were measured using a dynamic mechanical analyzer (Gabo, ExplexorTM 25N) in a tension mode. Temperature sweep (-70 to +60°C) and strain sweep (strain amplitude of 0 to 10%) tests were performed.

Results and Discussion

Swelling test

The swelling index of RHA-Si filled DPNR latex prevulcanizates is presented in Fig. 1. It is observed that the swelling index of prevulcanizates does not change with increasing RHA-Si loading until 10 phr, and then increases evidently with increasing filler loading more than 10 phr. It means that the high loading of RHA-Si decreases crosslink density, causing the increase in the penetration of the solvent in to the prevulcanizates. As loading of RHA-Si increases, the distribution of filler in rubber matrix decreases, and then crosslink density also decreases.

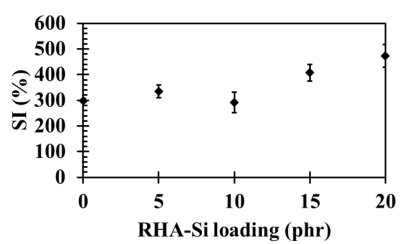


Fig. 1. Swelling index of prevulcanized DPNR latex film filled with various RHA-Si loadings

Tensile properties

The effects of RHA-Si loading on modulus at 100% strain (M100), tensile strength and elongation at break are shown in Fig. 2. It is evident from the relationship between M100 and RHA-Si loading (Fig. 2a) that the M100 increases with increasing filler loading up to 10 phr, and then M100 does not become different. There are three main possibility factors controlling M100, i.e., crosslink density, phase morphology and reinforcing effect. Regarding the crosslink density effect, it is known that the higher the crosslink density, the greater the M100, which is in good agreement with the results of swelling index as shown earlier. Moreover, the good filler distribution results in the improvement of M100. In the case of reinforcing effect, the higher the amount of RHA-Si, the larger the extent of rubber-filler interaction, and thus the greater the M100. In other word, the M100 results of prevulcanizates filled with high RHA-Si loading (i.e., filler loading of 15 and 20 phr) can be explained by the poor dispersion and distribution of filler in rubber matrix.

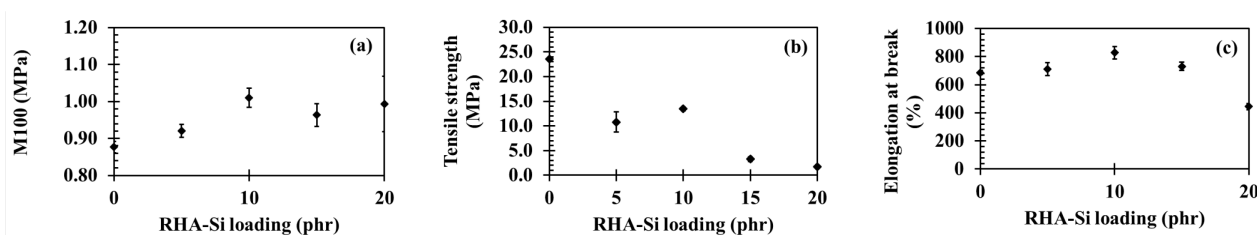


Fig. 2. Tensile properties of prevulcanized DPNR latex film filled with various RHA-Si loadings; (a) Modulus at 100% strain (M100), (b) Tensile strength and (c) Elongation at break

Tensile strength of DPNR latex filled with RHA-Si (as illustrated in Fig. 2b) is decreased with increasing filler loading. However, it seems that tensile strength does not change with increasing filler loading from 5 to 10 phr, and tensile strength decreases dramatically with filler loading more than 10 phr. This is due to crosslink density effect and poor filler-rubber interaction. In the case of elongation at break, it can be seen from Fig. 2c that the change of elongation at break is insignificant with increasing RHA-Si loading up to 10 phr, and then decreases with RHA-Si loading of 15 and 20 phr, which can be also explained by the crosslink density effect and poor filler-rubber interaction.

Morphology

Fig. 3 shows SEM micrographs of DPNR filled with various loadings of RHA-Si. The RHA-Si phase in prevulcanizates appears as bright in the micrographs. It is noted that the RHA-Si dose not distributes thoroughly in the rubber matrix, particularly at DPNR matrix filled with RHA-Si loading of 15 and 20 phr. Moreover, it can be seen that there are holes at the interface of rubber matrix and filler, indicating the poor filler-rubber interaction.

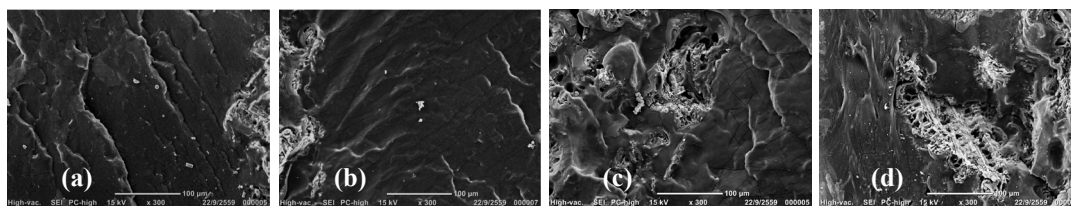


Fig. 3. SEM micrograph of DPNR filled with various RHA-Si loadings; (a) 5 phr, (b) 10 phr, (c) 15 phr and (d) 20 phr

Dynamic mechanical properties

Strain sweep test

Storage modulus (G') of DPNR prevulcanizates filled with RHA-Si as a function of strain amplitude is shown in Fig. 4a. It is evident that the unfilled prevulcanizate reveals the lowest G' and broadest plateau of linear viscoelastic region (LVE), which indicates the elastic or rubber-like response of prevulcanizate. Also, G' increases with increasing RHA-Si loading, which is due mainly to reinforcing effect, i.e., the hydrodynamic effect, the filler-filler interaction via hydrogen bonding as well as the filler-rubber interaction. Highly RHA-Si filled prevulcanizates, i.e. the prevulcanizates with 15 and 20 phr, show a strain-dependent G' as a result of strong filler-filler interaction (usually known as the Payne effect) [7].

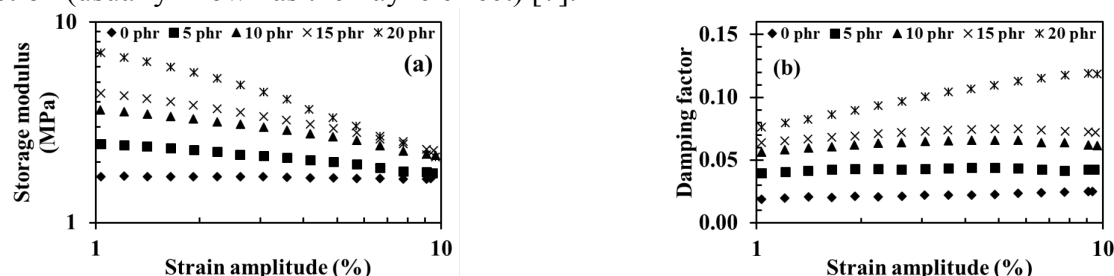


Fig. 4. Dynamic mechanical properties as a function of strain amplitude of prevulcanized DPNR latex film filled with various RHA-Si loadings at test temperature of 25°C; (a) Storage modulus (G') and (b) Damping factor ($\tan\delta$)

Fig. 4b shows the alteration in damping factor ($\tan\delta$) as a function of deformation strain. It is obvious that $\tan\delta$ increases with increasing RHA-Si loading. The crosslink density effect is used as the explanation. Furthermore, it is observed that the damping factor of prevulcanizates filled with RHA-Si loading of 15 and 20 phr increases with increasing strain amplitude. The increase in damping factor is reported to be the result of energy dissipation through a molecular slippage associated with the breakdown of the three dimensional filler transient network. This phenomenon is sometimes known as hysteretic process [8].

Temperature sweep test

Fig. 5a illustrates the influences of RHA-Si loading on G' of DPNR latex prevulcanizates over a temperature range of -70 to 60°C. It is evident that the values of glass transition temperature (T_g) as determined from abrupt change in G' of highly filled RHA-Si prevulcanizates (i.e., 15 and 20 phr) shift to the lower temperature with increasing RHA-Si loading. Generally, the increase in filler-rubber interaction leads to a shift in T_g to the high temperature as a result of molecular restriction. Conversely, the shift in T_g of filled vulcanizate to the low temperature indicates the poor filler-rubber interaction. As expected, the values of G' at temperature of 25°C agree well with those determined from the strain sweep test, as revealed earlier in Fig. 4a. The prevulcanisates with greater content of RHA-Si exhibit higher magnitude of reinforcement.

Damping factor as a function of temperature is given in Fig. 5b. The results of damping factor is in good agreement with the G' results, i.e. damping peak of highly filled films shifts to low temperature, indicating low T_g due to poor filler-rubber interaction. Clearly, the damping peaks of filled DPNR decrease with the increasing RHA-Si loading, implying the reduction in rubber volume fraction by the RHA-Si incorporation (dilution effect). On the contrary, the damping factor in the rubbery plateau appears to increase with increasing RHA-Si content, which is consistent with the results measured from the strain sweep test as shown previously in Fig. 4b.

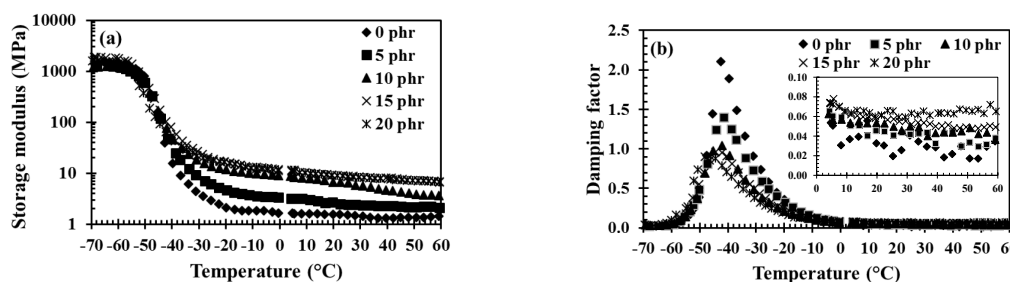


Fig. 5. Dynamic mechanical properties as a function of temperature of prevulcanized DPNR latex film filled with various RHA-Si loadings; (a) Storage modulus (G') and (b) Damping factor ($\tan\delta$)

Summary

DPNR prevulcanizates reinforced by RHA-Si were prepared. Swelling behavior was investigated. The results show that, the magnitude of crosslink density decrease with increasing loading of RHA-Si. This is attributed to the poor filler-rubber interaction between RHA-Si and DPNR, as evidenced by SEM micrograph. RHA-Si filled DPNR latex vulcanizates with higher loading tend to reduce the tensile strength and elongation at break, but G' and $\tan\delta$ as a function of strain show opposite trend with increasing the RHA-Si content. The increases in loading of RHA-Si reveal the increased extents of Payne effect and molecular slippage. The poor filler-rubber interaction in highly filled DPNR latex prevulcanizates with RHA-Si influence on a shift of T_g to low temperature. This study can be concluded that the poor interaction between RHA-Si and DPNR latex plays an important role towards the prevulcanizates properties.

Acknowledgements

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