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The effect of filler size on the cure characteristics, processability, mechanical properties, and morphology of stearic acid-coated $CaCO_3$ filled natural rubber compounds

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Abstract

The effects of filler loading and size on curing characteristics and mechanical properties of stearic acid-coated $CaCO_3$ filled natural rubber (NR) compounds have been studied. A two-stage conventional mixing procedure was used to incorporate two particle sizes, 1 and 5 μm, of stearic acid-coated $CaCO_3$ into natural rubber. Filler loading was varied from 0-60 parts per hundred of rubber (phr) at 15 phr intervals. The cure time (t_{90}) of both filler sizes decreased with increasing stearic acid-coated $CaCO_3$ loading. At a given filler loading, larger particle size coated $CaCO_3$ showed shorter t_{90}. The Mooney viscosity increased with an increase in filler loading and smaller particle size showed higher viscosity. Tensile strength of the coated $CaCO_3$ filled NR compounds increased with filler loading until a maximum level was reached (at approximately 30 phr) and then started to decrease with further increase in filler loading. As the coated $CaCO_3$ loading increased, the compounds became stiffer and harder. Thus, an increase in the modulus at 300% elongation with increasing filler loading was obtained. Again, the compounds filled with smaller coated $CaCO_3$ size showed higher tensile strength and 300% modulus.

Keywords: *natural rubber, filler, stearic acid-coated $CaCO_3$, mechanical properties*

บทคัดย่อ

การศึกษาอิทธิพลของปริมาณและขนาดของแคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริกเป็นสารตัวเติมในยางธรรมชาติคอมปาวด์ต่อคุณลักษณะการคงรูปและสมบัติเชิงกล ผสมแคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริกขนาด 1 และ 5 μm ร่วมกับยางธรรมชาติผ่านกระบวนการผสมแบบทั่วไปสองขั้นตอน โดยการเปลี่ยนแปลงปริมาณสารตัวเติมในช่วงระหว่าง 0-60 ส่วนในร้อยส่วน (phr) ด้วยการเพิ่มทุกๆ 15 phr เวลาการคงรูป (t_{90}) ของสารตัวเติมทั้งสองขนาดลดลงเมื่อปริมาณแคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริกเพิ่มขึ้น ที่ปริมาณสารตัวเติมคงที่ค่าหนึ่งเวลาการคงรูปของแคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริกที่มีขนาดใหญ่จะเร็วกว่าสารตัวเติมที่มีขนาดเล็ก ความหนืดมูนนี่เพิ่มขึ้นเมื่อเพิ่มปริมาณสารตัวเติมและความหนืดมูนนี่ของสารตัวเติมที่มีขนาดเล็กจะให้ค่าสูงกว่าสารตัวเติมที่มีขนาดใหญ่ ความทนทานต่อแรงดึงมีค่าเพิ่มขึ้นเมื่อปริมาณของสารตัวเติมเพิ่มขึ้นจนกระทั่งมีระดับสูงสุด (30 phr) ต่อจากนั้นเริ่มมีค่าลดลงเมื่อปริมาณของสารตัวเติมเพิ่มสูงขึ้น เมื่อปริมาณแคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริกเพิ่มขึ้นยางคอมปาวด์จะแข็งทื่อสูงขึ้น ด้วยเหตุนี้การเพิ่มปริมาณสารตัวเติมสูงขึ้นค่ามอดูลัส ณ เปอร์เซ็นต์ระยะยืดช่วง 300 เพิ่มสูงขึ้น และยางคอมปาวด์ที่ผสมสารตัวเติมขนาดเล็กจะแสดงค่าความทนทานต่อแรงดึงและ 300% มอดูลัสสูงกว่าสารตัวเติมขนาดใหญ่

คำสำคัญ: *ยางธรรมชาติ, สารตัวเติม, แคลเซียมคาร์บอเนตเคลือบผิวด้วยกรดสเตียริก, สมบัติเชิงกล*

1. Introduction

Natural and synthetic rubbers in vulcanized form are used to prepare various rubber products having a wide range of applications, ranging from footwear to automotive parts. In the vulcanization of rubber, carbon black and silica are the main fillers used in the compounding recipes (George, Varkey, Thomas, & Mathew, 2002; Chiu & Chiu, 1996). In spite of being well known for their capabilities as reinforcements, imparting strength and stiffness to the vulcanized rubber, these fillers are relatively expensive. Therefore, considerable R & D effort is being carried out to investigate the possibility of replacing these fillers with the goal to reduce the cost of rubber products while maintaining their desired properties. The effect of fillers on mechanical and other properties of the compounds depends strongly on their shape, size and size distribution of the primary particles and their aggregates, surface characteristics, and degree of dispersion and distribution (Chan, Wu, Li, & Cheung, 2002). One of the most important fillers used in large quantities in particulate filled polymers is calcium carbonate ($CaCO_3$). Much work has been done to study the use of $CaCO_3$ as a filler for polymeric materials (Atikler, Basalp, & Tihminlioğlu, 2006; Shah & Fuzail, 2006; Ismail, Nordin, & Noor, 2002; Arayapranee & Rempel, 2008). It not only lowers the cost but also improves mechanical properties such as modulus, hardness, toughness, dimensional stability, thermal resistance, and flame retardancy. However, all advantages offered by the use of fillers can be exploited only if the particles are distributed homogenously in the polymer matrix. In order to improve the interfacial adhesion, treatment of the filler with coupling agents or reactive surface modifiers is generally employed (Ess & Hornsby, 1986; Xu, Lei, & Xie, 2002). Kiss et al., 2007, investigated the effect of aggregation in polypropylene composites containing seven different precipitated $CaCO_3$ fillers coated with stearic acid (Kiss, Fekete, & Pukánszky, 2007). They observed that the coated fillers formed much looser aggregates with more diffuse interphases than the uncoated particles. Sahnoune et al., 2003, observed that the incorporation of $CaCO_3$ into a fixed 75:25 blend ratio (wt%) of high-density polyethylene (HDPE) and polystyrene (PS) led to an increased stiffness of the blends while the impact resistance showed a decrease (Sahnoune, Lopez Cuesta, & Crespy, 2003). Supaphol et al., 2003, studied the effects of $CaCO_3$ of varying particle size (1.9, 2.8, and 10.5 μm), content (0-40 wt%), and type of surface modification (uncoated, stearic acid-coated, and paraffin-coated) on the mechanical properties of syndiotactic polypropylene/calcium carbonate compounds (Supaphol, Harnsiri, & Junkasem, 2004). They reported that tensile strength was found to decrease while the Young's modulus increased with increasing $CaCO_3$ content. Both types of surface treatment on $CaCO_3$ particles reduced tensile strength and Young's modulus, but improved impact resistance.

The mechanical properties of filled rubbers usually are described in terms of tensile and tear strength, Young's modulus, and hardness. The mechanical properties of filled rubbers depend mainly on the type of filler, filler loading, filler dispersion, filler surface area, and the interaction between the filler and the rubber matrix. In this study, stearic acid-coated $CaCO_3$ particles of two sizes (1 and 5 μm) were incorporated into natural rubber and the effect of filler loading (0–60 phr) was investigated by examining processability and mechanical properties as performance indicators.

2. Meterials and methods

2.1 Materials

Details of the mixing ingredients and rubber formulations used are shown in Table 1. All mixing ingredients were used as received.

The surface area of the fillers was determined by the Brunauer-Emmett-Teller (BET) method using an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp.). The physical properties of fillers are presented in Table 2.

Table 1 Ingredients used in the present study

Ingredient	Amount phr[a]
NR	100
Zinc oxide (ZnO)	5.0
Stearic acid	2.0
N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS)	1.8
Sulfur (S)	2.4
Filler: Stearic acid-coated $CaCO_3$ (1 μm)	Variable (0-60)
Stearic acid-coated $CaCO_3$ (5 μm)	Variable (0-60)

[a] phr, parts per hundred of rubber

Table 2 Physical properties of the fillers

Filler	Mean particle size (μm)	Surface area (m^2/g)
Stearic acid-coated $CaCO_3$	1	18.09
Stearic acid-coated $CaCO_3$	5	3.24

2.2 Preparation of rubber compounds

A two-stage mixing procedure was employed to prepare all compounds. In the first stage, the mixing was carried out in a dispersion kneader machine with a fill factor of 0.7, a chamber temperature of 75°C, and a rotor speed of 40 rpm. Natural Rubber (NR) was initially masticated in the mixer for 2 min before the stearic acid and zinc oxide (ZnO) were added. After mixing for 1 min, the filler was added and the mixing process continued for a further 6 min. Finally, the N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS) accelerator was added and mixed for 3 min. The mixture was then discharged and sulfur was added for the second mixing step using a two-roll mill with a friction ratio 1:1.1 at 70°C for 3 min.

2.3 Cure characteristics and Mooney viscosity

Cure characteristics were studied using a moving die rheometer (model Rheo-Tech) manufactured from TECH-PRO according to ISO 3414 for 30 min at 150°C. The Mooney viscosity (ML_{1+4} at 100°C) was determined by using a Mooney viscometer (model Visc-Tech, TECH-PRO). The testing procedure was conducted according to the method described in ISO 289-1.

2.4 Vulcanization process

All compounds were compression molded at 150°C with a force of 17.5 MPa using a hydraulic hot press according to their respective cure time, $t_{90,}$ determined by the MDR.

2.5 Mechanical properties

Tensile properties were determined on an Instron Testing Instrument (Model 1011) using C-type Dumbbell-specimens, according to ASTM D412.

2.6 Scanning electron microscopy

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a Jeol Microscope (model JSM 5600 LV) at a magnification of 3000. The shape of fillers was also examined using the scanning electron microscope at 5000× magnification.

3. Results and discussion

3.1 SEM studies of filler particles

SEM micrographs of the filler particles at 5000× magnification are shown in Figure 1. As it can be seen, the $CaCO_3$ had irregular, approximately cubical particles. Figure 1 shows the formation of less aggregates in the 1 μm particle size of coated $CaCO_3$ [Figure 1(a)] compared to the 5 μm particle size of coated $CaCO_3$ [Figure 1(b)].

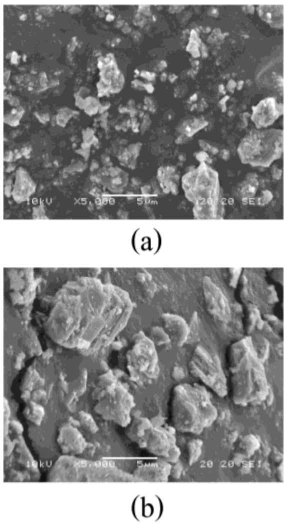


Figure 1 SEM micrographs at 5000× magnification of the fillers: (a) stearic acid-coated $CaCO_3$ (1 μm) and (b) stearic acid-coated $CaCO_3$ (5 μm)

3.2 Cure characteristics and processability of natural rubber compounds

Both particle sizes (1 and 5 μm) of coated $CaCO_3$ were incorporated with loadings ranging from 0 to 60 phr at 15 phr intervals to study the effect of filler loading on the cure properties of the compounds. The optimum cure time of compounds are given in Figure 2. It can be observed that compared to the unfilled compound, the optimum cure time of the coated $CaCO_3$ filled NR was higher than that of the unfilled compound. At low $CaCO_3$ loading, the chances of forming aggregates were less compared to high loading and hence good filler-rubber interaction was achieved. An increase in loading of coated $CaCO_3$ decreased the optimum cure time. This decrease may be attributed to a poor interaction between the $CaCO_3$ particles and the rubber matrix, which resulted in the tendency of the filled compounds to form filler agglomerates. However, at a given filler loading, larger particle size of coated $CaCO_3$ filled NR compounds showed shorter t_{90} than that of smaller particle size**.** Nasir and Choo, 1989, reported that the cure retardant was obtained with fillers having the smaller particle size, hence the larger surface area; there was the greater filler-rubber interaction (Nasir & Choo, 1989)**.**

The effect of filler loading on the Mooney viscosity of the compounds is shown in Figure 3. It can be seen that for $CaCO_3$ fillers, Mooney viscosity increased with an increase in filler loading. However, for larger particle sizes of coated $CaCO_3$ filled NR compound, the change of this property with filler loading was less pronounced. In the mixing state, the smaller the particle size, and hence the larger the specific surface area, the greater the interaction between the filler and rubber matrix was observed. Thus, a higher restriction to molecular motion of the NR compounds filled with two particle sizes of stearic acid-coated $CaCO_3$ was expected. In other words, the addition of fillers of a smaller size tended to impose extra resistance to flow. The lower Mooney viscosity of the compounds having larger particle size filler indicated that it could be processed more easily than those having smaller particle size filler.

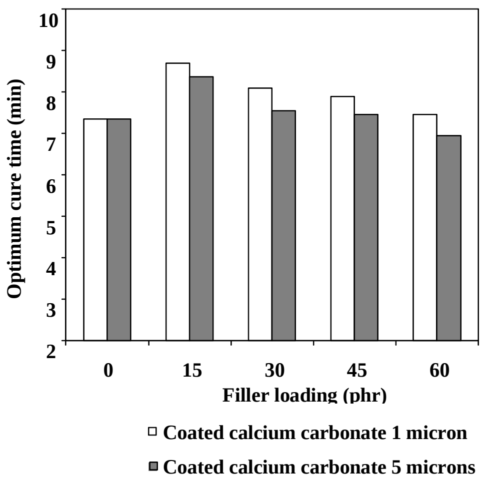


Figure 2 Relationship between filler loading and optimum cure time of NR compounds filled with two particle sizes of stearic acid-coated $CaCO_3$.

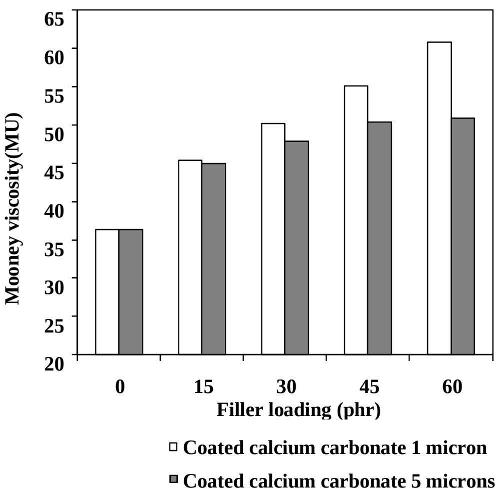


Figure 3 Relationship between filler loading and Mooney viscosity (ML_{1+4} at 100°C) of NR compounds filled with two particle sizes of stearic acid-coated $CaCO_3$.

3.3 Mechanical properties of NR compounds

3.3.1 Tensile properties

Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications. Coated $CaCO_3$ particles were incorporated at different loadings up to 60 phr in NR compounds to study the effect of filler loading on the mechanical properties of the filled NR compounds. Figure 4 shows the tensile strength of NR compounds as a function of filler loading. A decreasing trend in tensile strength was also observed with an increase of filler size. Large particle size of coated $CaCO_3$ can also diminish the tensile strength of compounds because of the partial aggregation of particles. It can be concluded from this observation that the size of the filler had a considerable influence on tensile strength even with non-bonded intermolecular interactions between polymer and filler particle. The effect of filler loading on tensile strength of NR compounds may increase or decrease with the incorporation of filler. Tensile strength of the coated $CaCO_3$ filled NR compounds increased with filler loading until reaching a maximum level (at approximately 30 phr) and then started to decrease with further increase in filler loading. The detrimental effect on tensile strength at high loadings may be attributed to aggregation of the filler resulting in inhomogeneous distribution which weakens the interaction between the filler and the matrix, leading to an undesirable material property. Rigbi (Rigbi, 1982) reported that the reinforcing filler increased the tensile strength up to maximum filler loading, after which a decrease in tensile strength at high loadings that may be attributed to the dilution effect or agglomeration of filler.

Figure 5 shows the effect of filler loading on modulus at 300% elongation of the rubber compounds, which is an indication of material stiffness for filler filled NR compounds. Fillers are known to increase modulus provided that the modulus of the filler is higher than that of the polymer matrix. Modulus of the filled compounds increased with an increase in filler loading. As more filler particles are introduced into the rubber, the rubber portion is reduced, resulting in higher stiffness properties. Increasing particle size led to a decrease in 300% modulus. It appears from the results that with the reduction in filler size, the stiffness of the polymer and the attractive interaction energy between the polymer and filler particles at the interface increased.

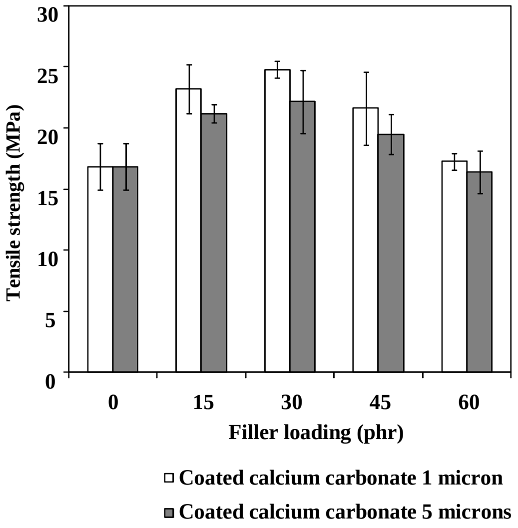


Figure 4 The effect of filler loading on tensile strength of 1 μm stearic acid-coated $CaCO_3$ and 5 μm stearic acid-coated $CaCO_3$ filled NR compounds.

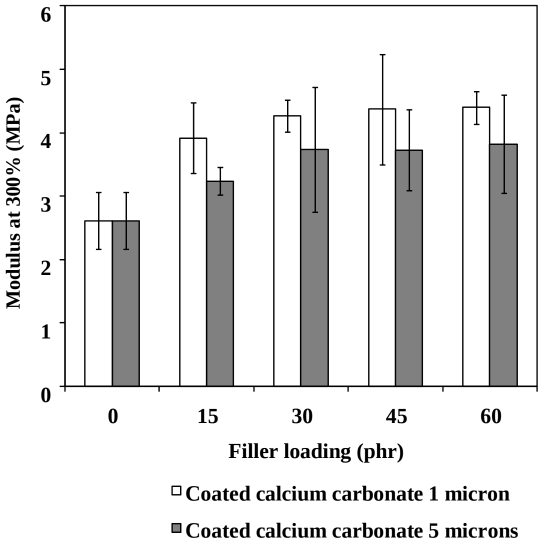
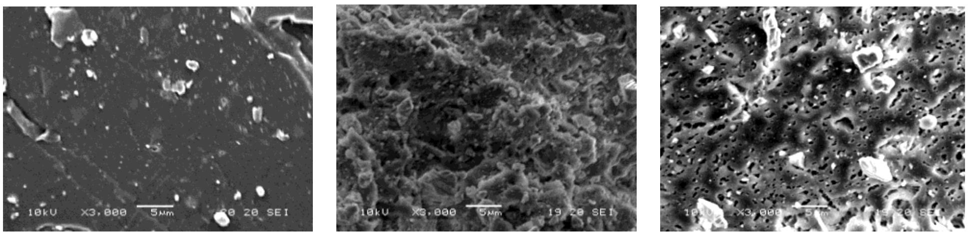


Figure 5 The effect of filler loading on modulus values at 300% of 1 μm stearic acid-coated $CaCO_3$ and 5 μm stearic acid-coated $CaCO_3$ filled NR compounds.

3.4 Morphology

The morphology of unfilled and coated $CaCO_3$ filled NR compounds at 30 phr filler loading after tensile fracture is shown in Figure 6. The surface of the unfilled NR compounds is smooth [Figure 6(a)]. For the fracture surface of coated $CaCO_3$ filled NR compounds [Figure 6(b) and (c)], the separation at the edge of the particle–matrix interface still can be observed, which led to void formation. Aggregation will cause defects to the compound because of the presence of voids between the particles and the matrix. This means that aggregates resulting as a weak point in the compound material can lead to an undesirable material property due to poor adhesion. This subsequently reduced the mechanical properties of the coated $CaCO_3$ filled NR compound system. As shown in Figures 1(a) and 1(b); it can be seen that aggregation did occur to a greater extent on coated $CaCO_3$ of larger particle size. The fracture surface of the smaller particle size filler showed a more homogenous phase dispersion, resulting in a higher tensile strength. $CaCO_3$ is considered when incorporated with rubber, in which the filler/matrix interfaces were weak. The SEM photomicrographs shown in Figure 6 confirm that a smaller particle size of the coated $CaCO_3$ provided a better filler dispersion and interfacial bond between filler and rubber matrix. This might increase the strength of the compound. The observations were in agreement with the mechanical properties.



(a) (b) (c)

Figure 6 SEM micrographs of (a) unfilled NR compounds and (b) 1 μm stearic acid-coated $CaCO_3$ and (c) 5 μm stearic acid-coated $CaCO_3$ filled NR compounds after tensile fracture at 30 phr filler loading (× 3000).

4. Conclusion

In this study, stearic acid-coated $CaCO_3$ was incorporated into natural rubber and the effects of the particle size of coated $CaCO_3$ (1 and 5 μm) and filler loading (0–60 phr) were investigated:

1. There was a cure reduction of coated $CaCO_3$ filled NR compounds with increasing filler loading. At a given filler loading, coated $CaCO_3$ with larger particle size showed shorter cure time.

2. The Mooney viscosity increased with increasing coated $CaCO_3$ loading and at a given filler loading, the coated $CaCO_3$ with smaller particle size showed higher viscosity values.

3. With the addition of coated $CaCO_3$ in NR compounds, the tensile strength increased with an increase in filler loading up to 30 phr and then this property decreased with further increase in filler loading, whereas the 300% modulus of the compounds increased with increasing filler loading. Smaller particle size of coated $CaCO_3$ gave better mechanical properties.

4. The SEM micrographs showed the occurrences of void formation in the coated $CaCO_3$ filled NR compounds and, as expected, poor filler dispersion and weak filler-rubber interaction were observed. However, the smaller particle size of filler showed the formation of fewer holes, which provided better rubber-filler interactions. The results confirm that coated $CaCO_3$ filled NR compounds with the smaller particle size show better overall mechanical properties than those of larger particle size.

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6. References

Arayapranee, W., & Rempel, G. L. (2008). A comparison of the properties of rice husk ash, silica, and calcium carbonate filled 75 : 25 NR/EPDM blends. *J Appl Polym Sci, 110*, 1165-1174.

Atikler, U., Basalp, D., & Tihminlioğlu, F. (2006). Mechanical and morphological properties of recycled high-density polyethylene, filled with calcium carbonate and fly ash. *J Appl Polym Sci, 102*, 4460-4467.

Chan, C. M., Wu, J., Li, J.-X., & Cheung, Y.-K. (2002). Polypropylene/calcium carbonate nanocomposites. *Polymer, 43*, 2981-2992.

Chiu, H.-T., & Chiu, W.-M. (1996). Influence of mechanical properties in carbon black (CB) filled isotactic polypropylene (iPP) and propylene-ethylene block copolymer. *J Appl Polym Sci*, *61*, 607-612.

Ess, J. W., & Hornsby, P. R. (1986). Characterisation of distributive mixing in thermoplastics compositions. *Polym Test, 6*(3), 205-218.

George, K. M., Varkey, J. K., Thomas, K. T., & Mathew, N. M. (2002). Epoxidized natural rubber as a reinforcement modifier for silica-filled nitrile rubber. *J Appl Polym Sci*, *85*, 292-306.

Ismail, H., Nordin, R., & Noor, A. M. (2002). The comparison properties of recycle powder, carbon black, and calcium carbonate filled natural rubber compounds. *Polym-Plast Technol Eng, 41*, 847-862.

Kiss, A., Fekete, E., & Pukánszky, B. (2007). Aggregation of CaCO3 particles in PP composites: Effect of surface coating. *Compos Sci Technol*, *67*, 1574-1583.

Nasir, M, & Choo, C H (1989) Cure characteristics and mechanical properties of carbon black filled styrene-butadiene rubber and epoxidized natural rubber blends. *Eur Polym J, 25*, 355-359.

Rigbi, Z. (1982) Reinforcement of rubber by carbon black. *Rubber Chem Technol, 55*, 1180-1220.

Sahnoune, F., Lopez Cuesta, J. M., & Crespy, A. (2003). Improvement of the mechanical properties of an HDPE/PS blend by compatibilization and incorporation of $CaCO_3$. *Polym Eng Sci*, *43*(3), 647-660.

Shah, G. B., & Fuzail, M. (2006). Modification of polyethylene and incorporation of fillers for effective reinforcement of mechanical and better flame retardant properties. *J Appl Polym Sci*, *99*, 1928-1933.

Supaphol, P., Harnsiri, W., & Junkasem, J. (2004). Effects of calcium carbonate and its purity on crystallization and melting behavior, mechanical properties, and processability of syndiotactic polypropylene. *J Appl Polym Sci, 92*, 201-212.

Xu, T., Lei, H., & Xie, C. S. (2002). Investigation of impact fracture process with particle-filled polymer materials by acoustic emission. *Polym Test, 21*(3), 319-324.