Mechanical Properties of Filled NR/LLDPE Blends

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A B S T R A C T

Effects of filler (carbon black N110, silica and calcium carbonate) on the mechanical properties of natural rubber (NR) / linear low-density polyethylene (LLDPE) blends have been investigated. The blends were prepared by melt blending in a Haake Rheomix at 140°C, 15 min mixing time and a rotor speed of 50 rpm. Fillers were incorporated into the blends for 10-60 vol.%. The mechanical and physical properties of the blends were found dependent on the filler characterization. Swelling index and elongation-at-break showed a decreasing trend with increasing volume percent of filler loading in the blend. The significant changes in other physical properties included the gel content, and bound rubber of the samples indicated a strong interaction between the filler particles and polymer matrix. In conclusion, mean agglomerate particles size and polymer-filler interaction are the factors determining the mechanical and physical properties of NR/LLDPE blends.

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INTRODUCTION

A wide variety of particulate fillers such as carbon black, silica and calcium carbonate are used intensively in the rubber/polymer industry to improve and modify the physical properties of polymer materials [1]. The addition of filler usually leads to increase in modulus and significant improvement in abrasion and tear resistance. Essentially two classes of particulate fillers have been found to offer significant reinforcing effects: carbon black and high-structured silica [2]. Carbon black can be incorpo-

rated as reinforcement filler in NR/LLDPE blends [3]. Carbon black has a unique ability to enhance the physical properties of elastomers [4]. This well documented phenomenon [5,6], termed as "reinforcement", has a profound effect on the current tyre and rubber industries. However, carbon black is used in plastics to alter the key physical properties of a compound, which determines their applications in a given market segment [4]. Carbon black reinforcement had become a subject of scientific interest as early as in the 1940s. Silica reinforcement started to be considered in the 1980s when the benefit of surface treatment with silanes was recognized, with the need for lower rolling resistance tyre being an important driving force in recent research efforts. The interaction between carbon black and elastomer occurs spontaneously but in the case of silica, it is chemically modified [2]. The effects of carbon black filler loading on the mechanical properties of polymer blends were widely reported in the literature [7,8]. However, there is no study reported on the NR/LLDPE blend in the presence of silica and calcium carbonate. This study was basically aimed to investigate the effects of various filler loadings on the mechanical properties of natural rubber / linear low-density polyethylene blends.

EXPERIMENTAL

Materials
Natural rubber (SMR-L) was supplied by Rubber Research Institute of Malaysia (RRIM), linear low-density polyethylene (LLDPE), Etilinas LL0220SA from Polyethylene Malaysia Sdn. Bhd., and carbon black (N110) from Cabot Corporation, Malaysia. Precipitated silica and calcium carbonate were purchased from BDH (AnalarR) England.

Characterization of Filler Properties
Mean agglomerate particles size of fillers was measured by Microtrac particle size analyzer X-100.

Formulation
The 60/40 NR/LLDPE blend was prepared by mixing 60% by weight of NR and 40% by weight of LLDPE. Addition of fillers such as carbon black, silica and calcium carbonate was varied from 10-60% by volume.

Blend Preparations
NR/LLDPE Blends were prepared by melt blending in a Haake Rheomix at 140°C, a rotor speed of 50 rpm and 15 min mixing. The NR was charged into the mixing chamber and mixed for 1 min before addition of LNR. The blending was continued for a further 3 min and LLDPE was then charged to the mixing chamber. After 2 min of mixing, carbon black was charged and blending continued for another 9 min. The blend was taken out and compression moulded into 1 mm sheet under a pressure of 150 kg.cm^{-2} in an electrically heated hydraulic press at 140°C for 3 min. The sheets were immediately cooled between two plates of a cold press at 25°C.

Physical Testing
Tensile strength and modulus (M100) properties were measured on dumbell-shaped sample using a Toyoseiki model Strograph-RI with a load cell of 1 kN and a cross-head speed of 250 mm/min at room temperature. The sample dimensions were accordance to BS 6746 standard. The tests were carried out on a set of seven sample pieces for each blend and the result was averaged from the best five samples.

Gel Content and Swelling Index
Gel contents were determined by Soxhlet extraction technique using toluene as solvent. The samples were extracted for 24 h and dried in air and in vacuum oven at 60°C until constant weight.
The gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{\text{weight after extraction}}{\text{weight before extraction}} \times 100$$

For swelling test, ASTM D 3616 standard was followed. Weighed samples were immersed in toluene for 24 h at room temperature.

The surface of the swelled samples were then immediately blotted with filter paper and weighed. The swelling ratio was defined as:

$$\text{Swelling index} = \frac{W_s}{W_i}$$

where, W_s and W_i were weights of swelled and initial samples, respectively.

Bound Rubber

Small pieces of approximately 2.000 g of filled compound were immersed in 25 mL toluene for 7 days at room temperature. After extraction, the rubber-filler gel was dried in a vacuum oven at a temperature of 60°C until a constant weight was obtained. The percentage of bound rubber content was finally calculated from the equation below as:

$$\text{Bound rubber } (BdR) = \frac{W_{fg} - W_{[mf / (mf + mp)]}}{W_{[mp / (mf + mp)]}} \times 100$$

where, $W_{fg,\ mf,\ mp}$ and W are the weight of carbon black-rubber gel, filler in the compound, rubber in compound, and the test specimen, respectively [9].

RESULTS AND DISCUSSION
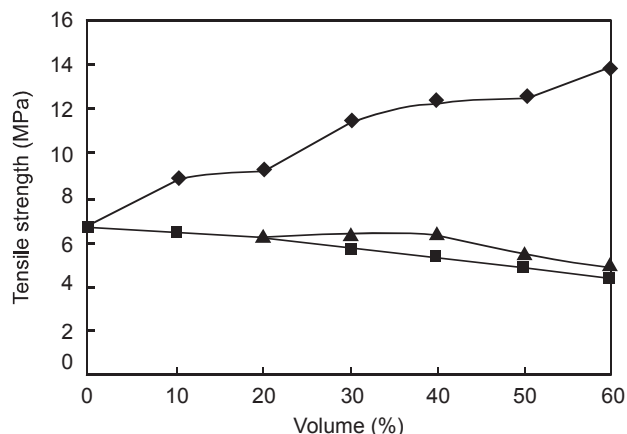
Filler Properties Characterization

Filler characteristics such as particles size, structure and surface properties have a large influence on the physical performance of the elastomeric material [10]. Mean agglomerate particles sizes of fillers used in this study are given in Table 1. The mean agglomerate particle sizes of all fillers are significantly different. The carbon black N110 has the smallest mean agglomerate particles size and followed by calcium carbonate and silica. On the other hand, carbon black has the largest surface area and followed by calcium carbonate and silica. Silica has the largest agglomerate size because of its highly reactive surface chemistry [11]. Measurement of surface area and density of carbon black, silica and calcium carbonate have been done by several authors [11,12].

Physical Testing

Figure 1 shows that tensile strength for carbon black

(—◆—) CBN110 (—■—) Silica (—▲—) CaCO$_3$

Figure 1. Effect of fillers loading on tensile strength.

filled NR/LLDPE blends significantly increase with increasing filler loading, whereas, silica and calcium carbonate show a decreasing trend. For silica and calcium carbonate filled NR/LLDPE blends, the tensile strengths are quite similar at lower loading up to 20 vol.%. At higher loading (30 vol.%), tensile strength for calcium carbonate filled NR/LLDPE blends is higher than silica filled NR/LLDPE blends.

At a fixed filler loading carbon black exhibits the highest value followed by calcium carbonate and silica. Tensile strength for carbon black filled NR/LLDPE blends increases are due to interaction between filler and polymer matrix. It is well known that the smaller particle size filler has a larger surface area and thus there is greater interaction between filler and polymer matrix. Generally, tensile strength increase is a result of the additional reinforcement of the polymer phase. The degree of reinforcement depends on the extent of polymer and filler interaction. The interactive forces increase with carbon black concentration and so does the degree of reinforcement. Carbon black is also believed to influence the thermally induced interaction between the natural rubber and low linear density polyethylene phases. Lower tensile strength for calcium carbonate filled NR/LLDPE blends is due to larger mean agglomerate particle size of filler (smaller surface area) and poor dispersion compared to carbon black. For silica filled NR/LLDPE blends, the lowest tensile strength observed is due to large mean agglomerate particles size of silica and weak interaction between filler and polymer matrix. It is well known that interaction between filler and filler is dominant in the

Table 1. Physical properties of carbon black, silica and calcium carbonate.

| Filler	Mean agglomerate particles size (μm)	Density (g/cm^3)
Carbon black N110	6.2	1.8
Precipitate silica	15.6	2.0
Calcium carbonate	7.2	1.0

case of silica filled polymer blends. These observations indicate that the mean agglomerate particles size play an important role in affecting the mechanical properties of NR/LLDPE blends.

Figure 2 shows the effect of filler loading and types on the modulus at 100%, M100 of NR/LLDPE blends. The M100 is observed to increase with increasing filler loading and the increment is almost similar at low filler loading for all the fillers. However, at higher filler loadings (>30 vol.%) the M100 for carbon black filled NR/LLDPE blend is higher and for silica and calcium carbonate fillers the increase is minimum. Several authors observed a similar trend for filled polymer blends [11,12]. These observations reveal that polymer matrix-filler interaction is an important factor controlling the modulus. It is well known that natural rubber forms a stronger adsorptive bond with carbon black than with silica, and followed by calcium carbonate [12]. Silica is better than calcium carbonate due to weak interaction formed between the filler and polymer matrix in the blend. However, silica is not well dispersed due to bigger agglomerate particles. Calcium carbonate is an inorganic filler, which acts as inert filler (non-reinforcing filler) due to non-reactive functional groups on the surface. Thus calcium carbonate is better dispersed and therefore, its non-reinforcing effect is more significant.

According to reinforcement concept, the main factors governing the reinforcement of elastomer, apart from filler loading are filler-particle size or specific surface area, filler structure and specific surface activity. Fine particles actually reflect their greater interface

between the polymer matrix and the filler, hence, provide a higher degree of reinforcement than the coarse ones. Higher filler structure is always associated with processing difficulty as it increases the viscosity of the compound considerably as well as the modulus of the vulcanizate. The surface activity is an important factor, indicating the extent of polymer-filler interaction. With good polymer-filler interaction, there would be increases in modulus as well as mechanical properties. Based on this concept, both carbon black and silica have very high surface activity, which provide greater reinforcement in comparison with the other filler such as calcium carbonate [11,12].

Figure 3 shows the effect of filler loading and type on elongation-at-break. It indicates that elongation-at-break (%) decreases gradually with increasing filler loading. The reduction of elongation-at-break is due to stiffening of the polymer matrix by the filler. Further increase in filler loading causes the molecular mobility decrease due to extensive formation of physical bond between the filler particles and the polymer chain that stiffen the matrix [13]. The increase in filler loading leads the matrix progressively becoming reinforced and hence lowering elongation-at-break at any filler loading greater than 20%. Elongation-at-break for carbon black filled NR/LLDPE blends is higher than calcium carbonate filled NR/LLDPE blends and then followed by silica. Carbon black provides greater reinforcement due to greater polymer matrix-filler particles interaction [13]. Polymer matrix-silica particles interaction is lower than polymer matrix-calcium carbonate interaction, which can be rationalized as due to the small size
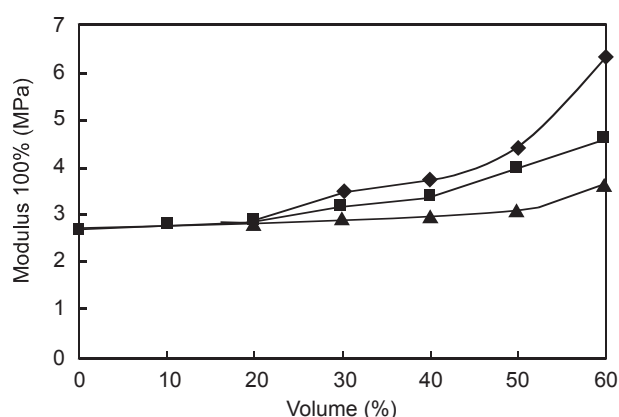
(—♦—) CBN110 (—■—) Silica (—▲—) CaCO₃

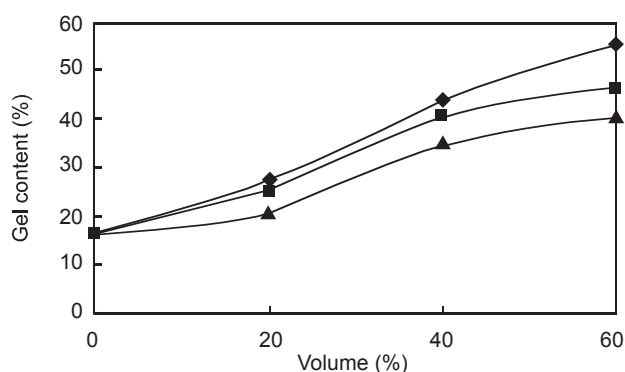**Figure 2.** Effect of filler loading on 100% modulus (M100).
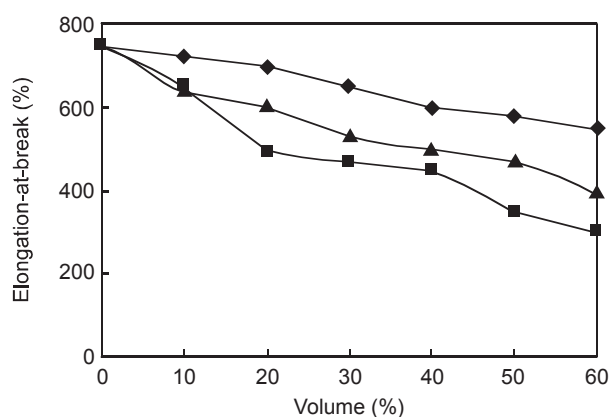
(—♦—) CBN110 (—■—) Silica (—▲—) CaCO₃

Figure 3. Effect of filler loading on elongation-at-break.

of the $CaCO_3$ particles, as they can be more homogeneously distributed in the matrix.
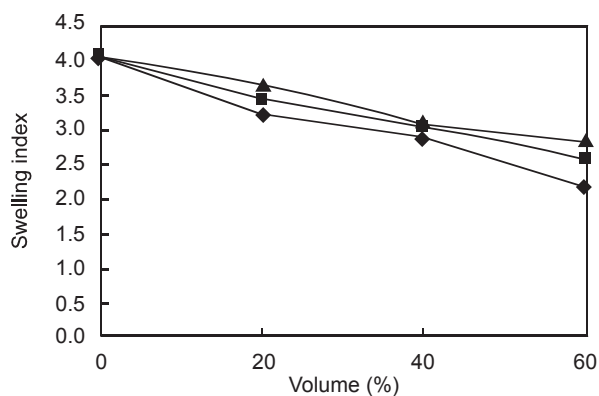
Gel Content and Swelling Index

Figure 4 shows that the percentage of gel content increases with the volume percent of filler loading. However, swelling index in Figure 5 decreases with the amount of filler loaded into the blends. Insoluble gel is formed when cross-linking reactions occur within the rubber and plastic phases as well as interaction at the rubber-plastic interphases. It is believed that strong interaction occurs between the rubber and plastic phases and the matrix-filler interphase. The increase of insoluble gel content and decrease in swelling with filler loading is due to the formation of a network structure pronounced by the filler. Reactions involving radical-radical recombination and macro-radical additions across the double bonds are expected to enhance in the presence of fillers. Swelling index can be used as an
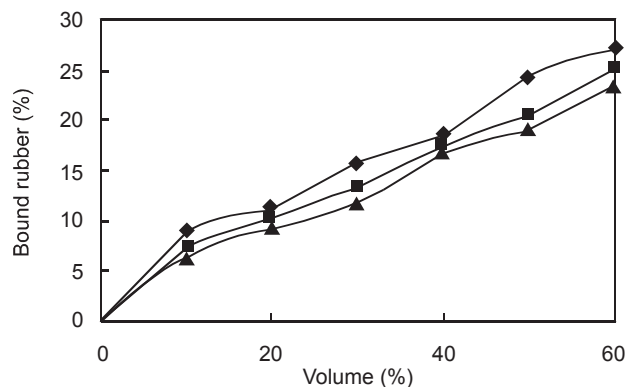

(—◆—) CBN110 (—■—) Silica (—▲—) $CaCO_3$

Figure 4. Effect of filler loading on insoluble gel content.

indicator for the formation of cross-links in the blends. Swelling index decreases with increasing filler loading which indicates an increase in the cross-link density.

Bound Rubber

When an elastomer, such as natural rubber and reinforcing filler are mixed, strong interactions occur in such manner that a good solvent of the polymer can extract only the free rubber portion, leaving a highly swollen rubber-filler gel. Bound rubber (BdR) is, by definition, the rubber content of that gel [2]. Bound rubber is formed in filled rubber/polymer compounds by physical adsorption, chemisorption and mechanical interaction [14].

Formation of bound rubber depends on the polarity and microstructure of the polymer and the structure and surface activity of filler. The filler-polymer interaction affects the level of bound rubber content. Figure 6 shows the effect of filler loading and types on the percentage of bound rubber. It is observed that bound rubber (%) increases with increasing filler loading. At a fixed filler loading, bound rubber content of carbon black filled NR/LLDPE blends is higher than silica filled NR/LLDPE blends. Calcium carbonate filled NR/LLDPE blends show the lowest bound rubber content. This is to be expected that rubber-filler interaction for carbon black filled NR/LLDPE blends is higher than other fillers. It is well known that carbon black particles interact strongly with rubber chain and thus chemical bonds are formed [15]. Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions. Since intermolecular hydrogen

(—◆—) CBN110 (—■—) Silica (—▲—) $CaCO_3$

Figure 5. Effect of filler loading on swelling index.

(—◆—) CBN110 (—■—) Silica (—▲—) $CaCO_3$

Figure 6. Effect of filler loading on bound rubber.

bonds between hydroxyl groups on the surface of silica are very strong, they can aggregate tightly and thus leads to the formation of filler networking. This implies that the amount of the tightly bound rubber is larger in the carbon black than silica [15].

CONCLUSION

Mechanical properties of the samples changed significantly due to mean agglomerate particles size (surface area) and polymer-filler interaction. Reinforcement of filled NR/LLDPE arises from the strong interaction between filler and polymer matrix. A higher filler loading leads to a higher insoluble gel content and bound rubber in NR/LLDPE blends.

ACKNOWLEDGEMENTS

REFERENCES

1. Bokobza L. and Rapoport O., Reinforcement of natural rubber, *J. Appl. Polym. Sci.,* **85**, 2301-2316 (2002).

2. Leblance J.L., Rubber-filler interaction and rheological properties in filled compounds, *Prog. Polym. Sci.,* **27**, 627-687 (2002).

3. Ahmad A., Mohd D.H., and Abdullah I., The effects of liquid natural rubber on the mechanical properties and morphology of carbon black filled NR/LLDPE blend, Chemical Process and Engineering, *Proc. of 2nd World Eng. Cong.,* Kuching, Sarawak, Malaysia, 264-267 (2002).

4. Donnet J.-B., Bansal R.C., and Wang M.-J., *Carbon Black: Science and Technology,* Marcel Dekker, New York, 2nd ed., 289 (1993).

5. Donnet J.-B. and Voet A., *Carbon Black, Physics, Chemistry and Elastomer Reinforcement,* Marcel Dekker, New York, Ch. 8, 272 (1976).

6. Kraus G., *Reinforcement of Elastomers,* Kraus G. Ed., Wiley Intersci., New York, Chs. 3 and 8 (1965).

7. Banik I. and Bhowmick A.K., Electron beam modification of filled fluorocarbon rubber, *J. Appl. Polym Sci.,* **76**, 2016-2025 (2000).

8. Katbab A.A, Nazockdast H., and Bazgir S., Carbon black-reinforced dynamically cured EPDM/PP thermoplastic elastomer. I. Morphology, rheology, and dynamic mechanical properties, *J. Appl. Polym. Sci.,* **75**, 1127-1137 (2000).

9. Sirisinha C. and Sittichokchuchai W., A study of relationships between state-of-mix, rheological properties, dynamic properties and bound rubber content, *J. Appl. Polym. Sci.,* **76**, 1542-1548 (2000).

10. Bokobza L. and Rapoport O., Reinforcement of natural rubber, *J. Appl. Polym. Sci.,* **85**, 2301-2316 (2002).

11. Sae-Oui P., Rakdee C., and Thanmathorn P., Use of rice husk ash as filler in natural rubber vulcanizates in comparison with other commercial fillers, *J. Appl. Polym. Sci.,* **83**, 2485-2493 (2002).

12. Poh B.T., Ismail H., and Tan K.S., Effect of filler loading on tensile and tear properties of SMR L/ENR 25 and SMR L/SBR blends cured via a semi-efficient vulcanization system, *Polym. Test.,* **21**, 801-806 (2002).

13. Sau K.P., Chaki T.K., and Khastgir D., Electrical and mechanical properties of conducting carbon black filled composites based on rubber and rubber blends, *J. Appl. Polym. Sci.,* **71**, 887-895 (1999).

14. Choi S.-S., Filler-polymer interaction in both silica and carbon black filled styrene-butadiene rubber compounds, *J. Polym. Sci. Part B: Polym. Phys.,* **39**, 439-445 (2001).

15. Choi S.-S., Difference in bound rubber formation of silica and carbon black with styrene-butadiene rubber, *Polym. Adv. Technol.,* **13**, 466-474 (2002).