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CURE CHARACTERISTICS AND MECHANICAL PROPERTIES OF NATURAL RUBBER/ORGANOCLAY NANOCOMPOSITES

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Abstract. Organoclay filler was added to natural rubber and cured by conventional vulcanization system. The filler loading was varied from 0–10 phr. The compounds were characterized in respect of their curing characteristics and mechanical properties. The cure characteristics: cure time and torque of the rubber compounds were studied by using the Monsanto MDR 2000 rheometer. The mechanical properties were investigated. The tensile strength, elongation at break and tear properties were improved at 2 phr organoclay. Further increase in organoclay loading decreases these properties. Modulus at 100% (M100) and modulus at 300% (M300) increased continuously with filler loading from 0–10 phr. Scanning electron microscopy was used to study the microstructure of the fracture surfaces.

Keywords: Nanocomposites, organoclay, natural rubber, cure characteristic and mechanical properties

Abstrak. Pengisi organoclay telah ditambahkan ke dalam getah asli dan dimatangkan dengan menggunakan sistem pemvulkanan konvensional. Kandungan pengisi yang ditambah adalah antara 0–10 phr. Penyebatian telah dicirikan mengikuti sifat pematangan dan sifat mekanikal. Sifat pematangan iaitu masa pematangan dan tork penyebatian getah telah dijalankan dengan menggunakan reometer Monsanto MDR 2000. Sifat mekanikal telah dikaji. Kekuatan tegangan, pemutusan pada takat putus dan sifat cabikan telah mencapai kemajuan pada takat 2 phr organoclay. Penambahan dalam kandungan organoclay yang seterusnya telah mengurangkan sifat-sifat tersebut. Modulus pada 100% pemanjangan (M100) dan modulus pada 300% pemanjangan (M300) telah bertambah secara berterusan dengan kandungan pengisi dari 0–10 phr. Mikroskopi Imbasan Elektron telah digunakan untuk mengkaji mikrostruktur pada permukaan sampel.

Kata kunci: Komposit nano, organoclay, getah asli, sifat pematangan dan sifat mekanikal

1.0 INTRODUCTION

The reinforcement of polymers with nano-sized particles is a promising technique that is capable of yielding materials with enhanced performance but without involving expensive synthesis procedures. Polymer/clay nanocomposites are being investigated and developed worldwide by a number of public, private and corporate entities [1]. Most research works on nanocomposites have been focused on either the thermoplastics or thermosets matrices [2-4]. However, recently there has been some studies on the

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efficiency of organoclay in reinforcement of elastomers such as butadiene rubber (BR), Styrene butadiene rubber (SBR), and Polyurethane (PU) [5,6].

An organoclay nanocomposite is a polymer system containing inorganic clay intercalated with organic cations with one dimension in the nanometer range i.e. one billionth of a metre [7]. This study reports on the cure characterisation and mechanical properties of Natural Rubber(NR)/organoclay nanocomposites. One of the requirements for a successful exploitation of organoclay as a filler is ensuring a good chemical interaction with the polymer matrices. Since NR does not have polar groups in its backbone, the NR/organoclay nanocomposites used in this project will be prepared by using a functionalised natural rubber i.e. epoxidized natural rubber (ENR) as a compatibilizer. The effect of organophilic nanoclays on the curing characteristics, mechanical properties, and thermoxidative ageing behaviour will be investigated.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials

Natural rubber grade SMR L and epoxidized natural rubber grade ENR 50 and organoclay grade 1.28E were used. Other compounding ingredients were sulphur, zinc oxide, stearic acid, N-isopropyl-N' -phenyl-p-phenylenediamine (IPPD), N-cyclohexyl-2-benzothiazyl sulphenamide (CBS).

2.2 Compounding

A conventional vulcanization system was used for compounding. Table 1 shows the composition of the rubber compound.

Table1 Composition of the rubber compound

Ingredients	Content (phr)[a]
Natural rubber	100
ENR50	10
Organoclay	2,4,6,8,10
Sulphur	2.5
Zinx Oxide	5.0
IPPD	2.0
Stearic acid	1.0
CBS	0.5

ENR, Epoxidized natural rubber: IPPD, N-isopropyl-N' -phenyl-p-phenylenediamine: CBS, N-cyclohexyl-2-benzothiazyl sulphenamide:

[a] Parts Per Hundred parts of rubber

The master batch (MB) preparation was done by using an Banbury internal mixer model BR1600 at RRIM, Sungai Buloh, Selangor. The compounding was done at 80°C and 100 rpm for 3 minutes. While for the final mixing (FM) stages the compounding was done by using a two-roll mill. The FM compounds were prepared by mixing the curatives with the MB compounds for 2 minutes.

2.3 Cure Characterization

Compound cure characteristics were measured using a Monsanto Moving Die Rheometer (MDR 2000) at 150°C according to ASTM 2240-93.

2.4 Compression Molding

The vulcanizates were prepared by curing at 150°C with the respective cure time, t_{90} determined from MDR 2000 by using a KAO Tech hot press. The sample with thickness of 2 mm sheets was moulded.

2.5 Tensile Properties

Dumbbell-shaped samples were cut from the mould sheets according to ASTM D412-93. Tensile properties were determined on a Monsanto Tensometer M500 with a crosshead speed of 500 mm/min. A total of five samples were tested for each experiment.

2.6 Tear Properties

Crescent-shaped samples type die B were cut from the mould sheets according to ASTM D624-9. A nick (0.50 ± 0.05 mm) in depth was produced by using a sharp razor blade. Tear strength was determined on a Monsanto Tensometer M500 with a crosshead speed of 500 mm/min. Five samples were tested for each experiment.

2.7 Scanning Electron Microscopy (SEM)

The fracture surfaces of the compounds were studied with a Leica Cambridge S-360 scanning electron microscope. The fractures surfaces were coated by gold to prevent electrostatic charging during examination.

3.0 RESULT AND DISCUSSION

3.1 Cure Characterization

Figure 1 shows the influence of filler content on the cure characteristics of NR/organoclay compounds that was derived from MDR20000 measurements. It can be seen that the

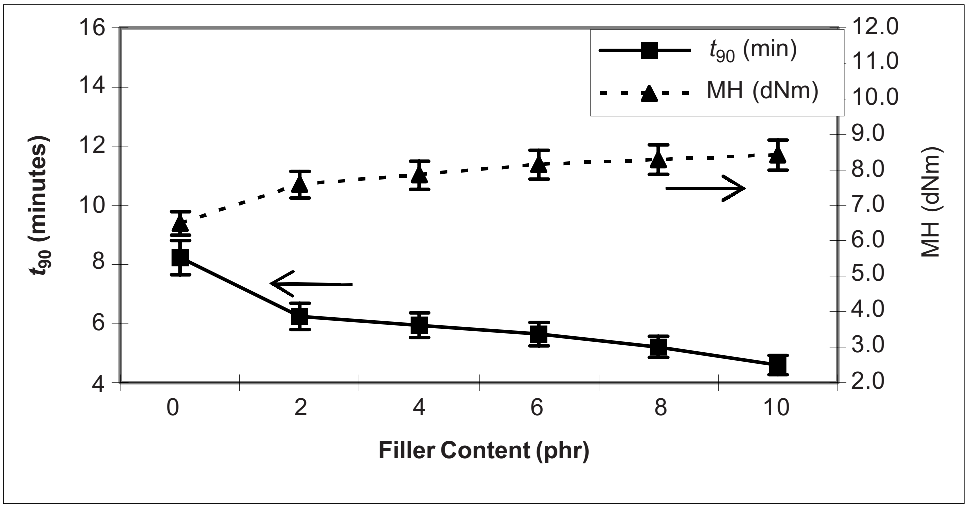

Figure 1 Cure time and maximum torque of the compounds with different filler content (phr)

t_{90} of the compounds reduced quite sharply at 2 phr filler content. Further addition of the filler resulted in a gradual reduction of t_{90}. This may be attributed to the amine functionality in the filler after the modification process or ion exchange process[8]. The amine containing compounds facilitate the curing reaction of natural rubber stocks.

The maximum torque (MH) is generally correlated with the durometer hardness and modulus. From Figure 1, the maximum torque increases with increasing filler content. This indicates that the incorporation of organoclay filler increases the stiffness of the rubber.

3.2 Tensile Properties

Figure 2 shows the effect of organoclay loading on the tensile properties of natural rubber/organoclay compounds. The tensile strength increases to a maximum at 2 phr and more or less stabilised up to 6 phr loading of organoclay. It is believed that further increase in loading resulted in a reduction of the property, up to 2 phr filler loading, the filler is uniformly dispersed in the natural rubber matrix. The filler has high aspect ratio which tends to improve interfacial bonding and form filler-rubber interaction because of the high specific surface area of the filler. However, when the filler content is high from 8 to 10 phr, the filler tends to form agglomerate and this leads to the reduction of tensile strength.

The elongation at break of the compounds initially remains unaffected with the incorporation of 2 phr filler content. A similar behaviour was reported by Mousa [8] for styrene butadiene rubber (SBR). This is believed to be related to the intercalation and exfoliation process of the organoclay that causes more crosslink between the

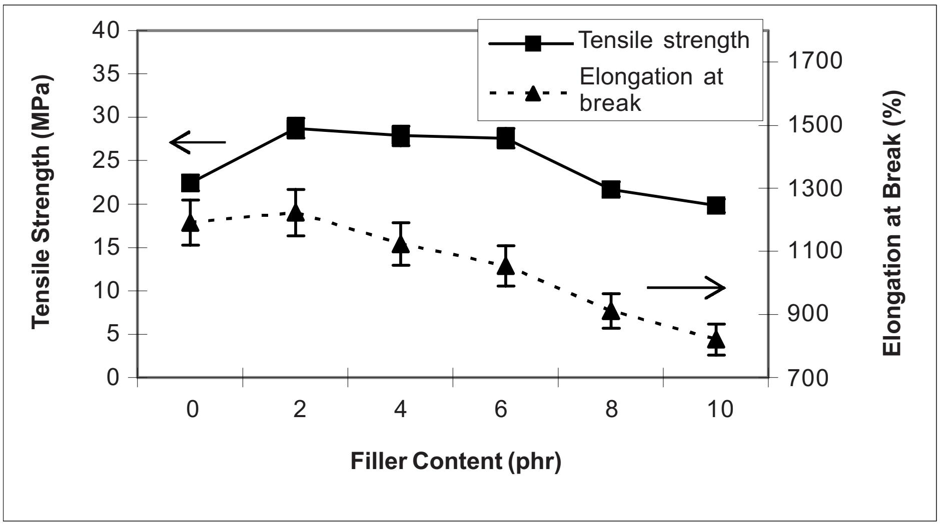

Figure 2 Effect of filler loading on tensile strength and elongation at break of natural rubber/organoclay compounds

rubber matrix and the organoclay. Further increase of filler loading after 2 phr of organoclay caused decreased elongation at break, it is due to the agglomerates at higher filler content. This can be explained by scanning electron micrographs of the fracture surfaces of the rubber compounds. This will be discussed later.

Figure 3 shows the tensile modulus, M100 (modulus at 100%) and M300 (modulus at 300%), which is a measure of stiffness of rubber compounds. Filler loading has

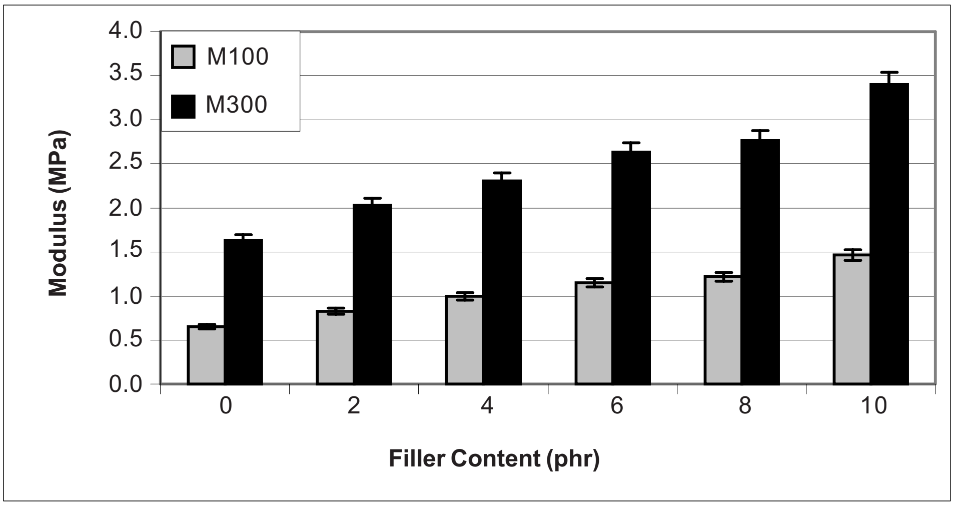

Figure 3 Effect of filler loading on modulus at 100% and modulus at 300% of natural rubber/organoclay compounds

similar effect on both M100 and M300, whereby both parameters increase with increasing filler content.

3.3 Tear Properties

Figure 4 shows the tear strength of natural/organoclay compounds with different filler loading. The tear strength increases gradually and remains relatively high up to 4 phr, after which it drops with further incorporation of organoclay. It is believed that at lower filler content the filler can be dispersed well in the rubber matrix and the filler can extent further propagation. However at higher filler content, the filler tends to form agglomerates, thus decrease the tear properties of composite.

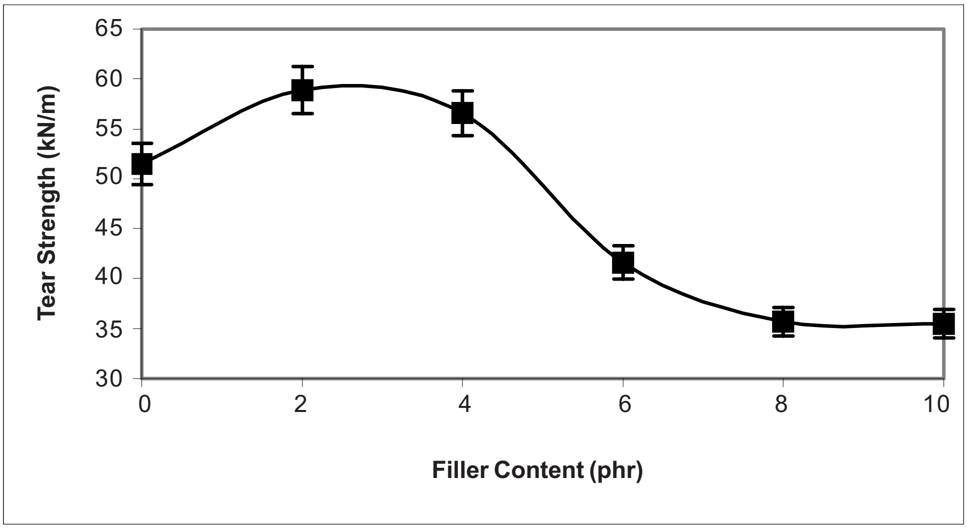

Figure 4 Effect of filler loading on tear strength of natural rubber/organoclay compound

3.4 Scanning Electron Microscopy (SEM)

Figures 5–7 show the failure surfaces of natural rubber gum compound, natural rubber compound filled with 2 phr organoclay and natural rubber compound filled with 10 phr organoclay, respectively. Figure 5 shows a very smooth surface, with some tear line in branching. Incorporation of 2 phr organoclay has transferred the morphology of the fracture surface. The surface becomes rougher and this may be attributed to the activation of failure mechanism associated with the presence of organoclay.

Figure 7 shows that the fracture surface of 10 phr sample has many holes compared with the fracture surface of 2 phr. This hole formation may be contributed to low rubber-filler interaction as a result of detachment of the filler from the natural rubber [9]. Such holes could act as initial flaws leading to localised stress concentration during

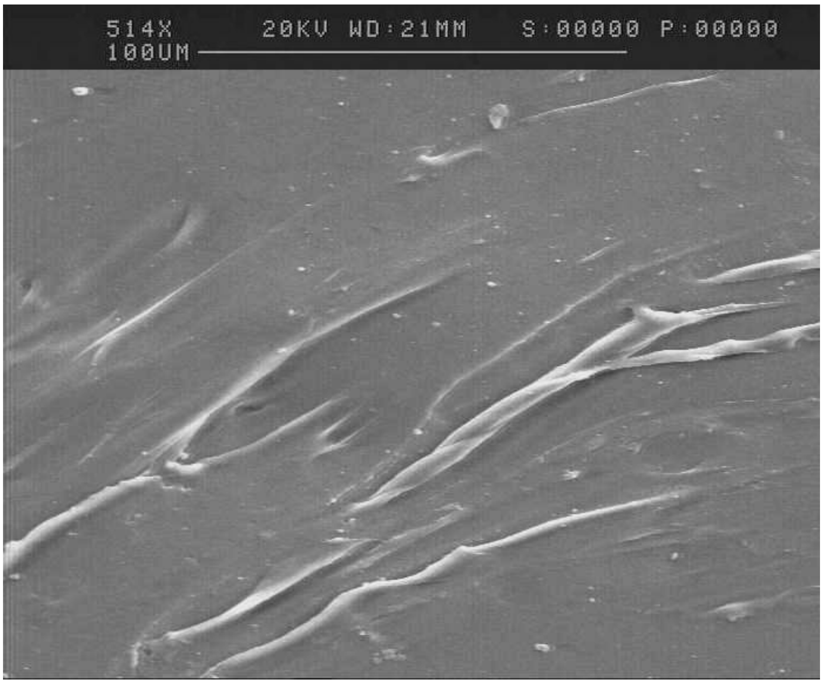

Figure 5 Tensile fracture surface of natural rubber gum compound

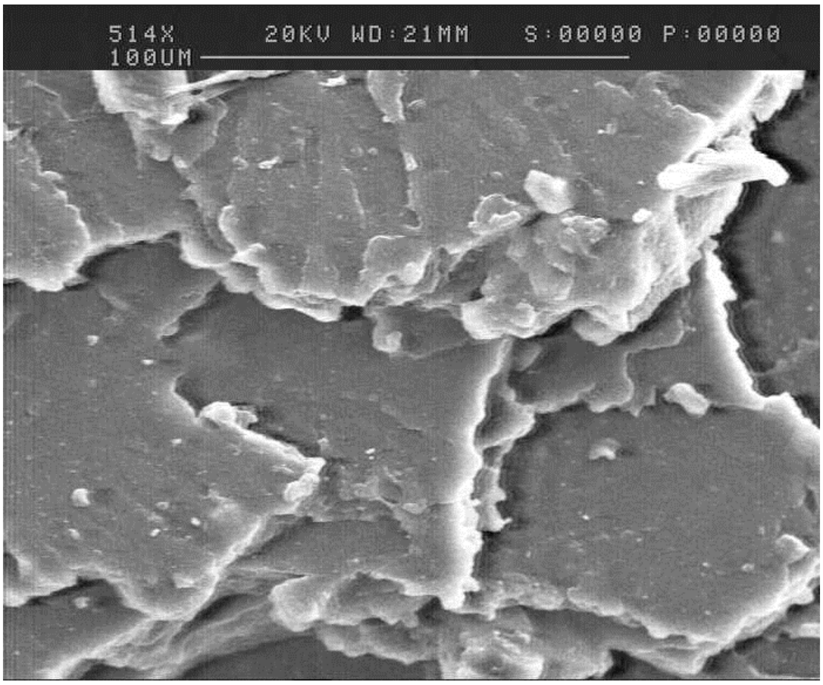

Figure 6 Tensile fracture surface of natural rubber compound filled with 2 phr of organoclay

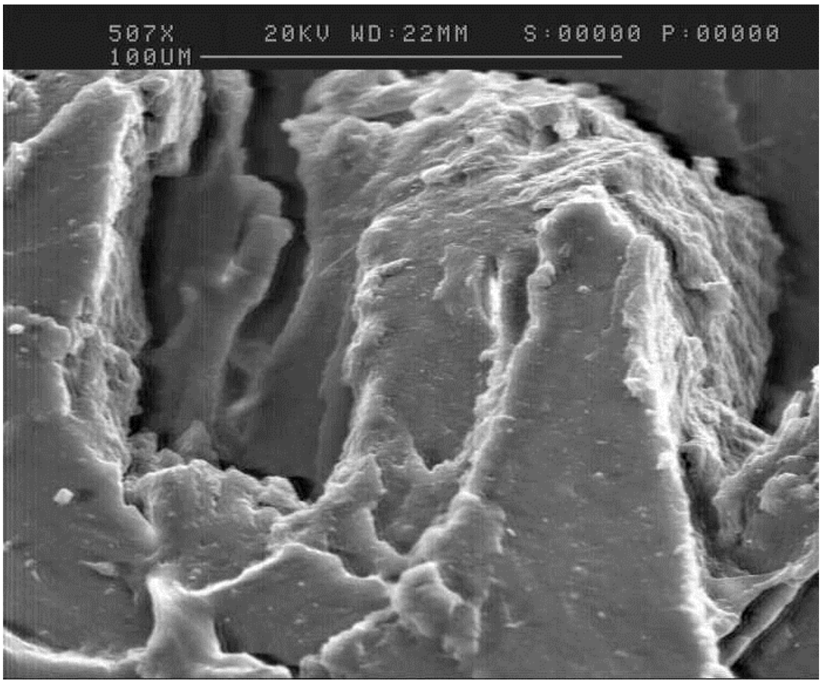

Figure 7 Tensile fracture surface of natural rubber compound filled with 10 phr of organoclay

deformation. Finally premature failure of the rubber compound occurred. This perhaps explains the reduction of both tensile and tear strength with higher filler content.

4.0 CONCLUSION

Cure characteristics of the natural rubber/organoclay compounds such as cure time (t_{90}) decreased with increasing filler content from 0–10 phr but showed slight increases in maximum torque. The mechanical properties: tensile strength increased gradually up to 2 phr filler loading, and more or less stabilised up to 6 phr loading of organoclay. Further increase in filler loading after 6 phr of organoclay resulted in a reduction in the tensile properties. The same trends are observed for elongation at breaks and tear strength. The tensile modulus M100 and M300 increased with increasing filler content.

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