

# Hindering crack growth in natural rubber and nanocomposites

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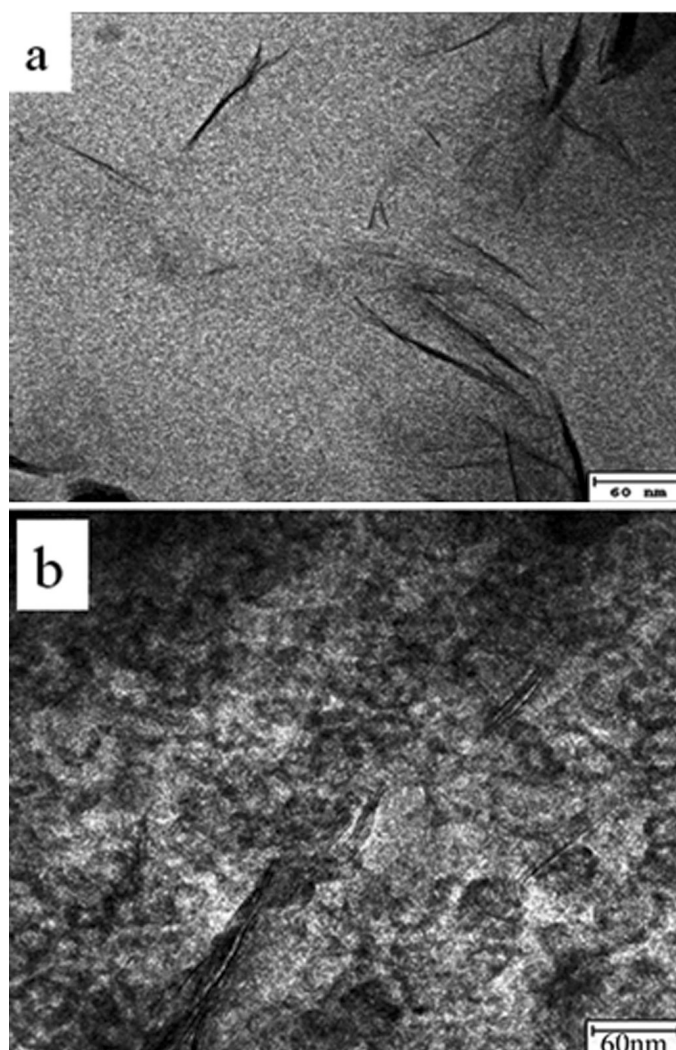
*Nanodispersed clay can greatly improve crack growth resistance by enhancing tensile strength under static conditions and improving flex-fatigue properties under dynamic conditions.*

Rubber is a key component in tires, which must resist cracking on the many occasions they come into contact with sharp objects such as rocks and gravel. Carbon black (CB) particles are widely used in the rubber industry to reinforce rubber; they are nanosized, so they endow rubber with excellent properties. However, CB is dependent on non-sustainable supplies of petroleum. Its production causes air pollution and gives the rubber products a black color. For the past several decades, researchers have sought substitutes for CB to reinforce rubber.

In recent years, polymer/clay nanocomposites have attracted considerable attention from academia and industry because of their high modulus and strength, low gas permeability, and low flammability.<sup>1-3</sup> However, the dearth of cost-effective methods for controlling the dispersion of the nanoparticles in polymeric hosts is the greatest technical challenge to the large-scale production and commercialization of nanocomposites.<sup>4</sup>

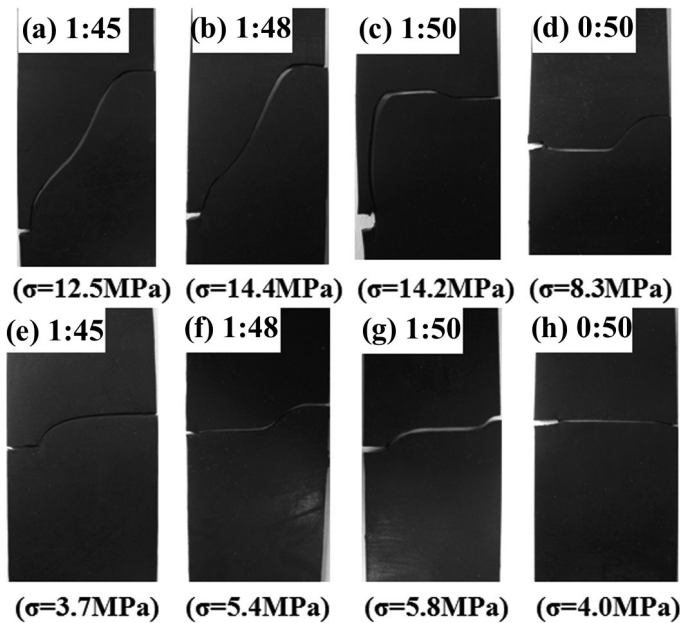
Generally, clay, as a reinforcing filler for rubber, has been widely used to prepare rubber nanocomposites through the following four methods: in-situ polymerization,<sup>5</sup> melt compounding,<sup>6</sup> solution compounding,<sup>7</sup> and latex compounding.<sup>8-10</sup> Compared with the other three methods, the latex compounding method, in which pristine clay (i.e., non-organoclay) co-coagulates with rubber latex in an aqueous suspension, is a promising candidate for industrialization due to the low cost of pristine clay, the simplicity of preparation process, and a superior cost/performance ratio.

We prepared natural rubber (NR)/clay nanocomposites by latex compounding and examined their nanostructures with a high-resolution transmission electron microscope (HR-TEM). These images clearly show that clay can be dispersed at the nanoscale in the rubber

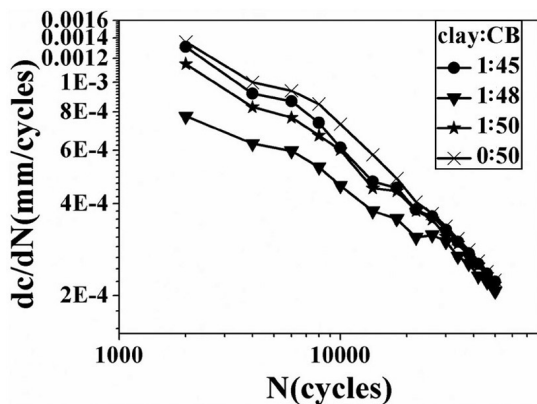


**Figure 1.** High-resolution transmission electron microscope images of nanocomposites. (a) Rubber/clay nanocomposites with 1 phr clay. (b) Rubber/clay/carbon-black (CB) nanocomposites with a clay:carbon-black ratio of 1:48. phr: Parts per hundred rubber.

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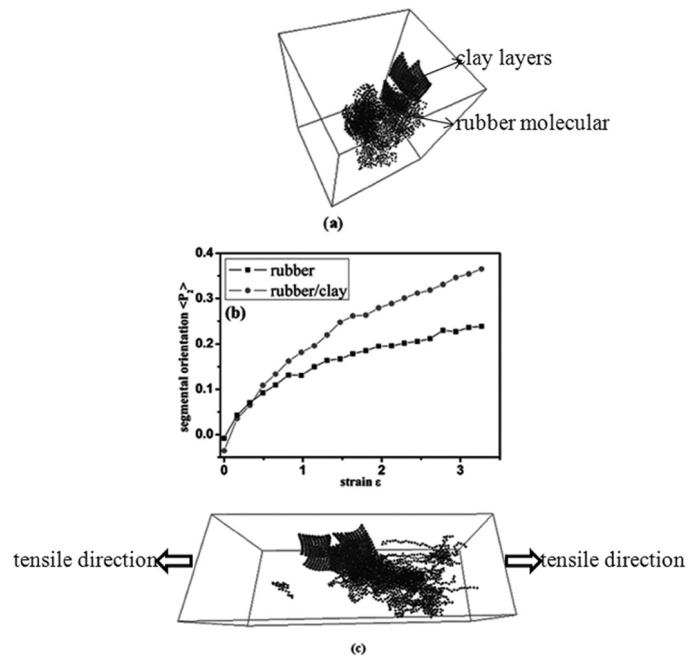
**Figure 2.** Effect of cut size ( $c$ ) on the tensile strength ( $\sigma$ ) and cracking patterns. 1:45, 1:48, 1:50, and 0:50 represent the clay:carbon-black ratio. Upper images:  $c = 1.0\text{mm}$ . Lower images:  $c = 4.5\text{mm}$ .



**Figure 3.** Fatigue crack growth rate as a function of flex times ( $N$ ) for various specimens. The original crack length is  $2.7\text{mm}$ .

matrices, and, therefore, a low loading of nano-dispersed clay can improve resistance to crack growth and have a strong reinforcement effect (see Figure 1). The CB aggregates and clay sheets are well dispersed with direct contact between each other. Furthermore, the CB aggregates are bridged through the clay sheets to form hybrid network, which contributes to the effective crack growth resistance.

To investigate the effect of clay on NR/CB nanocomposites, we mixed so-called N330 CB and other standard ingredients into the NR/clay nanocomposites in an open two-roll mill at room



**Figure 4.** Molecular dynamics simulation of orientation of rubbery chains and clay sheets during the deformation process. (a) Snapshot of polymer chains filled with clay sheets; note that for clarity only partial polymer chains and clay sheets are shown. (b) The chain segmental orientation as a function of the strain for rubber and rubber/clay systems. (c) Snapshot of the tensile state of polymer chains filled with clay sheets; only partial polymer chains and clay sheets are shown.

temperature at clay:CB ratios of 1:45, 1:48, 1:50 and 0:50. We used pre-cut strip specimens to examine crack growth resistances under static conditions.<sup>11</sup> Figure 2 shows the effect of cut size on the tensile strength and cracking patterns for appointed cut sizes. The crack in the NR/CB nanocomposites propagates rapidly to break in a simple lateral direction and leads to the lowest cut tensile strength. On the other hand, a more longitudinal crack is clearly observed in all NR/clay/CB nanocomposites. These longitudinal cracks result from the greater orientation of the NR chains caused by the clay layers, which prevents the crack from growing easily across the specimen.

We used pre-cut flex fatigue specimens to examine crack growth resistances under dynamic conditions.<sup>12</sup> We periodically monitored fatigue crack length and found that the crack of NR/clay/CB nanocomposites increases more slowly than with NR/CB nanocomposite (see Figure 3). Thus, although the ratio between clay and CB is different, clay could blunt the crack and block crack growth.

We simulated molecular dynamics to investigate the orientation of rubbery chains and clay sheets at rest (see Figure 4a) and during the



deformation process (see Figure 4c) at the molecular level.<sup>13–15</sup> Comparing Figure 4(a) and (c), we see that the clay layers are oriented with the rubber molecular ones along the tensile direction. We quantified this using second-order Legendre polynomials  $\langle P_2 \rangle$  to characterize the chain segmental orientation, where  $\langle P_2 \rangle = (3 \langle \cos^2 \theta \rangle - 1)/2$  and  $\theta$  is the angle between the orientation of the chain segment and the tensile direction. We found that, compared with the purely cross-linked system, the value of  $\langle P_2 \rangle$  for chains filled with clay became much larger with the strain, indicating that the chain segmental orientation was much higher (see Figure 4b).

In summary, we used pre-cut strip specimens under static conditions, pre-cut flex fatigue specimens under dynamic conditions, and molecular simulations to demonstrate the effect of the clay in a latex compounded NR/clay nanocomposites on crack growth resistance. We have shown that nanodispersed clay can effectively blunt the crack tip and hinder the crack growth, which is due to orientation of clay layers and polymer chains along the tensile direction. Our next step will be to show that NR/clay nanocomposites can improve crack growth resistance of off-road tires.

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