

EFFECT OF THERMAL AGING ON HARDNESS AND TENSILE FRACTURE OF NATURAL RUBBER COMPOSITES BASED ON SILICA AND MODIFIED/RAW BENTONITE FILLER SYSTEM

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ABSTRACT

Natural rubber (NR) composites filled with silica, modified bentonite (M-BNT), and raw bentonite (BNT) at varied amounts were prepared and tested for hardness and tensile fracture after thermal aging at 70 and 100 °C for 336 h. At 70 °C, the hardness of NR composites increased due to postcuring effect up to 336 h, while initial postcure for 48 h followed by degradation was observed at 100 °C. Measurements of tensile strength and elongation at break indicate a silica/M-BNT mixture filler would give good thermal resistance to NR composites. On the other hand, contour maps showed poor thermal resistance of NR composites filled with BNT. Attenuated total reflectance (ATR) – Fourier transform infrared (FTIR) spectra of aged NR composites show oxidation and chain scission during thermal aging.

Keywords: Natural rubber; Thermal aging; Bentonite; Silica; Mixture filler

INTRODUCTION

When exposed to high temperatures, natural rubber (NR), just like any other polymer, undergoes irreversible structural changes linked to its instability or to its interaction with atmospheric oxygen. These structural changes lead to changes of use properties [1]. The degree of degradation depends largely on the components added to NR. In this study, the effect of thermal aging on hardness and tensile fracture of NR composites was investigated based on a ternary filler system: silica, modified bentonite (M-BNT), and raw bentonite (BNT).

Most of the rubbers used in industry are subjected to heat which could result to drastic changes in the rubber properties. NR degrades in a wide variety of environments and service conditions. This degradation limits the service lifetime of NR [2, 3]. For instance, in oxygen containing environments, the mechanical strength of NR can be greatly affected by oxidation, especially at high temperatures. In order to determine the resistance of NR composites to oxidation, accelerated aging tests are typically used. During thermal aging, main-chain scission, crosslink formation, and crosslink breakage can occur, leading to severe changes in the mechanical properties of NR [4-6].

Particle-filled NR composites have recently attracted attention owing to their low cost and widespread industrial applications [7]. The usage of NR as an engineering material would be limited without the reinforcing character of certain fillers, which favorably modify properties such as stiffness, tensile strength, heat distortion, moldability, and several other important attributes. As of late, the use of clay fillers in increasing the thermal aging resistance of NR and other elastomers has gained the attention of some researchers. Rattanasom and Prasertsri [8] investigated the effect of partial replacement of calcined clay with various types of carbon black on the thermal aging resistance of NR vulcanizates, and found out that the thermal aging resistance of NR vulcanizates tend to be enhanced by the addition of various types of carbon black due to carbon black's higher reinforcing efficiency compared to that of the clay. In addition, Choudhury et al. [9] studied the effect of organo-modified clay on accelerated aging resistance of hydrogenated nitrile rubber nanocomposites. Their results suggest that the addition of organically modified clay improved the retention of physico-mechanical properties of the elastomer by disrupting the oxidative process. Likewise, Chen et al. [10] investigated the thermal degradation of hydrogenated nitrile-butadiene rubber (HNBR)/clay and HNBR/clay/carbon nanotubes (CNTs) nanocomposites, and observed that the coexistence of clay and CNTs could form compact char layers with better barrier property than clay, thereby improving the thermal stability of HNBR.

Although several hybrid filler systems have already been studied, the effect of replacement of silica with raw and modified bentonite has not been reported elsewhere. Therefore, in the present study, the effect of using a combination of three fillers, namely silica, M-BNT and BNT, on the thermal aging resistance of NR composites will be evaluated in light of hardness and tensile fracture property retention.

EXPERIMENTAL

Preparation of Modified Bentonite

One hundred grams of raw bentonite BNT (Saile Industries Inc.) was dispersed in 3 liters of distilled water (pre-heated at 80 °C) using a disperser (IKA T50 Digital Ultra-Turrax) for 1 min at 5000 rpm. Five grams of NaCl (AR grade, RTC Laboratory Services and Supply House) was then added to the hot clay slurry and mixed for another minute using the disperser. Using an overhead stirrer (IKA RW20 Digital), stirring was further carried out for 58 min at 1450 rpm while the temperature was maintained at 80 °C. Afterwards, a solution that was prepared by mixing 500 ml distilled water, 12.94 g tetradecyldimethylamine TDA (FARMIN DM4098, Pilipinas Kao Inc.), and 5.12 g HCl (AR grade, 37 wt%, RTC Laboratory Services and Supply House) was then added to the clay slurry. The slurry was dispersed for 1 min at 5000 rpm, and then stirred for 59 min at 1450 rpm while the temperature was kept at 80 °C. The resulting slurry was filtered, and the collected clay was dried in an oven for at least 24 h at 100 °C. Coco diethanolamide CDEA (Fil-Amide 182, Chemrez Technologies Inc.) weighing 3% of the mass of the dried clay was mixed with the dried clay on a porcelain mortar with a pestle. This process of heating then mixing was repeated three times to yield modified

bentonite (M-BNT). The produced M-BNT was placed in an oven at 80 °C for another 48 h to ensure dryness, and then stored in plastic containers before use in NR compounding.

Natural Rubber Formulations

Thirteen NR formulations were prepared for this study. Each formulation contains 100 phr NR, 5 phr zinc oxide, 2 phr stearic acid, 3.5 phr sulfur, 3.5 phr N- cyclohexyl-2-benzothiazole sulfenamide, and 15 phr filler. Another formulation without any filler was prepared as control. The filler was composed of a mixture of silica, M-BNT, and BNT at varied proportions, as dictated by a simplex lattice mixture design of experiment [11]. NR composites were prepared by compounding rubber and other ingredients in a two-roll mill. The rubber compounds were vulcanized in a compression molding press at 160 °C for 20 min.

Thermal Aging

Thermal aging of NR composites was conducted at 70 and 100 °C using a natural convection oven for 336 h. The aged specimens were left at room temperature for at least 16 h before testing for hardness and tensile fracture.

Measurement of Hardness and Tensile Properties

Aged and unaged samples were subjected to hardness and tensile fracture properties determination. Hardness was measured according to ASTM D2240 using a durometer (Kori Type KA). Tensile tests were performed on dumbbell shaped (Die C) specimens according to ASTM D412 using a universal testing machine (Shimadzu AGS-5kNX) at a crosshead speed of 500 mm/min. Three samples from each formulation were tested, and the average values were reported.

Characterization of Natural Rubber Composites

Attenuated total reflectance (ATR) – Fourier transform infrared (FTIR) spectra of NR composites before and after aging were obtained using a FTIR spectrometer (Thermo Nicolet 6700).

RESULTS AND DISCUSSION

Mechanical Properties of NR Composites.

Figure 1 shows the hardness (Shore A) of NR composites before and after 144 h of aging. The increase in hardness at 70 °C is attributed to a postcuring effect, wherein an increase in crosslinking leads to an increase in rigidity of the composites [1]. Durometer measurements over time show an increase in hardness for all formulations when aged at 70 °C up to 336 h. On the other hand, an increase during the initial phase then a continuous decrease in hardness after 48 h can be observed for NR composites when aged at 100 °C. The decrease can be attributed to the main-chain scission due to oxidative degradation of NR composites.

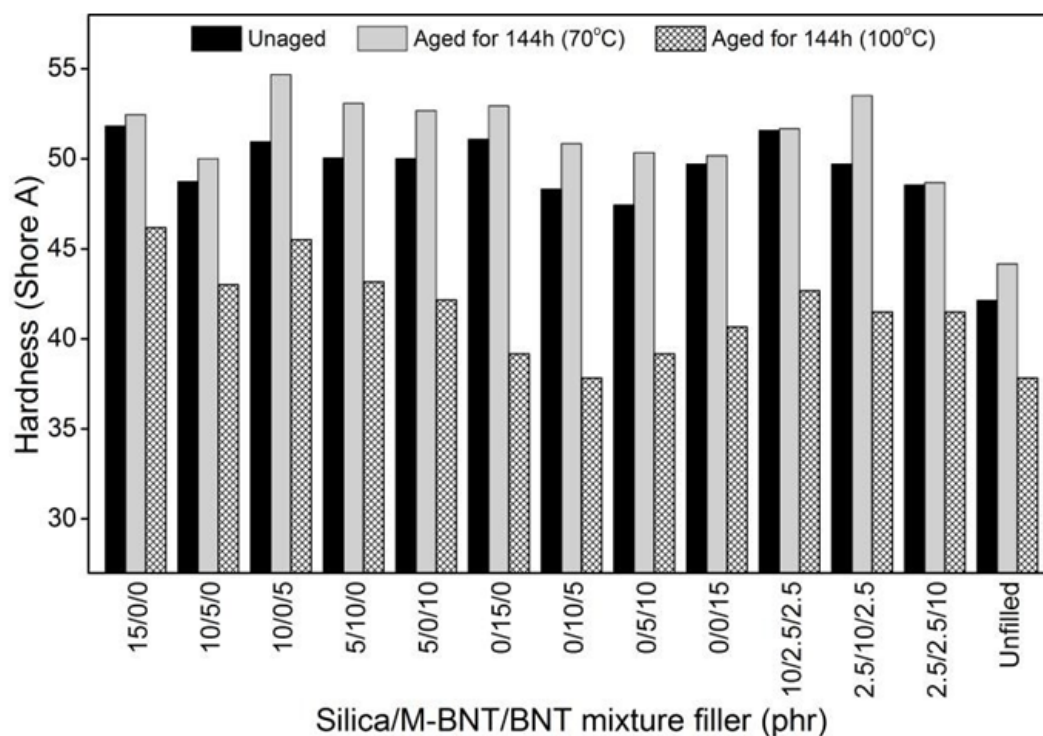


Figure 1: Hardness (Shore A) of NR composites before and after aging

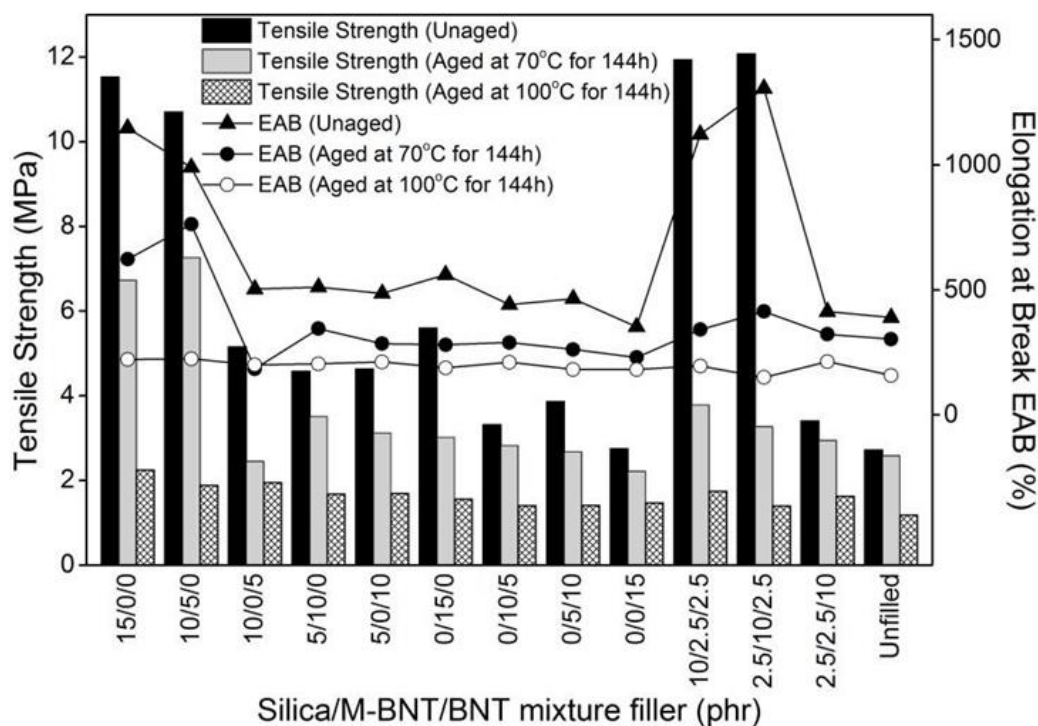


Figure 2: Tensile strength and elongation at break of NR composites before and after

Figure 2 shows the tensile strength and elongation at break of NR composites before and after 144 h of aging. The good thermal aging resistance exhibited by the composite filled with 10/5 phr silica/M-BNT mixture could be attributed to the formation of a barrier by the M-BNT platelets, thereby impeding the diffusion of oxygen through the NR matrix.

aging.

After extended periods of heating, NR composites became tacky and lost their tensile strength. This could be a result of excessive main chain scission and other chemical changes leading to a reduced tendency to crystallize at high strain. Superimposed ATR-FTIR spectra (Figure 3) show the presence of -OH groups ($3,570 - 3,200 \text{ cm}^{-1}$) and C=O groups (1690 cm^{-1}) after aging, indicating oxidation at the main polymeric chain of the NR composites [12].

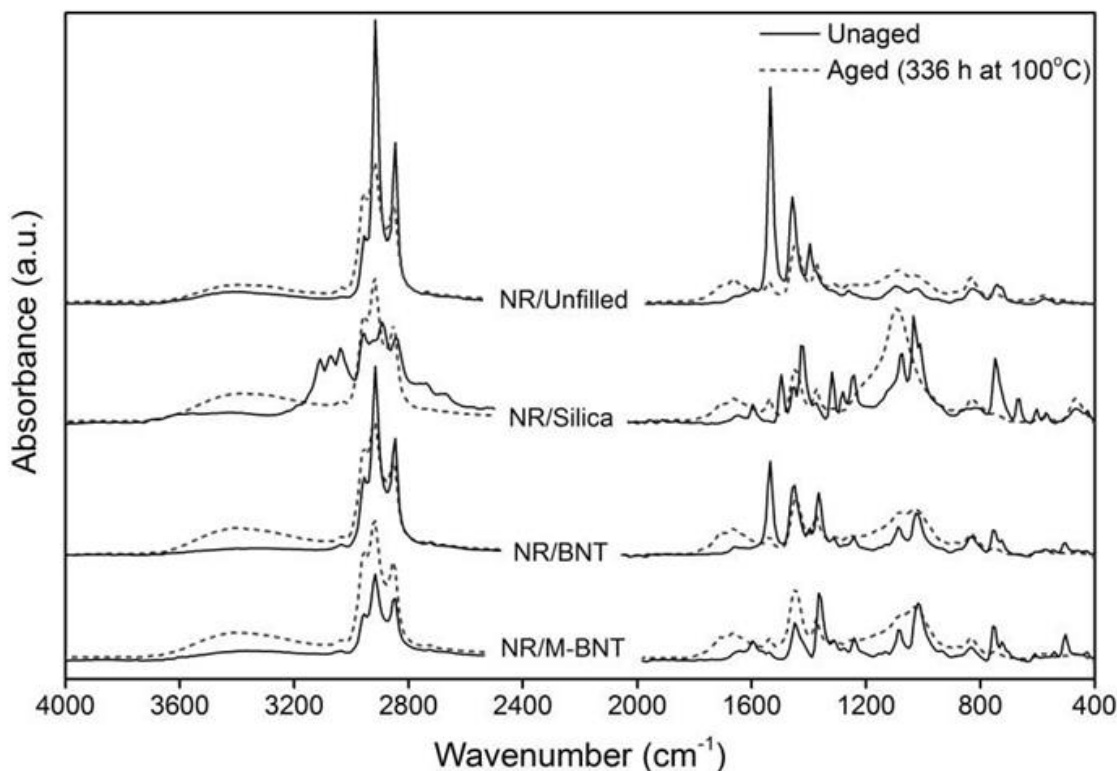


Figure 3: ATR-FTIR spectra of NR composites before and after aging for 336 h

Contour Plots

Ternary contour plots (Figure 4) reveal that among the three fillers, BNT imparted the least thermal aging resistance to NR composites. Moreover, the plots show an antagonistic effect between silica and BNT on resisting changes in the tensile strength and elongation at break of NR composites due to thermal aging. The plots are generated

according to equations 1-3:

$$\text{Hardness} = 3.4368 * \text{Silica} + 3.5127 * \text{M-BNT} + 3.2644 * \text{BNT} + 0.0518 * \text{Silica} * \text{BNT} \quad (1)$$

$$\text{Tensile Strength} = 0.4602 * \text{Silica} + 0.1958 * \text{M-BNT} + 0.1819 * \text{BNT} - 0.0417 * \text{Silica} * \text{BNT} \quad (2)$$

$$\text{EAB} = 44.2274 * \text{Silica} + 21.2095 * \text{M-BNT} + 19.1865 * \text{BNT} - 4.7143 * \text{Silica} * \text{BNT} \quad (3)$$

where “Hardness” is in the Shore A scale, “Tensile Strength” in MPa, “EAB” in %, and “Silica”, “M-BNT” and “BNT” in phr. These reduced hierarchical models are generated using the mixture design of experiment analyzer of Minitab 17.

Generally, positive interaction coefficients indicate synergism and negative interaction coefficients indicate antagonism [11]. The positive “Silica*BNT” cross product coefficient indicate that blending silica and BNT would be more effective in resisting changes in hardness levels when thermally aged at 70 °C than when used individually. On the other hand, negative “Silica*BNT” cross product coefficients indicate that blending silica and BNT would mean less thermal aging resistance at 70 °C in terms of tensile strength and EAB than when used individually.

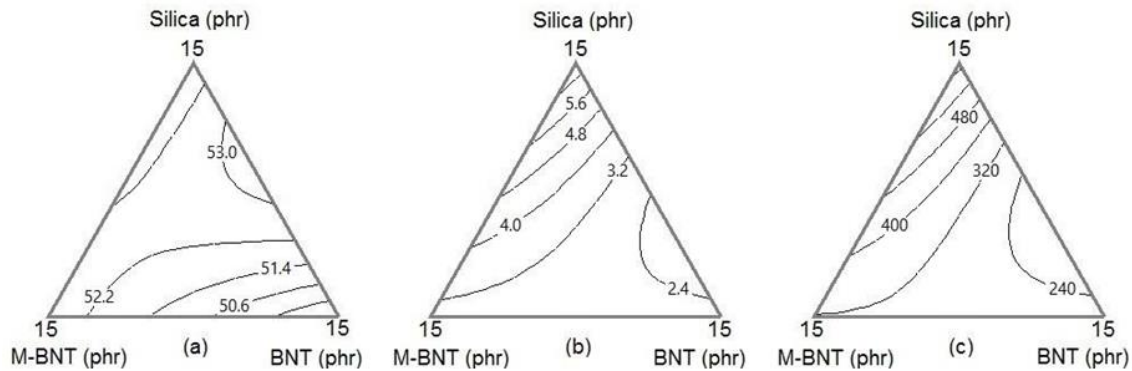


Figure 4: Ternary contour plots showing (a) Shore A hardness, (b) tensile strength in MPa, and (c) elongation at break in % of NR composites after thermal aging at 70 °C for 144 h

CONCLUSION

The effect of thermal aging on hardness and tensile fracture of NR composites based on silica/M- BNT/BNT ternary filler system was studied. The effect of aging was more pronounced at 100 °C than at 70 °C. The effect of postcure on hardness was predominant. Tensile strength and EAB decreased with aging time for both temperatures, but property loss was greater at 100 °C. Contour maps revealed poor thermal resistance of BNT-filled composites. For all NR composites, thermo- oxidative attack to the main polymeric chain, as manifested by ATR-FTIR peaks suggestive of chain scission and formation of C=O groups, could be the mechanism of degradation during thermal aging.

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