

Comparative Study of the Mechanical and Flame-Retarding Properties of Polybutadiene Rubber Filled with Nanoparticles and Fly Ash

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ABSTRACT: A comparative study was performed of fly ash and nano-CaCO₃ as fillers in polybutadiene rubber with 0, 4, 8 and 12% fly ash and nano-CaCO₃. Uniform sheets were prepared of well-compounded rubber. Nano-CaCO₃ was synthesized by *in situ* deposition. The CaCO₃ nanoparticles as reinforcing agents improved the tensile strength more than 50% than fly ash, and the toughness and hardness

also increased significantly. Up to a 75% reduction in flammability and a 100% improvement in the tear strength were observed with nano-CaCO₃. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 6–9, 2005

Key words: flame retardance; mechanical properties; nanocomposites; rubber

INTRODUCTION

Polybutadiene rubber (PBR), a useful and low-cost rubber, is widely available. It has been used for pneumatic tires, soles, gaskets, seals, and belts. PBR is more popular as a general-purpose rubber, so it is important to concentrate on all its properties. PBR can be modified for the enhancement of the mechanical properties, flame retardancy, and tear resistance with the addition of conventional fillers. However, an improvement in one property can adversely affect another. For optimum properties, a nanofiller is an interesting option for today's material research.

With a small size and a large surface area, nanoparticles have many special properties that are different from those of microparticles. The modification of a polymer with montmorillonite clay fillers results in excellent performance and a combination of properties.^{1–3} However, the method of preparation affects the properties, including the nanoparticle size, volume fraction, and dispersion of nanoparticles into the matrix; the methods of interfacial adhesion and dispersion are remarkably important.⁴

This article describes the results of a nano-CaCO₃ filler with a special synthesis method and compares it to commercial CaCO₃ and fly-ash composites of PBR. The mechanical, flame-retardancy, tear-resistance, and

hardness properties are examined for each case and compared with those from other fillers.

EXPERIMENTAL

Materials

PBR with a density of 0.91 g/cc, a hardness of 43–45 A, and a tensile strength of 7.3 kg/cm² was used. Compounding gradients such as steric acid, sulfur, zinc oxide, calcium carbonate, and potassium bicarbonate were procured from S.D. Fine Chemicals, Ltd. (Mumbai, India), and analytical-grade calcium chloride (CaCl₂) and K₂CO₃ were used for the synthesis of nanoparticles of calcium carbonate. Poly(ethylene glycol) (PEG; S.D. Fine Chemicals; molecular weight = 6000) was used to form the complex.

Nanoparticle synthesis

Nano-CaCO₃ was synthesized with *in situ* deposition. CaCl₂ (110 g) was placed in 100 mL of water. PEG (248 g) was diluted with 100 mL of water and mildly heated for proper mixing. The complex of CaCl₂ was prepared with PEG in a 4:1 molar ratio in distilled water. It was heated mildly for the mixing of CaCl₂ and PEG for its deposition. Another solution of K₂CO₃ (106 g) was prepared in distilled water.^{4–9} The first complex was kept for 12 h, and then the second complex was slowly added to it; the mixture was kept for 24 h. The precipitate was filtered, washed with water, and dried *in vacuo*. Nanosynthesis by *in situ* deposition is shown in Figure 1.

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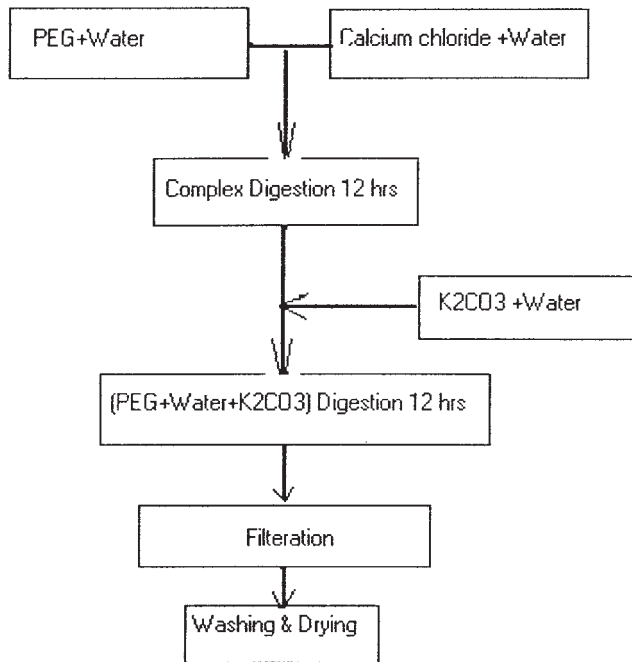


Figure 1 Synthesis of nano- CaCO_3 by *in situ* deposition.

Compounding

All the compounding ingredients were added according to the standard process. Nanoparticles were added homogeneously. The temperature and time were kept constant for each run.

Specimen preparation

The sheets from well-compounded rubber materials were prepared on a compression-molding machine in a simple flash-type chromium-plated mold with cavity dimensions of $130 \text{ mm} \times 130 \text{ mm} \times 3 \text{ mm}$. The samples were compressed under 100 kg/cm^2 of pressure at 145°C for 35 min of curing. The compositions of the fillers (nano- CaCO_3 , commercial CaCO_3 , and fly ash) were varied (0, 4, 8, and 12 wt % in PBR).

Tensile testing

Injection-molded tensile specimens per ASTM-D 638 were tested on a universal testing machine (model UT-2303, R&D Electronics, Mumbai, India). Testing was performed at room temperature. Modulus at 100% elongation and % elongation at break were determined at a deformation speed of 5.00 cm/min . The mean value of five measurements was taken.

Hardness

The compression-molded specimens were tested to determine the hardness data with a Shore A hardness

tester per ASTM D 2240. The data obtained represent the average values of five test specimens.

Flammability test

The tests were carried out according to ASTM D 4804, and the specimens ($1 \text{ cm} \times 8 \text{ cm} \times 0.5 \text{ cm}$) were tested for the burning rate of the materials.

Tear strength

The tear test specimens were prepared according to ASTM D 624. Weight was applied so that both ends apart from the notch tended to stretch in the opposite direction. The weight was gradually increased until spontaneous tearing occurred.

RESULTS AND DISCUSSION

Nanosize confirmation

Figure 2 shows X-ray diffraction scans for calcium carbonate synthesized in PEG. Nano- CaCO_3 was confirmed by X-ray diffraction scans with Scherer's formula:

$$d(\text{\AA}) = k\lambda / \Delta 2\theta \cos\theta \quad (1)$$

where d is the particle size (39 nm), k is the order of reflection, λ is 1.542, and θ is the diffraction angle.

Tensile properties

The relationship between the volume of the filler and the tensile strength of PBR/filler composites is shown in Figure 3. The tensile strength of the nano- CaCO_3 /rubber composites was higher than that of the other composites up to 8 wt % filler. The increase in the tensile strength of the fly-ash composite was less than that of the nano- CaCO_3 composite and commercial composite.

The increase in the tensile strength was the same (40%) for both nano- CaCO_3 and commercial CaCO_3 at 8 wt %. Above 8 wt %, the results for the nanofillers were not appreciable because the nanoparticles agglomerated at higher compositions, and so the results were almost the same as those of commercial calcium carbonate. For polymer nanocomposites, inorganic nanofillers freely disperse in polymers and increase the tensile properties drastically.¹⁰ However, for rubber, inorganic nanoparticles are strongly fixed by electrostatic forces, so it is necessary to add a hydrophobic layer with coupling agents to reduce the agglomeration problem and free dispersion of nanoparticles in rubber.¹¹ Hundiwale et al.¹² studied the mechanical properties of natural rubber filled with fly ash and micrometer-size calcium carbonate and observed that the fly-ash-filled composites were better with respect to mechanical properties than those filled with calcium carbonate.

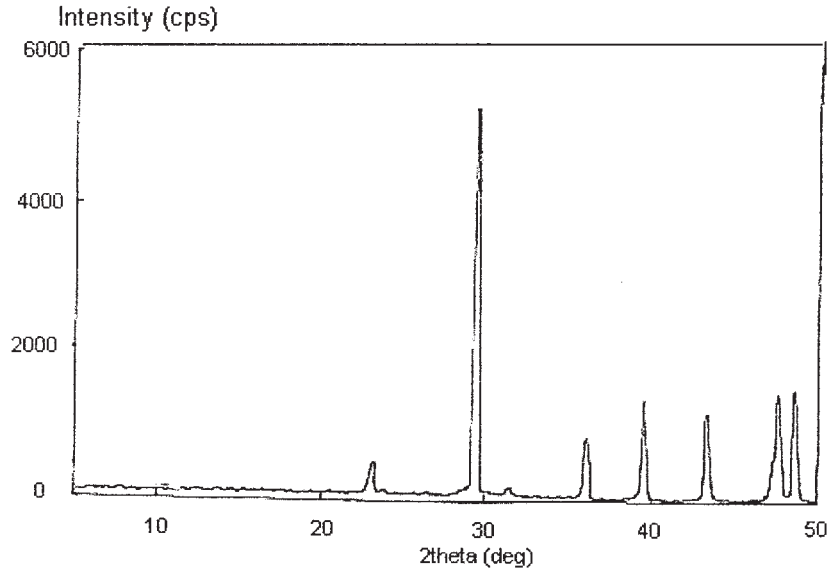


Figure 2 X-ray diffractogram of nano-CaCO₃.

Modulus at 100% elongation

The effect of different filler compositions on PBR is shown in Figure 4. The relationship indicates that Modulus at 100% elongation of fly ash was maximum in comparison with the moduli of the other fillers in the composites up to 4 wt %. At 8 wt % for all the fillers, Modulus was the same (0.73 MPa); the decrease in Modulus was sharp for nano-CaCO₃ filler concentrations greater than 8%.

Elongation at break and tear strength

Figure 5 illustrates the elongation at break of nano-CaCO₃, commercial CaCO₃, and fly ash. For all three compositions, the elongation at break increased with an increase in the filler content; for nano-CaCO₃, this

increment was sharp and almost 90% greater than that of the PBR control. The increases with commercial CaCO₃ and fly ash were 58 and 50%, respectively.

The relationship between the weight percentage of the fillers in PBR and the tear resistance of the PBR-filled composites is shown in Figure 6. The nanofilled rubber showed the greatest improvement in the tear strength with an increase in the filler concentrations. This effect was due to the very fine size of the particles, which produced more interfacial bonding along with good dispersion and homogeneity of bonding. This was substantiated by the results observed by Manchado et al.¹³ They reinforced natural rubber with modified bentonite clay and found that silicate nanolayers were exfoliated and uniformly dispersed in the rubber chains; elastomers crosslinked more in the presence of organoclay than natural rubber.

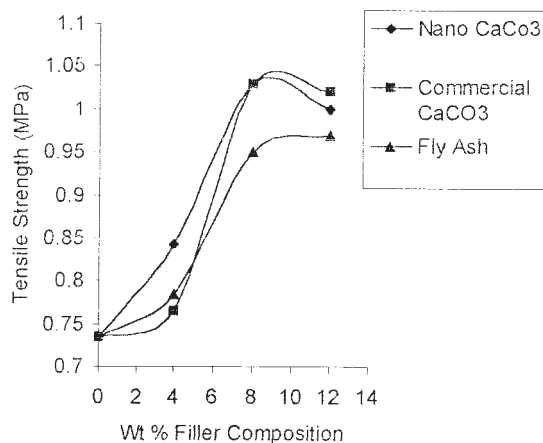


Figure 3 Tensile strength at break of PBR filled with different fillers.

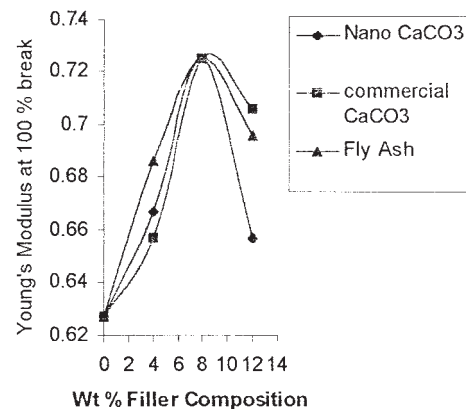


Figure 4 Modulus at 100% elongation of PBR filled with different fillers.

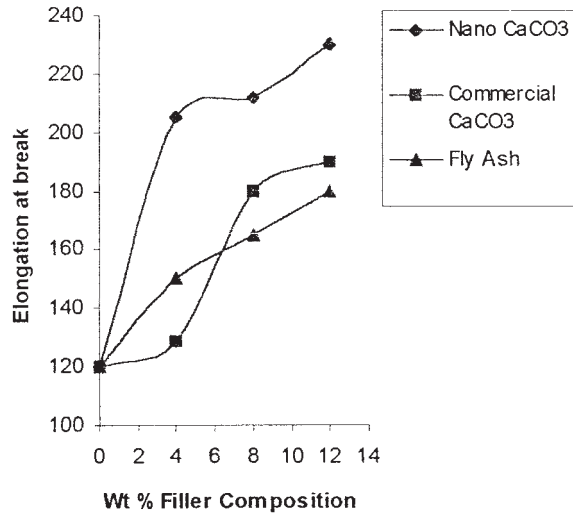


Figure 5 % elongation at break of PBR filled with different fillers.

Flammability

The rate of burning for different filler compositions is shown in Figure 7. The nano-CaCO₃-filled rubber showed a significant reduction in the rate of burning in comparison with rubber with commercial CaCO₃ or fly ash for all concentrations. The nanofiller formed an effective layer on the surface by its uniform dispersion. Thus, the absorption of energy by nanoparticles was uniform (endothermic), and the evolution of flue gases was hampered. This effect drastically reduced the burning phenomena in comparison with the other fillers.

CONCLUSIONS

The following conclusions could be drawn from this study:

1. The tensile strength and modulus at 100% elongation were more or less the same for the nano-CaCO₃ composites and commercial CaCO₃ composites up to 8% filler.

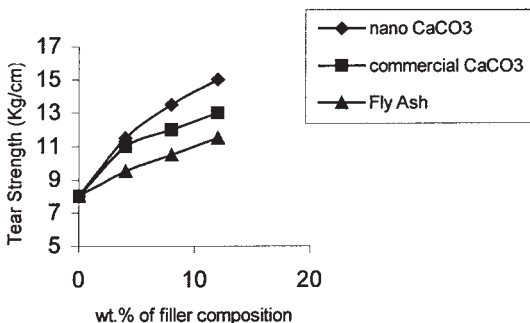


Figure 6 Tear strength of PBR filled with different fillers.

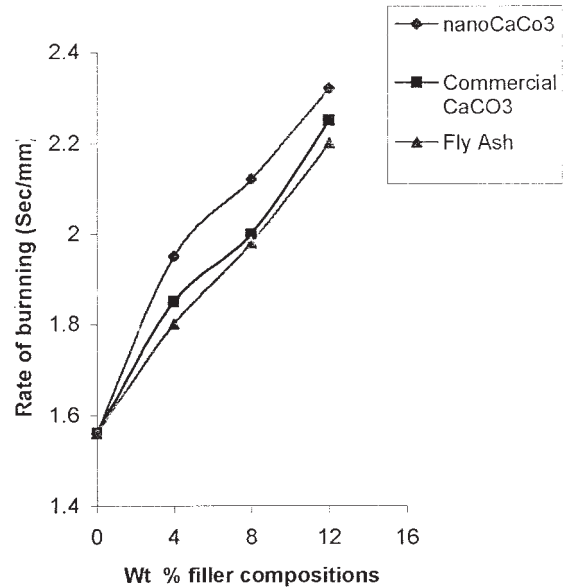


Figure 7 Flame retardancy of PBR filled with nano-CaCO₃, commercial CaCO₃, and fly-ash composites in various concentrations.

2. A sharp increment in the elongation at break was observed with an increase in nano-CaCO₃ from 2 to 12 wt %; it was almost 100% more than that of the control. Commercial CaCO₃ and fly ash showed an increase of only about 50%.
3. Like the elongation at break, the tear strength also was improved approximately 100% for 12 wt % nano-CaCO₃; it was much higher than that of commercial CaCO₃- and fly-ash-filled rubber composites.
4. The rate of burning was much lower than that for commercial CaCO₃- and fly-ash-filled rubber composites.
5. The improvement in all the properties was due to the uniform dispersion of nanoparticles in the rubber matrix.

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