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Study of the mechanical, dynamic mechanical and dielectric properties of natural rubber/barium titanate composites

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Abstract

The focus of the paper is to investigate the effect of barium titanate ($BaTiO_3$) particles on the mechanical, dynamic mechanical, and dielectric properties of natural rubber (NR) composites. The natural rubber/barium titanate composites with different volume fractions of barium titanate were prepared via the two-roll mill process. A silane coupling agent was used to modify the surface of the barium titanate particles. The curing characteristics of the composites were determined and the composites were vulcanized at 150 °C using a hot press. The mechanical properties, dynamic mechanical properties, and dielectric properties of the composites were studied. The mechanical properties indicated that the incorporation of barium titanate caused the tensile strength and hardness of natural rubber to be improved. Dynamic mechanical analysis results show that the incorporation of barium titanate particles into the natural rubber matrix resulted in a decrease of the height of the loss tangent (tanδ) peak and the T_g values shifted slightly to a higher temperature with the addition of barium titanate particles. The dielectric properties of the natural rubber/barium titanate composites were enhanced with increased barium titanate loading. Moreover, the morphology of the composites was also studied using scanning electron microscopy. A microstructure analysis was performed to verify and better assess the performance properties of the natural rubber/barium titanate composites.

Keywords: Natural rubber composites; Barium titanate; Mechanical properties; Dynamic mechanical properties; Dielectric properties

1. Introduction

Thailand is currently the world's number one rubber producer with 4.50 million tonnes of output, or 35.70% of total production [1]. The government has formulated policies to enhance the development of the natural rubber industry and support research into natural rubber since this is crucial to the sector's performance. Natural rubber is important because of its suitability for numerous industrial rubber applications due to having considerable strength, elasticity, and resilience. The developing rubber industry provided, therefore, a market for a wide variety of materials, although natural rubber technology requires extensive compounding.

The use of fillers in rubber is almost as old as the use of rubber itself. Fillers, such as calcium carbonate, carbon black, silica or clay, are added to cheapen the products. Incorporation of fillers in rubber is a common practice, as it typically reduces the costs and modifies the physical and mechanical properties. This alteration of properties in rubber depends on the nature of the fillers as well as of the polymers [2]. For dielectric polymer composites, the use of barium titanate fillers in polymer composites has attracted interest due to the high dielectric constant, high flexibility, and low dielectric loss. Although barium titanate particles have a high dielectric constant the application has been limited because of low breakdown strength, brittleness, and high dielectric loss. On the other hand, polymer materials exhibit low dielectric loss and high breakdown strength. Both high dielectric constant and low dielectric loss are desired for dielectric polymer composites. The incorporation of barium titanate into the natural rubber matrix could obtain a high dielectric constant and low dielectric loss. While previous studies have reported the use of barium titanate as filler in the polymer matrix [3 – 7], there have been very few studies reporting on the properties of natural rubber/barium titanate composites. Hence, in the present study, natural rubber filled with different barium titanate contents was prepared. The influence of the barium titanate content on the mechanical, dynamic mechanical, and dielectric properties was then investigated.

2. Materials and methods

Materials

Natural rubber (NR) grade-STR 5L and other compounding ingredients including zinc oxide, stearic acid, sulphur, 2-Mercaptobenzothiazole (MBT) and silane-69 were supplied by Kij Paiboon Chemical Limited Partnership (Bangkok, Thailand). Barium titanate was obtained from Sigma-Aldrich Co., LLC. Bis[3-(triethoxysilyl)-propyl]tetrasulfide (si-69) was selected as the coupling agent for surface modification of barium titanate particles [8]. The amount of si-69 was also kept constant in all formulations (6 wt% of the particles).

Preparation and testing of rubber compounds

The details of the materials are shown in Table 1. The rubber compounds were prepared using a laboratory two-roll mill (model LRM-S-110/3E, Labtech Engineering) with the temperature maintained at 50 °C. Nip gap, mill roll speed ratio, time of mixing and sequence of addition of the ingredients were kept the same for all rubber compounds. The compounding ingredients were added in the following order: activators, filler, accelerators, and then sulphur. After mixing, the rubber compound was taken out and sheeted through a laboratory mill at a 2 mm nip setting. The curing characteristics of the rubber compounds were studied using a moving die rheometer (model EKT 2001M, Ektron) in accordance with ASTM 5289-95. Compounded rubber samples weighing 25 g were placed between a pair of rotating disks which was set at the temperature of 150 °C. The cure times, T_{C90} (optimum cure time to achieve 90% of full torque development) were then evaluated.

Mechanical analysis

A compression molding process was used to prepare specimen sheets at 150 °C according to their respective T_{C90}. Tensile testing was carried out using a universal testing machine (model M500-25AT, Testometric). Specimens were made in accordance with ASTM D412. The instrument was operated at a crosshead speed of 500 mm min^{-1} using a 2,500 kgf load cell. The hardness was tested using a shore hardness tester (model shore A, Desik) in accordance with ASTM D2240.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of rubber composites were assessed from –100 °C to 100 °C in a nitrogen atmosphere using a dynamic mechanical analyzer (model DMA/SDTA 861e, Mettler Toledo). DMA specimens were cut from the compression molded sheet to dimensions of 25 mm length, 7 mm width, and 2 mm thickness. The specimens were deformed under tension at a constant frequency of 10 Hz and a heating rate of 2 °C min^{-1}.

Dielectric properties

Dielectric constant and dielectric loss of rubber composites were assessed using a precision impedance analyzer (model 4294A, Agilent Technologies, Japan). The instrument was operated in the range of 1 KHz to 1 MHz.

Morphological analysis

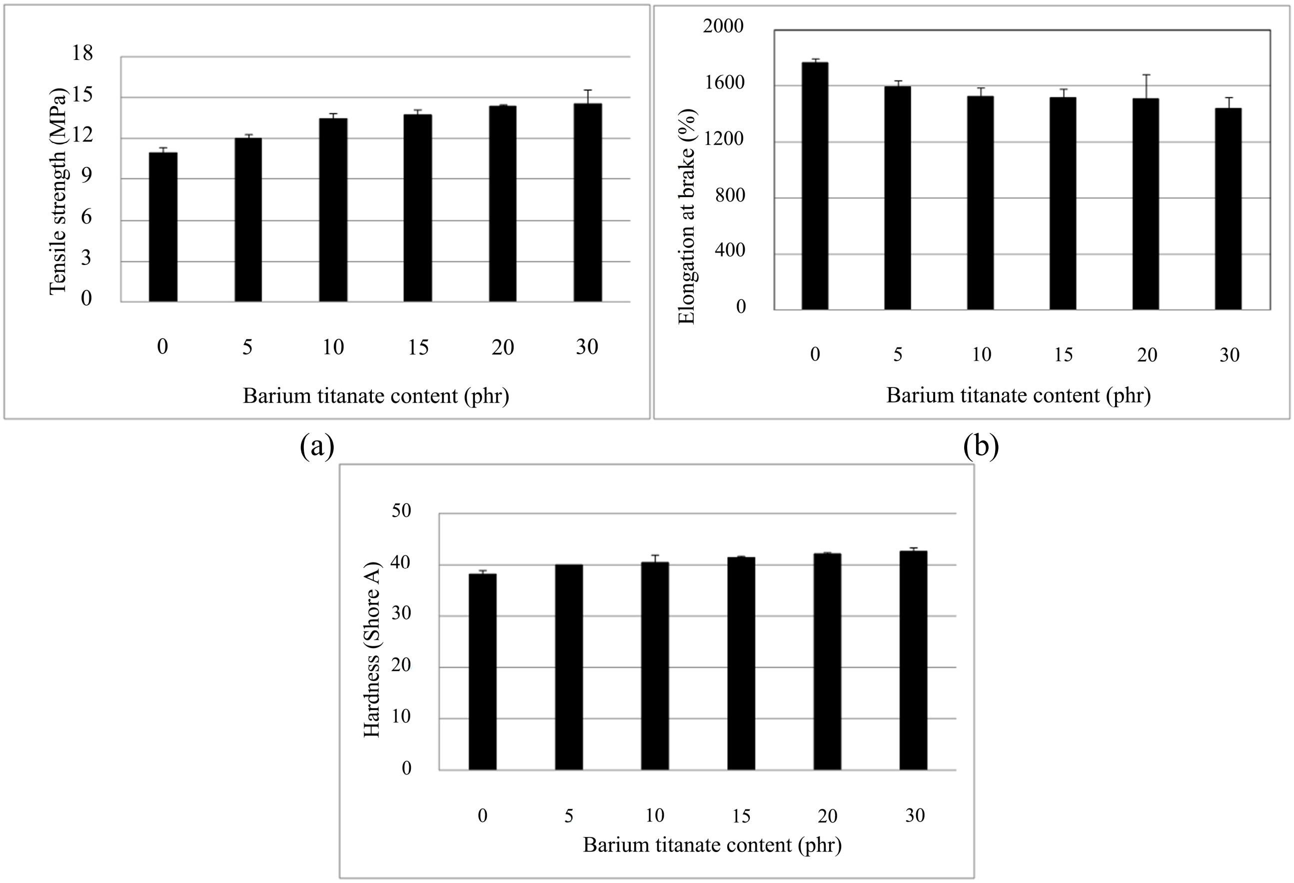
The dispersion morphology of silicon carbide in rubber composites was observed by scanning electron microscopy (model S-4800, Hitachi). The samples were soaked in liquid nitrogen and then were fractured. The test samples were mounted on stubs and gold coated in order to avoid electric charge accumulation during examination.

Table 1 Materials used in the present study.

Materials	Function	Amount (phr)
Natural rubber (STR 5L grade)	Raw material	100
Zinc oxide	Activator	4
Stearic acid	Activator	2
2-Mercaptobenzothiazole	Accelerator	0.70
Sulphur	Curing agent	3
Barium titanate	Filler	0, 5, 10, 15, 20 and 30
Si-69 level (wt%)	Coupling agent	6

3. Results and Discussion

The mechanical properties of natural rubber and natural rubber/barium titanate composites with different barium titanate contents are presented in Fig. 1(a) – Fig. 1(c). The results of the tensile studies are given in Fig. 1(a) – Fig. 1(b). As seen in these figures, the tensile strength values of the samples improved whereas the elongation at brake values decreased with the increasing barium titanate content. It is clear from the figures that natural rubber exhibited tensile strength of 10.94 MPa whereas natural rubber/barium titanate composites exhibited tensile strength of 12.01, 13.51, 13.74, 14.42 and 14.54 MPa at 5, 10, 15, 20 and 30 phr filler content respectively. These results indicated that barium titanate can reinforce the mechanical properties of natural rubber, when the load applied to the rubber composites is absorbed by the fillers before being distributed throughout the matrix [9]. On the other hand, the decrease in the elongation at break denotes that barium titanate cannot provide extra stiffness to the polymer. This can be related to the lack of strong interfacial adhesion between the polymer and fillers. Fig. 1(c) illustrates the variation in surface hardness of natural rubber/barium titanate composites according to the Shore A scale. The hardness increased with increasing barium titanate content.

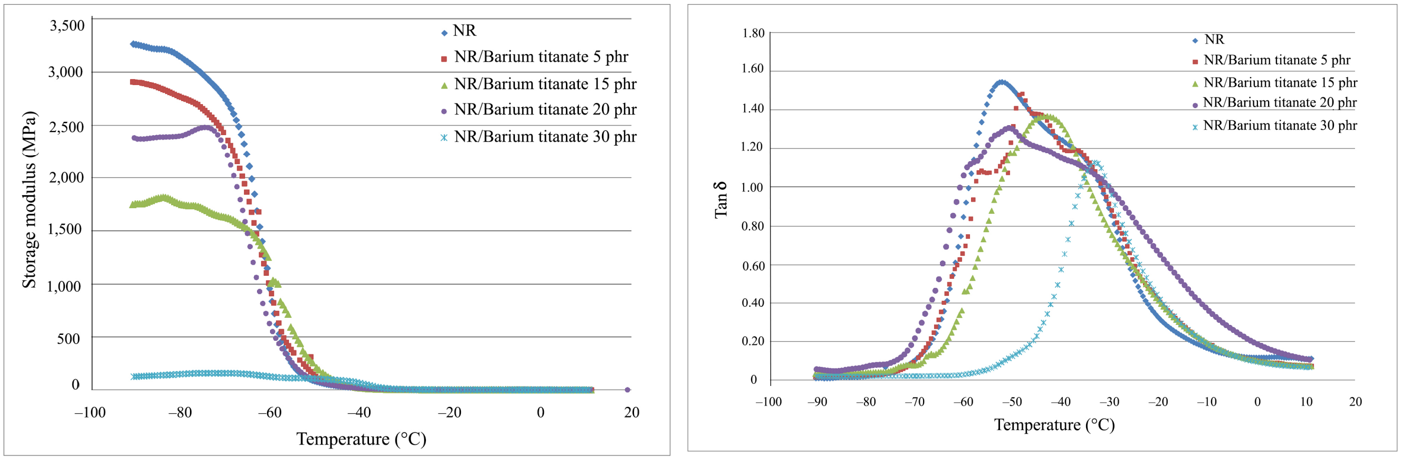


(c)

Fig. 1 Mechanical properties of natural rubber/barium titanate composites: (a) tensile strength; (b) elongation at break; (c) hardness.

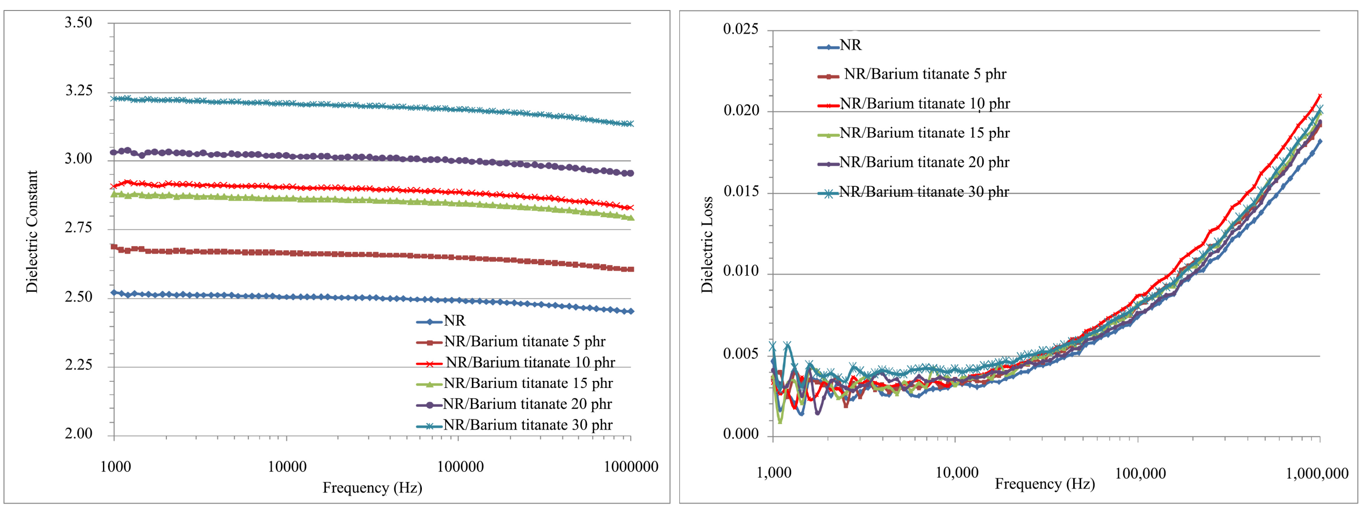
The dynamic mechanical properties of pure natural rubber and rubber composites with different filler contents were examined to determine the storage modulus (E′) and tanδ as a function of temperature. The storage modulus refers to the elasticity properties that describe the energy stored in the system. Fig. 2 (a) shows the storage modulus of pure natural rubber and of natural rubber/barium titanate composites with different filler contents as a function of temperature. It can be seen that the storage modulus of all the samples decreased with an increase in temperature. It decreased quickly in the temperature range from -70 °C to -50 °C due to the glass transition temperature. These results were consistent with Moayad Husein Flaifel et al. who studied the dynamic mechanical properties of NiZn ferrite nanoparticle-filled thermoplastic natural rubber nanocomposites. They found that the decreasing rate of storage modulus over the entire temperature range is not constant, and a significant drop in its value occurs within the temperature range of -70 °C to -50 °C [10]. Furthermore, the barium titanate had an influence upon the storage modulus of the rubber composites, which could be decreased with an increase in temperature.

The tangent delta (tanδ) is the ratio of loss modulus to the storage modulus. The tanδ peak can also provide information on the glass transition temperature (T_g) and energy dissipation of materials [10]. Fig. 2 (b) shows tanδ of pure natural rubber and natural rubber/barium titanate composites with different filler contents as a function of temperature. From Fig. 2 (b), pure natural rubber presents the highest magnitude of tanδ. The incorporation of barium titanate into the natural rubber matrix decreases the height of the tanδ peak. The reduction in the height of the tanδ peak for rubber composites with higher filler content is due to the strengthening effect provided by the fillers. The tanδ peak of natural rubber is shifted to a higher temperature with the addition of barium titanate. This indicated that the T_g values of the samples shifted to a higher temperature with an increase in barium titanate content. It can be explained that the strengthening effect of the filler has limited the mobility of the rubber chain.



(a) (b)

Fig. 2 Dynamic mechanical properties of natural rubber/barium titanate composites: (a) storage modulus; (b) tanδ.



(a) (b)

Fig. 3 Dielectric properties of natural rubber/barium titanate composites: (a) dielectric constant; (b) dielectric loss.

The dielectric properties of pure natural rubber and natural rubber/barium titanate composites were measured by precision impedance analyzer. The dielectric constants of pure natural rubber and natural rubber/barium titanate composites with different filler contents at frequencies from 1 KHz to 1 MHz are shown in Fig. 3 (a). It is observed that the incorporation of barium titanate can improve the dielectric constant of natural rubber and the filler content can enhance the dielectric constant of rubber composites. A similar finding was also observed by Jun Su and Jun Zhang that the increasing barium titanate content can increase the dielectric constant of polymer composites [4].

Fig. 3 (b) shows the curve of the dielectric loss of pure natural rubber and natural rubber/barium titanate composites with different filler contents. It was found that the dielectric loss of all the rubber composites showed similar trends in which the dielectric loss is unstable at frequencies below 10,000 Hz; when the frequency became higher the dielectric loss became stable. The dielectric loss increases with increasing frequency.

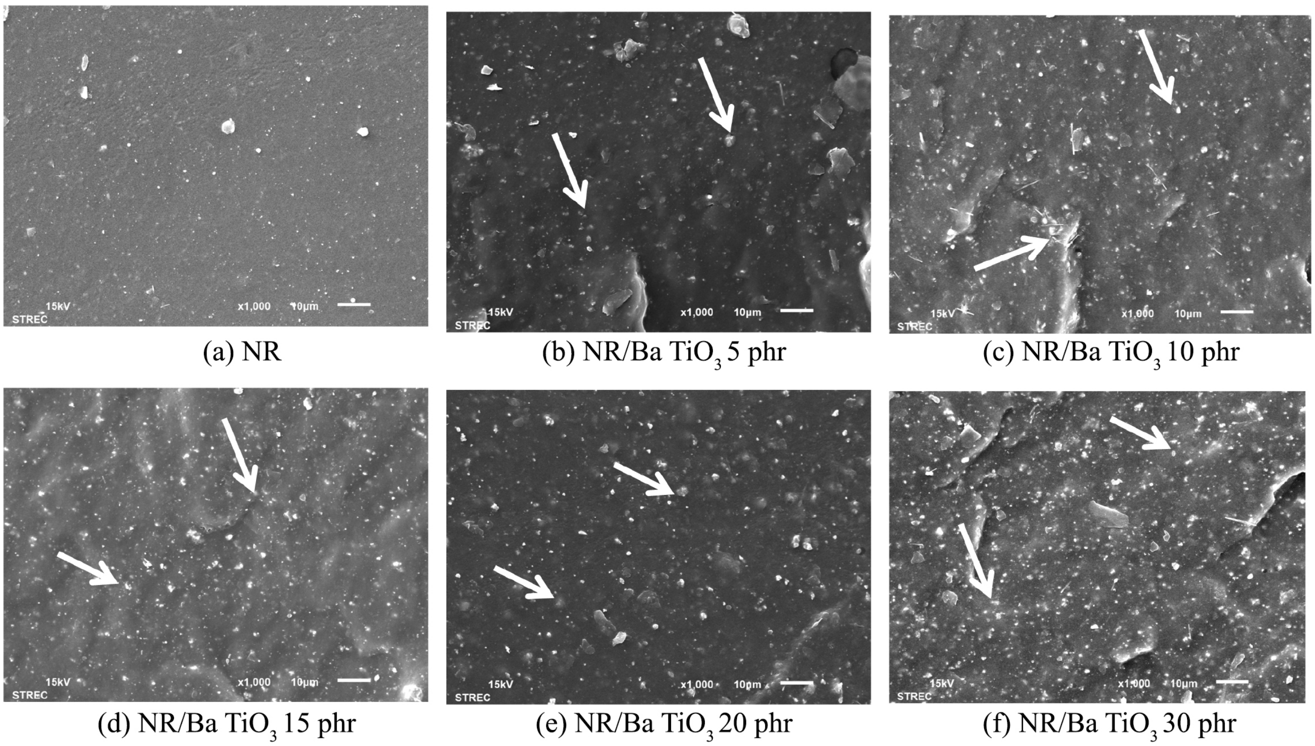


Fig. 4 SEM images of natural rubber/barium titanate composites: (a) NR; (b) NR/$BaTiO_3$ 5 phr; (c) NR/$BaTiO_3$ 10 phr; (d) NR/$BaTiO_3$ 15 phr; (e) NR/$BaTiO_3$ 20 phr; (f) NR/$BaTiO_3$ 30 phr.

Fig. 4 shows the SEM images of the fracture surface of natural rubber/barium titanate composites. It can be seen that the barium titanate particles are well dispersed in the natural rubber matrix, as indicated by the white arrows. The good dispersion may be due to the surface modification of barium titanate with si-69 improved interfacial adhesion between barium titanate particles and natural rubber [8]. Improvements in the properties of the rubber composites were obtained.

4. Conclusion

From the results explained above, it was found that the natural rubber/barium titanate composites have been successfully developed. The incorporation of barium titanate enhanced the tensile strength and hardness of natural rubber. In terms of dynamic mechanical properties, the addition of barium titanate decreased the height of the tanδ peak and the T_g values shifted slightly to a higher temperature. In addition, the dielectric properties of the natural rubber/barium titanate composites were enhanced with increasing barium titanate content. The good dispersion of barium titanate obtained in the rubber composites produced enhancement of the properties. Both results indicated that the addition of barium titanate in the natural rubber matrix has significantly improved the mechanical, dynamic mechanical and dielectric properties.

5. Acknowledgement

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