

EXPERIMENTAL AND MODELING STUDY ON THE EFFECT OF CARBON BLACK SUBSTITUTION WITH MODIFIED AND RAW BENTONITE ON THE TENSILE PROPERTIES OF NATURAL RUBBER COMPOSITES

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ABSTRACT

The effect of carbon black (CB) substitution with modified (M-BNT) and raw (BNT) bentonite on the tensile properties of natural rubber (NR) composites is investigated in this paper. NR composites are prepared using a third degree simplex lattice mixture design of experiment, where proportions of CB, M-BNT, and BNT are varied in the rubber formulations. M-BNT is produced by modifying sodium-activated bentonite with tetradecyl dimethylamine (TDA) salt and cocamide diethanolamine (CDEA). Results from tensile testing of NR composites reveal the optimum composition of mixture filler to be 10 phr CB, 5 phr M-BNT, and 0 phr BNT for tensile modulus, tensile strength and stresses at different strains (100, 200 and 300 %). Observed synergistic effect on tensile properties can be attributed to the formation of dual filler system between CB and M-BNT. Better dispersion of clay fillers in the rubber matrix was achieved due to organic modification of bentonite. Generated contour plots based on reduced hierarchical models show same trend demonstrating synergy between CB and M-BNT.

Keywords: Natural rubber; Carbon black; Bentonite; Design of experiment; Mixture filler

INTRODUCTION

Carbon black (CB) is considered to be the most widely used filler in rubber processing due to its reinforcing effect on material properties. However, researchers and rubber manufacturers today aim to look for filler substitutes due to the color limitations of carbon black and the devastating effect of its production on the environment [1].

Recently, layered silicates (clay) are gaining attention as potential filler substitutes not only to reduce polymer consumption and cost of production [2], but also to substantially improve the mechanical properties and thermal stability of produced rubber composites upon addition of organically modified clays [3, 4]. There are two characteristic

properties of layered silicates which give rise to improvement of mechanical properties of rubber composites: 1) high aspect ratio of layers/nanoparticles and 2) presence of exchangeable cations in the layer gaps which allows them to be modified chemically [4-6]. Chemical modification not only brings the reinforcing effect but also renders improvement in the filler-polymer compatibility. In addition to these properties, the platelet structure of clay offers a tortuous path for oxygen diffusion which thereby increases the thermal stability of rubber products [6].

Bentonite (BNT) is one of the most known and widely used natural clays for the preparation of organoclays. It also offers many advantages as rubber filler for it is naturally abundant, cheap, environmentally friendly and easy to modify because of its high cation exchange capacity (CEC) [7]. Ion-exchange with alkylammonium ions (cationic surfactant) is the most widely employed method in modifying clay minerals [8] which renders organophilicity to the filler [9].

In this present study, BNT clay is modified using a two-step organic treatment method. The first organic modification is done through the addition of tetradecyl dimethylamine (TDA) salt on sodium-activated BNT while the second organic modification is done through the addition of a non-ionic surfactant cocamide diethanolamine (CDEA). This paper aims to investigate the effect of replacing CB with modified (M-BNT) and raw (BNT) bentonite on the tensile properties of NR composites. Tensile modulus, tensile strength and stresses at different strains (100, 200 and 300 %) are measured. This study also aims to model the tensile properties of natural rubber (NR) composites as function of CB, M-BNT, and BNT proportions in the rubber formulations using reduced hierarchical models.

EXPERIMENTAL

Materials

All analytical grade reagents and industrial grade BNT used in clay modification and preparation of NR composites were sourced from local suppliers. NR and compounding ingredients were provided by Rhodoco Rubber Processing Services, Inc.

NR Composite Preparation

Plain NR and thirteen NR composites with varying mixture filler proportions of CB, M-BNT and BNT were prepared for this study. M-BNT was produced by modifying sodium chloride - activated BNT with TDA salt (1 times the CEC of BNT) and CDEA (3 wt. % of dried clay). These formulations were dictated by a third degree simplex lattice mixture design of experiment (DOE) [10]. Each formulation contains 100 phr NR, 5 phr zinc oxide, 2 phr stearic acid, 1.4 phr sulfur, 1.4 phr n-tert-butyl-2-benzothiazole sulfenamide (TBBS), and 15 phr mixture filler. NR composites were prepared by compounding rubber and other ingredients in a two-roll mill. Rubber compounds were vulcanized in a compression moulding press at 160 °C for 20 mins. Compounding and vulcanization of rubber was performed by Rhodoco Rubber Processing Services, Inc.

BNT and M-BNT Characterization

X-Ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy using attenuated total reflectance (ATR) analyses were employed to determine the effect of organic modifications performed on BNT. Diffraction patterns were recorded using an x-ray diffractometer (Shimadzu XRD 7000) with Cu-K α target $\lambda = 1.54 \text{ \AA}$ and a scanning rate of $2^\circ/\text{min}$. Infrared spectra were recorded using a spectrometer (Thermo-Scientific Nicolet 6700) equipped with ATR accessory.

Tensile Property Testing.

Tensile tests were performed on dumbbell-shaped specimens using a universal testing machine (Shimadzu AGS-5kNX) to obtain values of tensile modulus, tensile strength and stresses at different strains (100, 200 and 300 %).

Modeling of Tensile Properties

Empirical modeling was applied on the tensile properties of NR samples. Minitab 17 was used to generate the models and contour plots as function of CB, M-BNT and BNT proportions. Reduced hierarchical models were established by considering only the significant terms ($p < 0.05$) in the full cubic model as given by the analysis of variance (ANOVA).

RESULTS AND DISCUSSION

BNT and M-BNT Characterization

Figure 1 shows the XRD and FTIR-ATR results of BNT and M-BNT. Figure 1(a) shows XRD diffraction peaks at 2θ values of 5.72° and 5.06° which were exhibited by BNT and M-BNT, respectively, as computed using Bragg's Law ($\lambda = 2d\sin\theta$) [11]. This 2θ values correspond to d values of $15.45 \text{ \AA}$ and $17.46 \text{ \AA}$. It is observed that the XRD peak of M-BNT exhibited a displacement from a higher to lower 2θ value. This observation is attributed to the intercalation of the organic species in the silicate galleries of BNT. This phenomenon caused the expansion of interlayer spacing from $15.45 \text{ \AA}$ (BNT) to $17.46 \text{ \AA}$ (M-BNT). The expansion of the interlayer spacing in M-BNT suggests the effectiveness of the organic treatments employed to BNT. Figure 2(b) shows the appearance of three new peaks on the FTIR-ATR spectrum of M-BNT. The band at 1465 cm^{-1} is attributed to the C-H bending vibrations (medium intensity) of methylene groups. Bands at 2846 cm^{-1} and 2916 cm^{-1} are attributed to the C-H asymmetric (medium intensity) and symmetric (strong intensity) stretching vibrations, respectively [12]. The formation of these bands suggests the incidence of aliphatic groups on M-BNT clay surface. This observation agrees with the XRD results confirming the effectiveness of the two-step organic treatment.

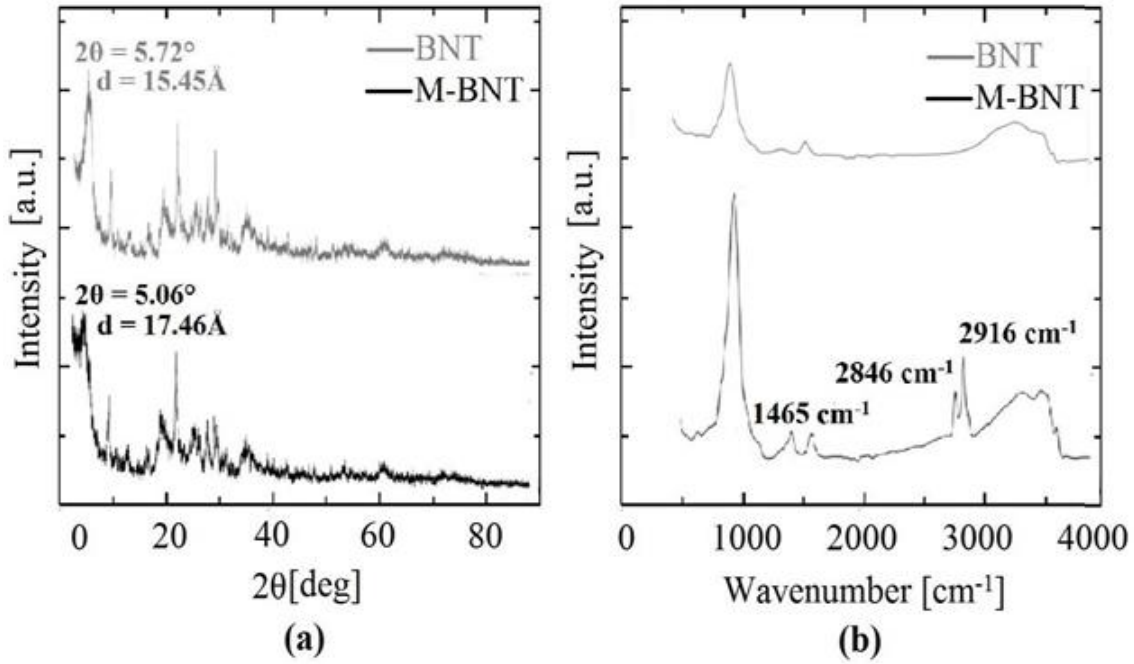


Figure 1: (a) XRD and (b) FTIR-ATR results of BNT and M-BNT

Tensile Properties

Figure 2 shows a graphical summary of the tensile properties of NR composites. Line plots represent the magnitudes of tensile modulus and tensile strength of plain NR (control) and 13 NR composites while bar plots represent the magnitudes of the stresses at different strains (100, 200 and 300 %).

NR composite with mixture filler CB/M-BNT/BNT 10/5/0 exhibits superior tensile properties relative to all samples. This composite gives the highest value for all tensile properties: tensile modulus (1.14 MPa), tensile strength (5.91 MPa), stress at 100 % strain (0.85 MPa), stress at 200 % strain (1.39 MPa) and stress at 300 % strain (1.96 MPa). NR composite with pure BNT filler shows to have the least tensile performance for all composites: tensile modulus (0.63 MPa), tensile strength (2.55 MPa), stress at 100 % strain (0.54 MPa), stress at 200 % strain (0.79 MPa) and stress at 300 % strain (1.02 MPa) which is due to the incompatibility of BNT filler to non-polar NR.

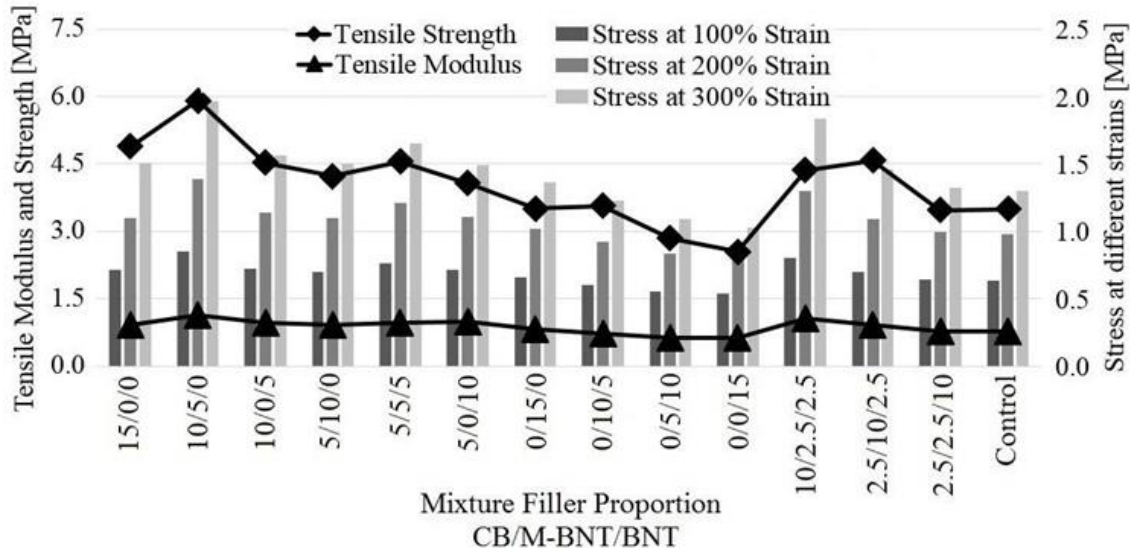


Figure 2: Tensile properties of NR composites at varied proportions of CB, M-BNT, and BNT fillers

After partial replacement of CB with 5 phr of M-BNT, 23.06 % improvement in tensile modulus, 21.10 % improvement in tensile strength, 19.53 % improvement in stress at 100 % strain, 26.14 % improvement in stress at 200 % strain, 30.35 % improvement in stress at 300 % strain are observed as compared to NR composites with pure CB filler. The above observations serve as evidence on how partially replacing CB with M-BNT can significantly improve tensile properties of NR composites. The remarkable improvement in tensile properties is attributed to the synergistic effect of CB and M-BNT fillers due to the formation of a dual filler structure. [13-15]. M-BNT gets associated with CB particles forming a hybrid filler network. This structure renders more chain mobility which contributes to the increase in tensile modulus and strength of the composites [14]. Furthermore, the layered structure of M-BNT allows slippage of rubber chains which renders resistance to deformation even at higher strains [15].

Modeling of Tensile Properties.

Figure 3 shows the contour plots of (a) tensile modulus, (b) tensile strength and (c-e) stresses at different strains (100, 200 and 300 %) as function of CB, M- BNT, and BNT proportions. Dark-shaded regions represent high values of tensile properties while light-shaded regions represent low values. All contour plots exhibit a similar trend. High tensile properties are located on the CB and CB/M-BNT side of the contour plots. This demonstrates synergy between CB and M-BNT upon partial replacement of CB with 5 phr of M-BNT. On the other hand, low tensile properties can be found on the BNT side. The difference in the reinforcing effect of BNT and M-BNT fillers on the NR composites confirms the significance of surface modification on bentonite in order to provide enhancement in the tensile performance of rubber composites.

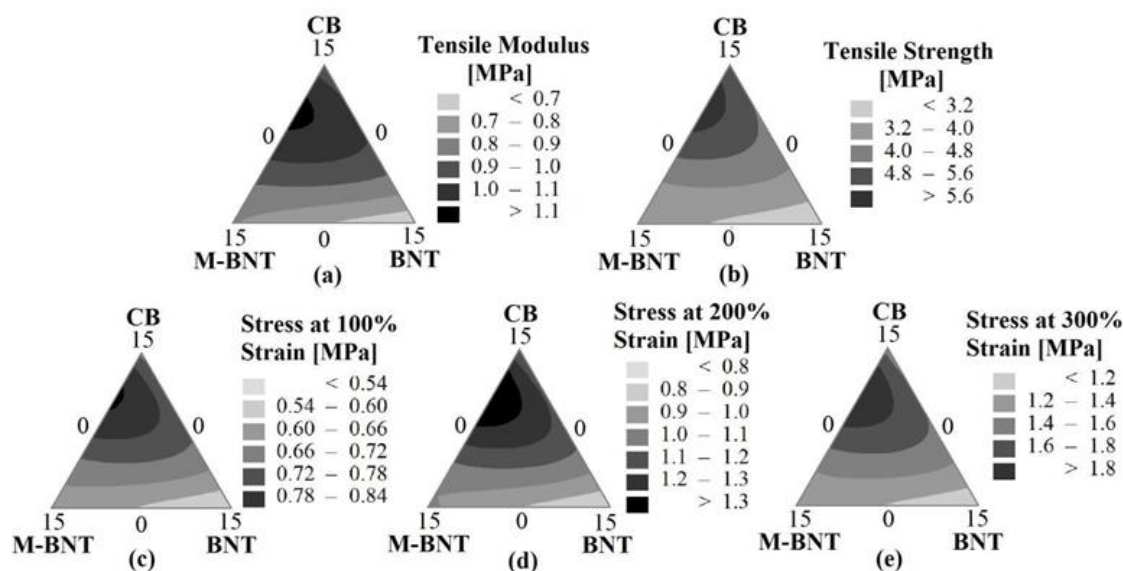


Figure 3: Contour plots of (a) Tensile Modulus, (b) Tensile Strength, Stresses at different strains (c) 100 %, (d) 200 % and (e) 300 %

CONCLUSION

M-BNT is a promising filler substitute to carbon black in terms of improving the tensile properties of NR composites. Synergistic effect on tensile properties of NR composite is achieved at 10 phr CB and 5 phr M-BNT which is found to be the optimum mixture filler proportion in this study. XRD and FTIR-ATR results confirm the effectiveness of surface modification performed on BNT. Contour plots based on reduced hierarchical models show same trend demonstrating synergy between CB and M-BNT which leads to improved tensile performance of filled NR composites.

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