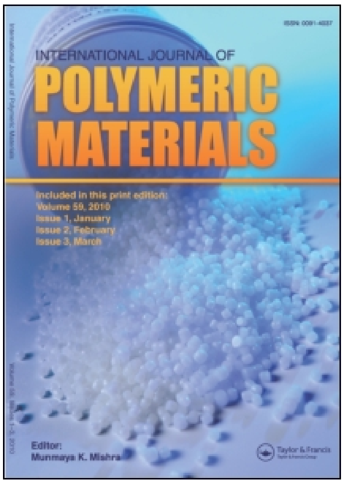

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Ahmad Mousa[a]
[a] Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan

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Evolution of the Mechanical Properties of EPDM Vulcanizates by Compounding with Layered Organo-Montmorillonite

Ahmad Mousa
Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan

Organoclay was compounded with EPDM using a two roll and cured by conventional sulfur curing system. The organoclay content was progressively increased from 0 to 15 phr of the EPDM rubber. The mechanical properties of the EPDM vulcanizates were evaluated by an Ekktron tensile testing machine. It has been found that tensile properties increased with nanoclay content. The observed trend was related mainly to the strong interaction between the rubber matrix and the nanoscaled filler (organoclay in this case) and subsequently to the improved crosslink density. Such improvement was attributed to the small size of the filler particles and to the amine functionality in the organoclay structure.

Keywords: EPDM vulcanizates, clay, compounding, mechanical properties, montmorillonite

INTRODUCTION

The concept of polymer/organoclay nanovulcanizates, credited to researchers to Toyota Central Research and Development Laboratories (Japan) is a new type of polymeric materials from the late 1980s with one component having dimensions in the nanometer range. Such materials give a combination of properties that are not available in any of the single components. Reinforcement is possible at very low loading of filler compared to the conventional filler vulcanizates, which require much higher quantities. Organoclay is a filler containing layered silicates with a very high aspect ratio as their thickness

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Address correspondence to Ahmad Mousa, Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt 19117, Jordan. E-mail: mousa@rocketmail.com

is 1 nm and their length can reach up to 2 μm. The aspect ratio is up to 2000, offering very large polymer/silicate interface area. Layered silicates surfaces are normally occupied by cations such as Na^+ and Ca^+, which are usually replaced by organoammonium cations via ion exchange reaction making the layered silicates surfaces organophilic [1]. Such onium cations increase the initial interlayer distance (initially at about 1 nm). So, the interlayer distance of commercially available montomorillonite-based clays is usually enough for polymer molecules to be inserted between the silicate layers, or the individual silicate layers are dispersed in the polymer matrix structure [2]. The intercalation/exfoliation of layered silicates are governed by the compatibility, polymer diffusivity and processing variables. Rubber should be preferred polymer matrices to accommodate the organo clays to produce nanovulcanizates. This claim is argued as follows. First, amine compounds, used as low molecular weight intercalants/surfactants/ in organophilic silicates, act in sulfur curing rubber recipes as activators. Thus, layered silicates intercalated by amine-compounds containing primary, tertiary, and quaternary amines may be involved in the sulfur curing reactions. Second, rubbers are high molecular weight polymers showing extremely high viscosities during melt compounding. Owing to the latter, high shear stresses may operate locally on the layered silicate stacks causing them to shear and peel apart [3–4]. Despite the aforementioned properties, the overwhelming majority of the work done was devoted to thermoplastic [2–3] and little attention was paid to thermoset rubbers until now. This investigation reports the influence of organoclay on the mechanical behavior of sulfur cured ethylene-propylene-diene terpolymer (EPDM rubber).

EXPERIMENTAL

Materials

EPDM showing a mooney viscosity of ML $(1+4)$ at 125°C was supplied by Bayer AG, Germany. Montmorillonite modified by octadecyltrimethylamine; Nanomer 1.28E® were obtained from Noncor Inc. USA. Stearic acid, zinc oxide, MBTS, and sulfur were donated by local industry. The mixing recipes used were as follows in phr based on EPDM: rubber 100, organoclay: Various, ZnO: 5, Stearic acid 1, MBTS 1, and Sulfur 2.

Mixing

Mixing was carried out on a Brabender two roll mill with a nip clearance of 1 mm and friction ratio 1.3. Incorporation of the curing agents took place on the two roll mill at room temperature. The cure characteristics were determined at 160°C using an Ekktron oscillating disc rheometer at 1.66 Hz frequency and 0.5 arc.

Hot Pressing

Sheets of 2 mm thickness were molded with a Carver auto series compression molding machine using a force of 30,000 Ibs at 160°C according to their t_{90} derived from Ekktron oscillating disc rheometer.

Mechanical Testing

Tensile Testing

Tensile tests were carried out on EKKTRON tensile testing machine, according to ASTM D412. The samples were tested at a deformation rate of 500 mm/min at room temperature. Five samples were tested and the average value was recorded.

Swelling Index

Circular discs of 2 mm thickness and 20 mm diameter were immersed in Toluene. The swelling ratio was determined gravimetrically, by weighing the polymer sample prior to immersion in the toluene (W_i) and after equilibration in the solvent (W_t).

$$Swelling\ index = \frac{Final\ mass}{Initial\ mass}$$

Impact Test

Izod impact tests were carried out with an instrumented custom scientific pendulum impact tester, model Ceast, in accordance with ASTM 256.

Morphology

The fracture surface of the tensile test samples was inspected using scanning electron microscope model EDAX CDU XL-30. The samples were sputtered by carbon using sputter coater model BAL-TEL SCD 005, prior to testing.

RESULTS AND DISCUSSIONS

Tensile Properties

Figure 1 shows the effect of the organoclay on tensile strength of EPDM/organoclay composite at various organoclay loading. It can

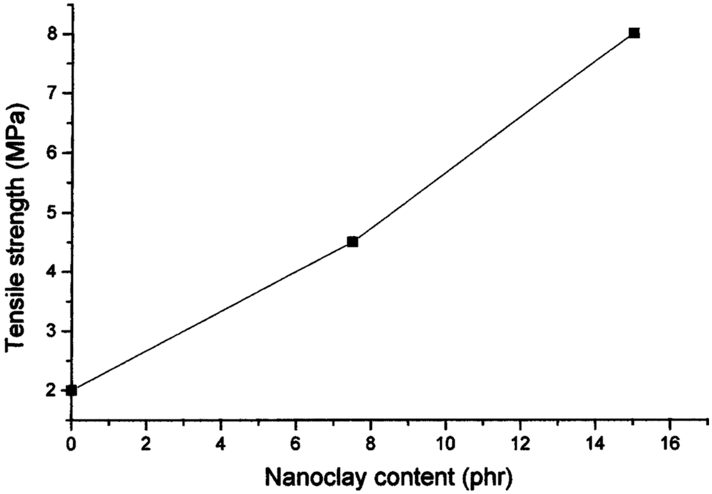

FIGURE 1 The effect of nanoclay loading on tensile strength of EPDM vulcanizates.

be seen that the tensile strength of the formulations has increased with increase of organoclay content. This is in line with previous investigations on various rubber stocks [5–6]. The improved reinforcement efficiency of organoclay may be attributed to the interaction between organoclay and the EPDM rubber [6]. Two reasons might hold for this scenario: First the small particle size, the high aspect ratio, and platelet structure of the organoclay filler expected to provide a larger surface area for the interaction between the rubber and filler. Second, the incorporation of the amine modified nanoclay is expected to enhance the sulfur based curing reaction, due to the amine functionality in the organoclay structure, which results from the ion exchange modification process. Recall that nitrogen containing compounds act as accelerators for sulfur induced vulcanization [7]. Thus it might be inferred that organoclay is not just a filler. Instead, it acts as a secondary curing agent that could facilitate the curing reaction of the EPDM formulations. Thus, it is expected that the degree of curing will be enhanced with increased organoclay content. Such an increment is evidenced by two means: First, the increment in the state of cure, which is (elastic torque at maximum value, MH – elastic torque at minimum value ML) derived from the moving die rhemoter and presented in Figure 2. Recall that the torque difference indirectly indicates the degree of curing according to previous investigations on various rubber systems [8–10]. Second, the swelling index data of

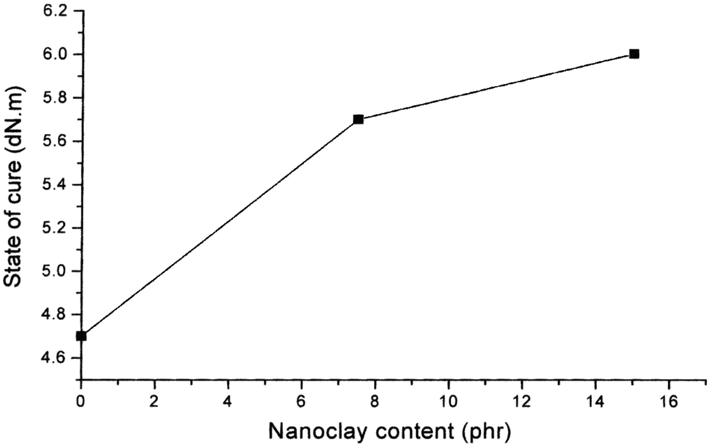

FIGURE 2 State of cure as a function of nanoclay content of EPDM vulcanizates.

the EPDM vulcanizates were evaluated and presented in Figure 3. It is observed that the swelling index of the vulcanizates decreased with filler content. This may be, again, due to the enhanced degree of curing as well as the filler dispersion that is expected to decrease the solvent

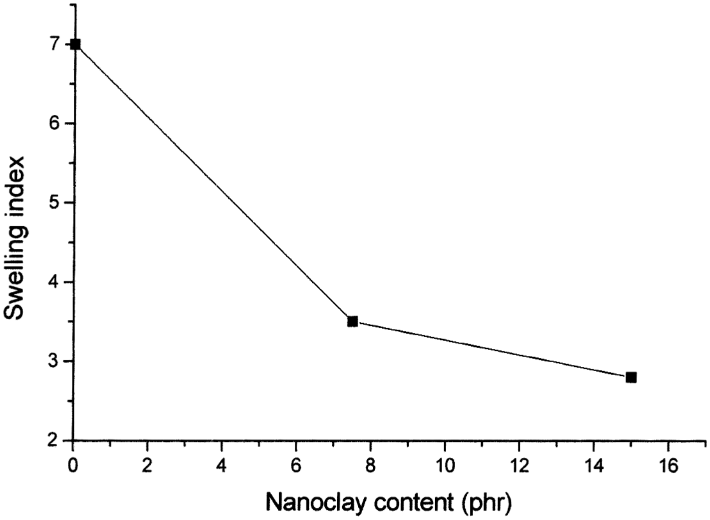

FIGURE 3 The influence of nanoclay loading on the swelling index of EPDM vulcanizates.

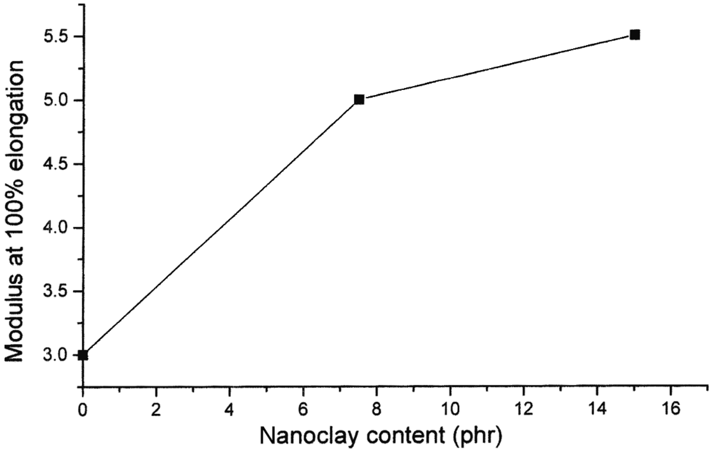

FIGURE 4 The influence of nanoclay loading on M100 of the EPDM vulcanizates.

penetration into the EPDM vulcanizates. Figure 4 shows the effect of organoclay content on the modulus at 100% elongation for the EPDM vulcanizates at various organoclay contents. Note that M100 increased with organoclay content. This, again, may be related to the presence of the organoclay filler, which improves the composites' strength and modulus at relatively low filler loading as compared to the conventional fillers [11–12]. This trend is similar to that recorded in the case of tensile strength. Further, the elongation at break of the EPDM vulcanizates is presented in Figure 5. It is obvious that the elongation at break increased with organoclay loading. This can only be explained by intercalated/exfoliated structure of the organoclay filled EPDM vulcanizates, which allows an easy reorientation of the platelets.

Impact Energy

Figure 6 illustrates the influence of organoclay loading on the impact energy of the EPDM/organoclay composite. The improvement in the impact strength could be due to the increase crosslink density of the EPDM vulcanizates. This is expected to improve the elastic properties and the molecular retractability of network.

Morphological Studies

The fracture surfaces of both unfilled and filled EPDM/organoclay vulcanizates are presented in Figure 7a and b, respectively. It is

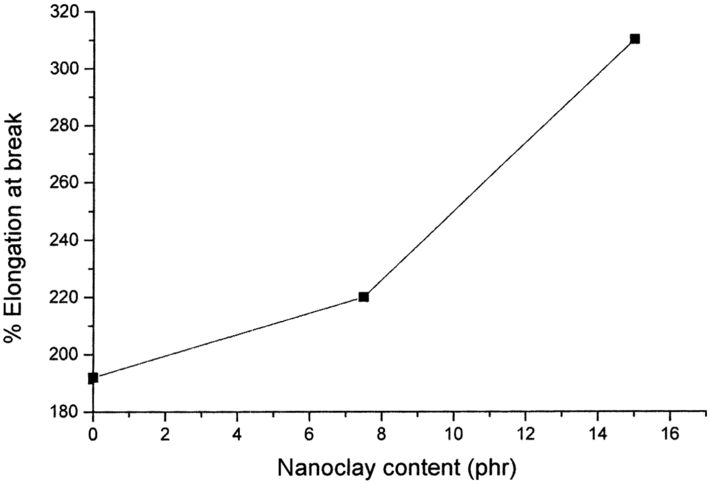

FIGURE 5 Elongation at break against nanoclay loading for EPDM vulcanizates.

obvious that the fracture of the unfilled system was initiated on several planes prior to the formation of major crack with the existence of some micro voids. This is due to the absence of organoclay as well

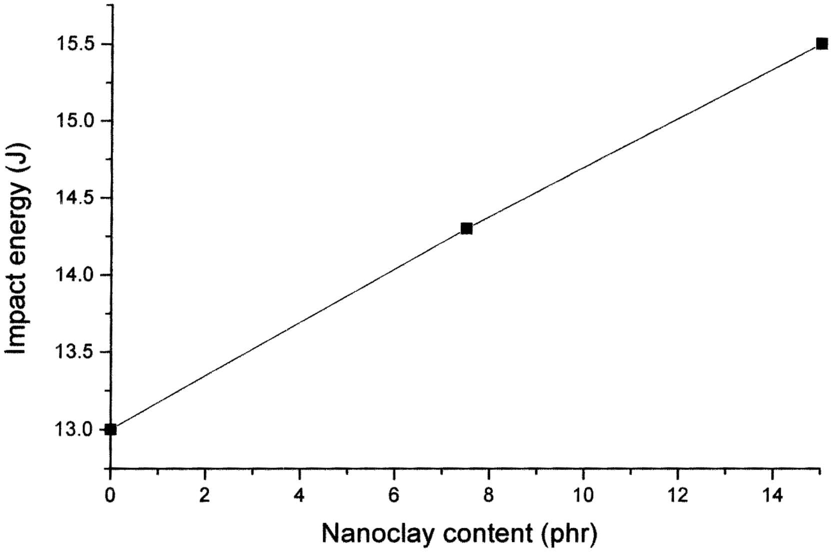

FIGURE 6 The influence of nanoclay loading on the impact energy of the EPDM vulcanizates.

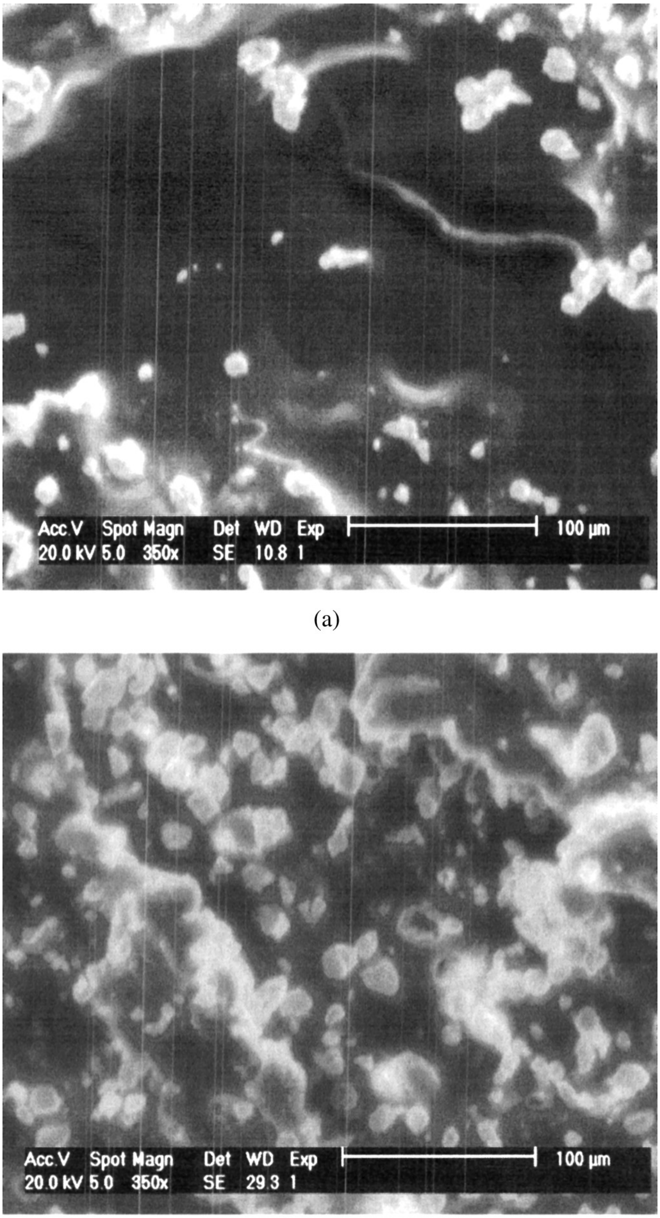

FIGURE 7 Scanning electron micrographs of EPDM/organo clay vulcanizates: (a) unfilled system, (b) filled system.

as reduced crosslink density. On the contrary, the presence of the organoclay has transformed the fracture surface to rugged plane with better matrix tearing and less signs for secondary cracks as indicated in Figure 7b. This might be associated with the improved mechanical properties.

CONCLUSIONS

Based in the earlier results the following conclusions can be drawn: The organoclay increase has strongly affected the tensile strength, modulus of elasticity and elongation, positively. This is due to an increase of the cohesive force between the organoclay layers and the rubber matrix accompanied by the crosslinking force generated from the sulfur content. The increase of organoclay content accompanied with increase in degree of crosslinking due to the amine functionality of the organoclay, resulting from the modification process.

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