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# Expanded Organo-Bentonite Nano Filler for High-Value Added Rubber Products

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## ABSTRACT

Manufacturers add carbon black, precipitated silica, and natural clay fillers in formulations of rubber products to improve processability, enhance mechanical properties, and cut material cost. However, carbon black is harmful in nature and limits product color; precipitated silica is costly and decreases productivity; and natural clay has poor reinforcing ability. To reduce carbon black and precipitated silica in formulations and improve material performance, we propose the use of expanded organo-bentonite (EO-BNT) nano filler as an eco-friendly and cost-effective additive to rubber products. EO-BNT nano filler is produced from two-step chemical treatment of natural clay. We believe that the use of EO-BNT nano filler will introduce new formulations and improve the competitiveness of rubber products in the market. Our aim is to use EO-BNT nano filler as an effective additive to improve material properties and lower the consumption of carbon black and precipitated silica during rubber compounding. We are currently testing amine salts and non-ionic surfactants as feasible chemicals for modification of local bentonite clay.

**KEYWORDS:** nano filler, rubber, bentonite, organo-clay

## 1 INTRODUCTION

The rubber manufacturing industry has long been dependent on the use of conventional fillers such as carbon black, precipitated silica and natural clay in their product formulations. Fillers are used in rubber products for special purposes, such as enhancement of mechanical properties, improvement of processability, and reduction of material cost. However, the application of these conventional fillers is accompanied by several problems. For instance, carbon black is polluting in nature due to its dependence on petroleum; its black color also restricts product design leading to importation of expensive non-black fillers such as precipitated silica. On the other hand, precipitated silica offers lower mechanical properties as compared to carbon black due to its inability to achieve good dispersion during rubber compounding (Ismael and Mathialagan, 2012). Natural clay, although abundant and relatively inexpensive, only provides low reinforcing ability due to its large particle size and low surface activity (El-Nashar et al., 2012).

To solve the problem of large particle size and low surface activity of inexpensive clay, organic modification is applied to enhance the interaction between clay particles and rubber molecules. During organic modification, the distance between clay layer gaps is increased, causing collapse of stacked layered structure and reduction of clay particle size to nanoscale thickness. Figure 1 illustrates the expected dispersion of natural and organo-treated clay fillers in rubber. Because of the intercalation (Figure 1b) and exfoliation (Figure 1c) of the silicate layers using organo-treated clay fillers, there is improvement in material properties of rubber products. Sengupta et al. (2007) reported fast curing rates, improved gas barrier properties, solvent resistance and thermal stability as positive results after incorporation of small amounts of organo-clay nano filler in rubber formulations.

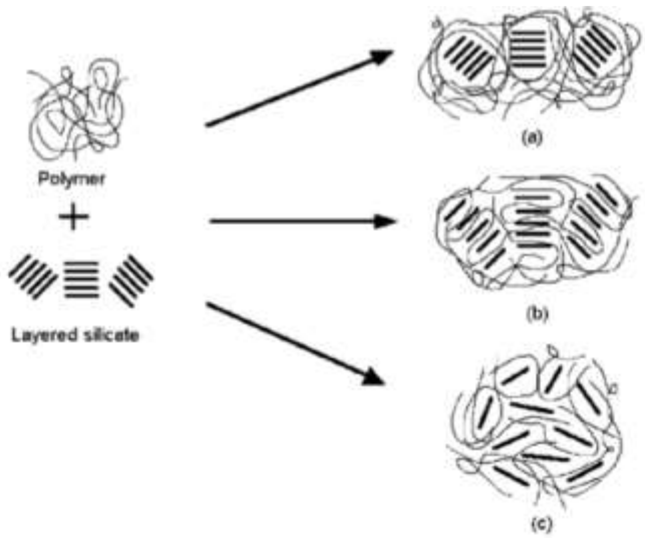


Figure 1 Expected dispersion of (a) natural and (b,c) organo-treated clay fillers in rubber (Sengupta et al., 2007).

However, in practice, the use of organo-treated clays as filler does not always result to significant improvement of material properties due to non-uniform dispersion and large aggregate formation of clay fillers in the rubber matrix (Das et al., 2011). The current organic treatment is not sufficient to consistently improve material properties of rubber products. This project proposes the use of expanded organo-bentonite (EO-BNT) nano filler to improve material properties and possibly reduce or replace carbon black and precipitated silica in rubber product formulations. Figure 2 illustrates the proposed method of preparing EO-BNT nano filler.

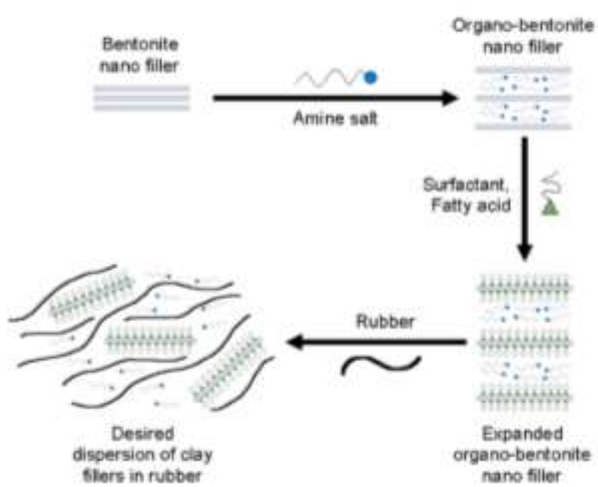


Figure 2 Preparation of proposed expanded organo-bentonite (EO-BNT) nano filler and its expected dispersion in rubber.

The project will apply a "propping-open" procedure to stepwise expand the gap space between clay layers (Das et al., 2011). The first organic modification of bentonite clay using amine salt solution will primarily swell and expand the clay layer spacing. The secondary organic modification using a surfactant or fatty acid will further expand the gap space and enhance the surface activity of clay layers to rubber molecules (Rooj et al., 2012). The use of EO-BNT nano filler in rubber formulations is expected to ensure consistent improvement in material properties than using natural bentonite clay and organo-bentonite fillers due to increased exfoliation and uniform dispersion. EO-BNT nano filler may also partially or totally replace expensive conventional fillers such as carbon black and precipitated silica in rubber compounds.

## 2 PROJECT GOALS AND OBJECTIVES

This project study has the following goals and specific objectives:

Goal #1 – To effectively use expanded organo-bentonite (EO-BNT) nano filler in improvement of material performance of rubber products.

- Objective #1.1 – To successfully prepare EO-BNT nano filler from available local natural clay and chemicals.
- Objective #1.2 – To utilize the prepared EO-BNT nano filler in optimized compounding and vulcanization of a rubber product.
- Objective #1.3 – To determine the processing conditions of EO-BNT nano filler that will yield the optimum improvement in material properties of a rubber product.
- Objective #1.4 – To measure the material properties of a rubber product compounded with prepared and optimized EO-BNT nano filler as compared to compounded with usual organo- and natural bentonite nano filler – viscoelastic, thermo-mechanical, and chemical stability.

Goal #2 – To reduce the amount of carbon black and precipitated silica in rubber product formulations, resulting to less importation of expensive fillers and reduction of manufacturing cost.

- Objective #2.1 – To use EO-BNT nano filler as a partial and full substitute for carbon black in compounding and vulcanization of a rubber product.
- Objective #2.2 – To measure the material properties of a rubber product partially and fully compounded with EO-BNT nano filler as compared to that compounded with only carbon black.
- Objective #2.3 – To use EO-BNT nano filler as a partial and full substitute for precipitated silica in compounding and vulcanization of a rubber product.
- Objective #2.4 – To measure the material properties of a rubber product partially and fully compounded with EO-BNT nano filler as compared to compounded with only precipitated silica.

Goal #3 – To enhance the capacity of the University of the Philippines Diliman (UPD) to work with the local rubber manufacturing industry on joint university-industry applied research projects.

- Objective #3.1 – To recruit a group of undergraduate and graduate students at the Department of Chemical Engineering (DChE), UPD, who will work on the "Expanded organo-bentonite nano filler for high value-added rubber products" research project.
- Objective #3.2 – To provide a training program for the recruited students that covers a) polymer and nano-structured material design, synthesis and characterization methods hosted by US partner Case Western Reserve University (CWRU); b) rubber product compounding and vulcanization hosted by industry partner Philippine Rubber Industries Association (PRIA); and c) rubber product testing methods hosted by DChE-UPD.
- Objective #3.3 – To present and publish the significant results of the research project in an international conference and academic journal, respectively.
- Objective #3.4 – To provide member companies of PRIA with relevant R&D directions and resources regarding a) application of EO-BNT nano filler in rubber product formulations; and b) latest advances in rubber research and innovation.

# 3 METHODS AND ACTIVITIES

## 3.1 Preparation of expanded organo-bentonite (EO-BNT) nano filler

Natural bentonite clay will be dispersed in deionized water, followed by treatment with sodium chloride salt. The primary organic modification will be done through the addition of tertiary amine dissolved in hot concentrated hydrochloric acid solution and added to the hot clay slurry. The forming sediment will be collected by vacuum filtration and will be washed repeatedly with hot water. The filtered sediment will then be dried in a vacuum oven at an elevated temperature to yield organo-modified bentonite clay. Subsequently, the secondary organic modification will be done by mixing a fatty acid or surfactant to the organo-modified bentonite clay at an elevated temperature. The expanded organo-bentonite (EO-BNT) nano filler will be formed after cooling the treated clay to room temperature. EO-BNT will further be grinded in a planetary ball mill for size reduction.

## 3.2 Rubber compounding and vulcanization

Rubber will initially be masticated and mixed with zinc oxide in an open two-roll mixing mill at an elevated temperature. Stearic acid, EO-BNT nano filler and other additives will then be incorporated in the mix. The compounded master batch will then be extruded, cooled and aged at room temperature for at least 24 hours. After aging, the compound will be mixed with vulcanization accelerators and sulfur. The amount of additives, accelerators and sulfur that will be mixed with rubber will be dictated by a list of formulations developed using active design of experiment (DOE). The final compound will be vulcanized by compression moulding in an electric hydraulic press at an elevated temperature for a specific time. Vulcanized rubber article will be shaped in sheet and button form as required by material property test methods.

## 3.3 Measurement of material properties and characteristics of bentonite nano filler and vulcanized rubber article

The material properties and characteristics of the bentonite nano filler to be measured are a) physical properties such as cation exchange capacity (CEC) of received natural bentonite clay and bulk density, b) solid state structure in terms of basal spacing by X-ray diffraction, c) confirmation of organic modification by Fourier Transform Infrared Spectroscopy (FTIR) using Attenuated Total Reflectance (ATR) accessory and d) surface characteristics using high-end optical microscopy. For the vulcanized rubber article, properties to be measured are a) rheometric properties and curing characteristics using a moving die rheometer, b) physical properties such as bulk density and hardness, c) mechanical properties using universal testing machine (UTM) and chemical stability by monitoring the change in weight with time during exposure to a chemical environment.

## 3.4 Optimization of processing conditions of EO-BNT nano filler

Design of experiments (DOE) will be used to find the processing conditions of EO-BNT nano filler that will give the most desirable responses in terms of rheometric properties, curing conditions, hardness, mechanical properties and chemical stability of vulcanized rubber article. The five processing conditions of EO-BNT nano filler that will be considered in this project are: a) amount of salt used during sodium activation of ground clay, b) type of tertiary amine salt used during first organic modification, c) amount of tertiary amine salt used, d) type of chemical used during second organic modification, and e) amount of chemical used during second organic modification. A $2^{5-1}$ fractional factorial DOE study is employed which instructs us to prepare at least 16 different rubber compounds (Lazic, 2004).

### 3.5 Effect of bentonite clay modification on intercalation and material properties of vulcanized rubber

DOE will also be employed to study the effect of several factors during physical and chemical modification of bentonite clay in terms of intercalation and material properties. The factors that will be studied will be the presence of the following processes during synthesis: sodium activation, organic modification with tertiary amine salt, organic modification with surfactant, and grinding time. A $2^4$ full factorial DOE study suggests at least 16 rubber compounds to prepare for the experiments (Lazic, 2004).

### 3.6 Feasibility of partial and/or full replacement of carbon black and precipitated silica with EO-BNT nano filler in rubber compounds

The idea of partial and/or full replacement of carbon black and precipitated silica with bentonite clay filler in rubber compounds will also be investigated. After determining the optimum processing conditions of bentonite nano filler, two (2) rubber product formulations containing carbon black and precipitated silica will be selected and tested (Chandrasekaran, 2007). The amount of carbon black and precipitated silica in the rubber formulations will be decreased systematically, while the amount of bentonite nano filler is simultaneously increased. The optimum loading of bentonite nano filler in the chosen formulations will then be determined.

## 4 ACKNOWLEDGEMENTS

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