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*Corresponding author

Ali Ansarifar, Department of Materials,
Loughborough University, Leicestershire,
LE11 3TU, UK

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Mineral Kaolin - A Highly Versatile Filler for Rubber

Ali Ansarifar*

Department of Materials, Loughborough University, Leicestershire, LE11 3TU, UK

Opinion

Reinforcement by solid fillers improves the mechanical and dynamic properties of the rubber vulcanizates and has been a major achievement for rubber compounders. Carbon blacks (CBs) derived from petroleum, synthetic silicas (SS), and, more recently, carbon nanotubes (CNTs) have all been shown to improve rubber properties. However, there are some serious health and safety, cost, and technical issues related to their use in rubber. For example, CBs contain polycyclic aromatic hydrocarbons (PAHs) [1], which makes them highly toxic depending on the extent of exposure, the amount to which one is exposed, and the method of exposure (inhalation, ingestion, or skin contact). There is a considerable health risk associated with their use in rubber compounds [2]. SS such as precipitated silica (PS) are very effective fillers and have been shown to improve the rubber properties, but they retard sulfur vulcanization [3,4]. To minimise this adverse effect, silanes are used with silica. For example, bis[3-triethoxysilylpropyl]tetrasulfane (TESPT), a bifunctional organosilane also known as Si69 coupling agent, is widely used in tyre tread rubber compound formulations with PS [5,6]. Carbon nanotubes have performed unsatisfactorily in natural rubber, and their use in rubber reinforcement has been highly problematic. When the interactions of CNTs with the natural rubber (NR) matrix were examined, the CNT bundles emerged from the side surfaces of the rubber samples tested and slowly slid back in when the deformation was removed. In these tests, the protruded lengths were many times larger than the nanotube bundle diameters. This suggested that the interfacial interactions between CNTs and NR were very weak [7]. Strong rubber-filler interaction, either by chemical bonding of the rubber with the filler or by the formation of physically bound rubber on the filler surface, is essential in rubber reinforcement [8,9]. Hydrous aluminium phyllosilicates or clay minerals such as montmorillonite (MMT) and kaolin have received much attention in recent years because they are relatively inexpensive and non-toxic. Since MMT consists of a triple-layer sandwich structure, its dispersion mechanism in rubber is different from that of kaolin. Intercalation and exfoliation morphologies are used to characterise the layer dispersion in clay/polymer nanocomposites. The latter morphology is more desirable due to its high surface area, which is important in rubber reinforcement [10]. But producing a high level of MMT clay dispersion in rubber is still a challenge [11,12], and moreover, MMT is often treated organically to improve its exfoliation and dispersion in the rubber matrix. Exfoliation of MMT at a high loading, e.g., 15 parts per hundred (phr) by weight, in the rubber matrix is very difficult to achieve [13].

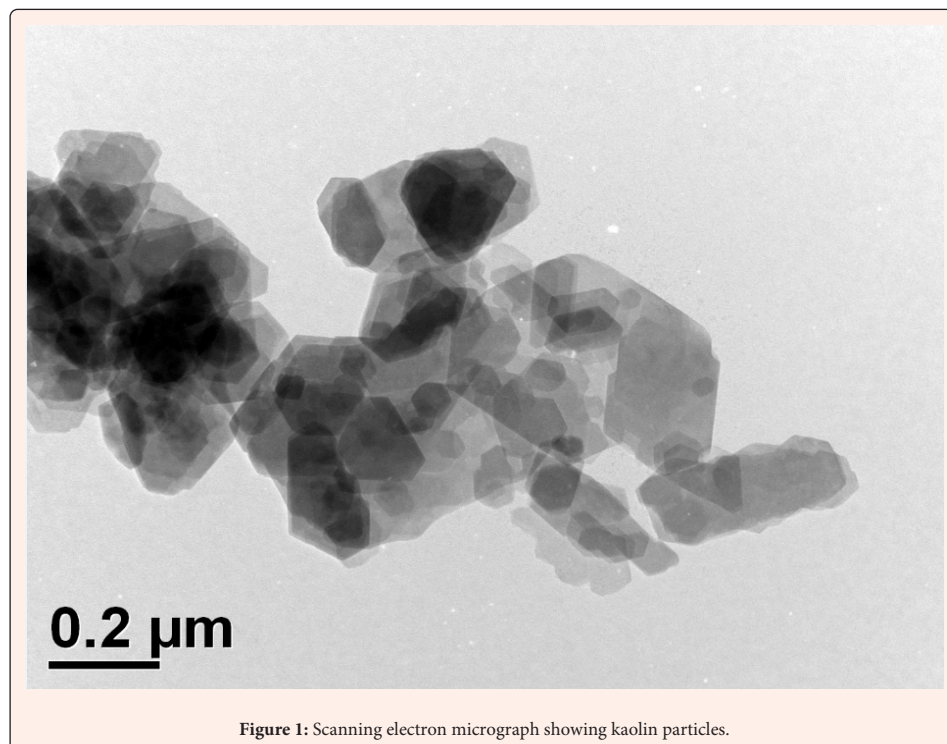


Figure 1: Scanning electron micrograph showing kaolin particles.

Recent studies have shown that mineral kaolin can be used in rubber reinforcement effectively at high loadings without a need for intercalation and exfoliation, and it has significant benefits for sulfur vulcanization. Rubber grade kaolin, Mercap 100 (China clay; $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), was used for this study. The surface of kaolin was pre-treated with 3-mercaptopropyl-trimethoxysilane (MPTS) to reduce its polarity and prevent it from adsorbing moisture. MPTS contains less than 2 wt% sulfur, has a fine particle size of about 0.3 μm, and a 25 m²/g surface area measured by nitrogen adsorption. It contains approximately 90 parts per million (ppm) of sulfur, primarily from trace secondary minerals, mainly pyrite (FeS₂), with a melting point of 1100 °C. Kaolin has a flat lamellar structure (Figure 1). The powder was stored at 80 °C for 48 hours to remove moisture if any before mixing it with NR. The other ingredients were sulfur, N-tert-butyl-2-benzothiazole sulfenamide (Santocure TBBS), and

zinc oxide (ZnO). The loading of kaolin was increased from 0 phr to 60 phr and 140 phr to make rubber compounds which were tested at 160 °C in a curemeter to produce cure traces from which the cure properties were measured (Figure 2). The cure system consisted of 4 phr sulfur, 3.5 phr TBBS, and 0.2 phr ZnO. The rubber compounds were cured to produce vulcanizates for measuring the mechanical properties. The study showed a significant reduction in the scorch time by 55% and in the optimum cure time by 63%, as well as a large increase in the cure rate by 72% and an increase of 60% in the crosslink density when the loading of kaolin was raised from 0 phr to 140 phr. Some of the mechanical properties were improved by a large margin. For example, while hardness and Young's modulus increased by 109% and 570%, respectively, tensile strength and tearing energy were unaffected, and elongation at break, compression set, and stored energy density at break deteriorated when the loading of kaolin was raised to 140 phr. Kaolin improved all the mechanical properties mentioned above for polybutadiene (BR) and ethylene-propylene-diene (EPDM) rubbers, but the compression set deteriorated when kaolin was added [14].

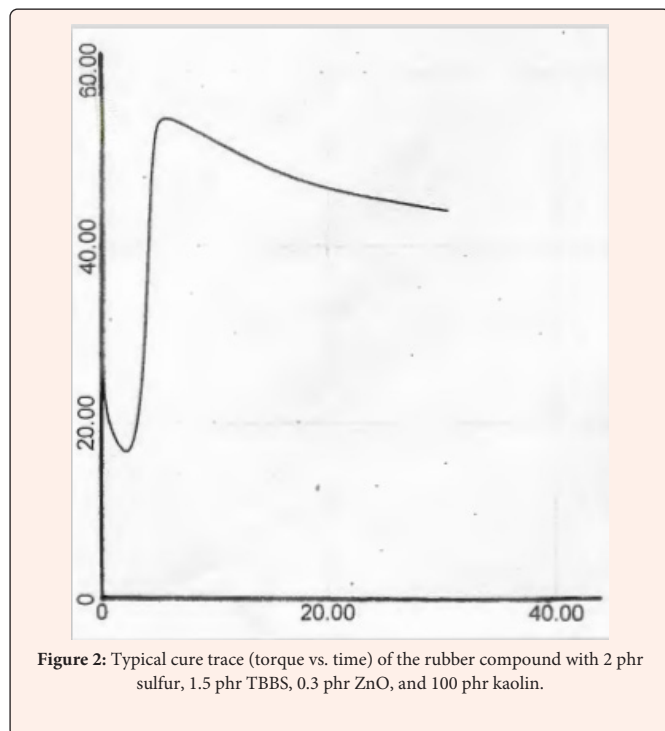


Figure 2: Typical cure trace (torque vs. time) of the rubber compound with 2 phr sulfur, 1.5 phr TBBS, 0.3 phr ZnO, and 100 phr kaolin.

In another study, the effect of kaolin on the curing properties of the rubber at 1 phr, 2 phr, 3 phr, and 4 phr sulfur was examined. The rubber compounds with 1-3 phr sulfur had 1.5 phr TBBS and 0.2 phr ZnO, and the rubber compound with 4 phr sulfur had 3.5 phr TBBS and 0.2 phr ZnO for optimum cure. The crosslink density as indicated by Δ torque (Figure 3), cure rate index (CRI) (Figure 4), and the scorch and optimum times (Figures 5 & 6), were affected when the kaolin loading was increased from 60 phr to 100 phr and 140 phr at 1 phr, 2 phr, 3 phr, and 4 phr sulfur loading. The rubber with 140 phr kaolin and 4 phr sulfur produced the best results because it had the highest crosslink density, the fastest cure rate, and the shortest scorch and optimum cure times. Mineral kaolin improves the mechanical and curing properties of the rubber at high sulfur loading, according to the data. Since kaolin is environmentally safe, abundant in nature, and highly effective in curing and reinforcing the rubber properties, it may be the filler of choice for rubber compounders. Kaolin can be used at very high loadings, i.e., 140 phr or even higher, for optimum reinforcement without the need for intercalation and exfoliation, which are essential requirements for the effective use of other clays such as MMT at much lower concentrations. A future study should consider treating the kaolin

with a sulfur-bearing bifunctional organosilane such as TESPT. TESPT enables stable covalent sulfur chemical bonding between the filler and rubber to produce strong rubber-filler interaction for optimum property reinforcement as well as good dispersion of the filler particles in the rubber [15] MPTS can perform the latter function but not the former.

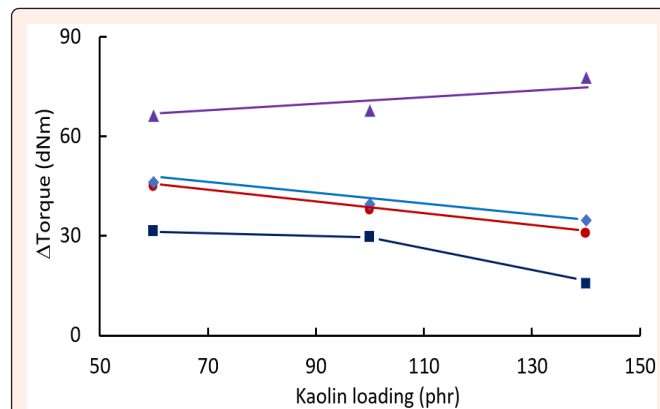


Figure 3: Δ Torque vs. kaolin loading at different levels of sulfur loading. (■) with 1 phr sulfur; (●) with 2 phr sulfur; (◆) with 3 phr sulfur; (▲) with 4 phr sulfur.

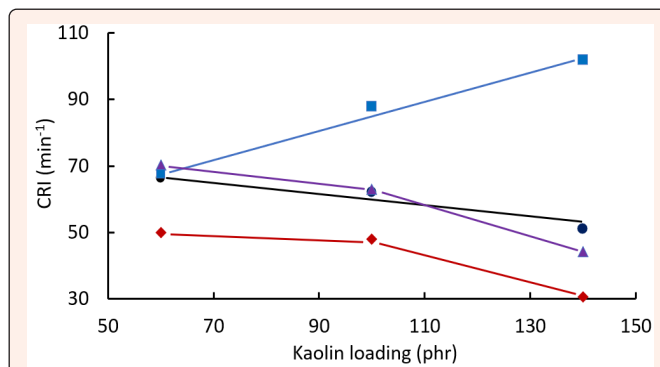


Figure 4: CRI vs. kaolin loading at different levels of sulfur loading. (◆) with 1 phr sulfur; (●) with 2 phr sulfur; (▲) with 3 phr sulfur; (■) with 4 phr sulfur.

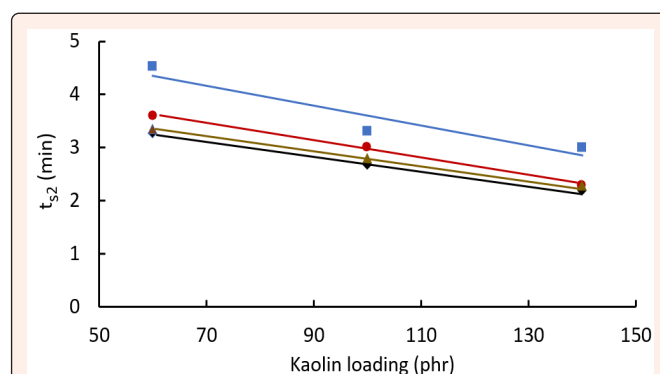


Figure 5: Scorch time vs. kaolin loading at different levels of sulfur loading. (■) with 1 phr sulfur; (●) with 2 phr sulfur; (◆) with 3 phr sulfur; (▲) with 4 phr sulfur.

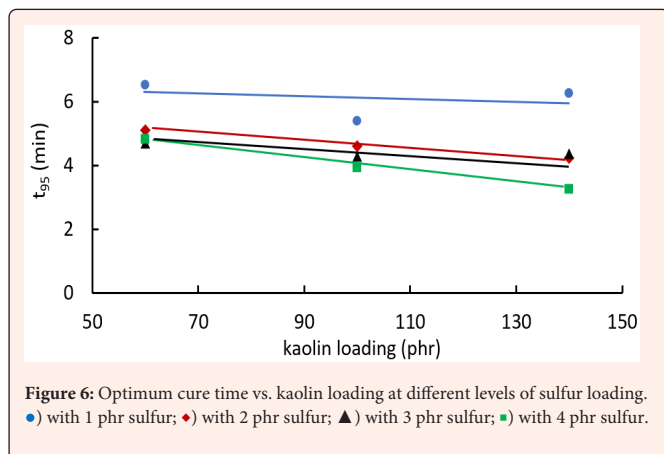


Figure 6: Optimum cure time vs. kaolin loading at different levels of sulfur loading. ● with 1 phr sulfur; ◆ with 2 phr sulfur; ▲ with 3 phr sulfur; ■ with 4 phr sulfur.

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