

EFFECT OF DIFFERENT ORIGINS OF NATURAL RUBBER ON THE PROPERTIES OF CARBON BLACK FILLED NATURAL RUBBER COMPOSITES

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Received Date: July 3, 2012

Abstract

Two different origins of natural rubber (NR) from Malaysia; SMR CV60 and Vietnam; SVR 3L filled with 0 and 30phr carbon black (CB) were investigated. Compounds were prepared by a two-roll mill with conventional (CV) and efficient (EV) cure systems. Results obtained show that SVR 3L has higher Mooney viscosity compared to SMR CV60. A different origin of NR has influenced the cure characteristics of rubber compounds. In EV system, SVR 3L compounds showed faster cure rate index (CRI) while in CV system showed contrary results. However, CRI of NR compounds with EV system increased with addition of CB due to high amount of accelerator while CRI in CV system decreased with addition of CB. Torque difference for both NR compounds with each cured system showed similar value. However, mechanical and physical properties were dependent on addition of CB. SVR 3L composites exhibited better tensile strength and recovery from loading force compared to SMR CV60.

Keywords: Cure characteristics, Mechanical properties, Natural rubber, Vulcanization systems

Introduction

Natural rubber contains high molecular weight, mainly organic with long-chain molecules made up of repeating units of polyisoprene [1]. It has excellent mechanical and physical properties (tensile strength, tensile modulus, tear strength and hardness) [1,2]. However, NR is easy to be attacked by solvents, deteriorated by oxygen, ozone, sun light, UV rays as well as humidity [3,4]. With addition of filler such as silica, carbon black, etc, rubber composites are used in many applications to produce different type of products such as engine mounts, truck tires, passenger tires, hose, conveyor belts, tank lining, etc. [5]. NR has better properties over synthetic polymer due to a small proportion of protein and fatty acids which, help to increase the cure rate. NR also has better toughness, green strength, plasticity retention index [4-6]. Rubber properties are depending on compounding ingredients especially vulcanization system, type and amount of filler and other special ingredients for better degradation resistance. Katrina Cornish [7] made comparison of different rubber biochemistry including *Hevea brasiliensis*, *Parthenium argentatum* and *Ficus elastic*. The particle size, components of rubber and molecular weight showed that rubber molecule initiation, biosynthetic rate and molecular weight, in vitro, are dependent upon substrate concentration and the ratio of isopentenyl pyrophosphate (IPP, the elongation substrate, or monomer) and farnesyl pyrophosphate (FPP, an initiator), but these parameters are affected by intrinsic properties of the rubber transferees as well. Ismail et al. [2] made comparison of different types of accelerators on carbon black filled NR composites. Cetyltrimethylammonium maleate (CTMAM) can work as accelerator for sulphur vulcanization better than N-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS) without activators, zinc oxide and stearic acid. In present work, comparison of different

origins of NR filled carbon black was investigated. Mooney viscosity of each SMR CV60 and SVR 3L were discussed. Cure characteristics such as scorch time, cure time, cure rate index and torque difference, physical and mechanical properties of CB filled NR composites were investigated.

Experimental

Materials

Natural rubber (SMR CV60) and Vietnamese natural rubber (SVR 3L) were supplied by Zarm Scientific Sdn. Bhd. Zinc oxide, stearic acid, sulphur, N-Cyclohexyl-2-benzothiazole sulfonamide (CBS) were obtained from Bayer Sdn. Bhd and carbon black (CB) was obtained from Cabot Cans Sdn. Bhd.

Compounding and Cured Characteristics

A typical formulation used in this work is shown in Table 1. The compounding process was carried out in accordance with ASTM D 3184 using a two-roll mill. The Mooney viscosity of raw NR was determined by using a Monsanto automatic Mooney viscometer (MV 2000) at 100°C. The test procedure was conducted according to the method described in ASTM 1646-00. The cure characteristics were carried out followed by ASTM D 2084, using Monsanto Moving Die Rheometer (MDR 2000) at 160°C for scorch time (t_{s2}), cure time (t_{90}), cure rate index (CRI) and torque difference (MH - ML). The compounds were vulcanized into test sheets using a hot press moulding machine at 160°C with respective cure time t_{90} from the MDR 2000, and pressure of 1000 psi.

Table 1. The Formulation for Rubber Compounds

Material	CV System	EV System
	phr*	phr*
NR	100	100
Carbon black	**	**
Zinc oxide	5.00	5.00
Stearic acid	2.00	2.00
CBS	0.50	5.00
Sulphur	3.50	0.50
Antioxidant	2.00	2.00

* phr – parts per hundred rubber

** 0, 30

Swelling Test

Swelling test (ASTM D471) was performed on 30 mm x 5 mm x 2 mm sample from the compression-molded samples, by immersion in solvent (toluene) at 25 °C for 24 hours. The test sample was taken out and blotted with filter paper. The swelling ratio is defined as (Equation 1):

$$Q\% = \frac{M_t - M_0}{M_0} \times 100 \quad (\text{Equation 1})$$

where M_0 and M_t are the mass of the test piece before swelling and after swelling, respectively. The mass of the sample was measured by electronic digital balance with 0.0001 g accuracy.

Tensile and Tear Tests

Tensile properties of specimens were measured according ASTM D 412, dumbbell shaped samples were cut from the mould sheets. The crosshead rate for tensile test was 500 mm/min which was carried out with a Tensometer Monsanto T10. Tear properties of specimens were determined according ASTM D 624 with trousers test pieces. The crosshead rate for tear test was 100 mm/min.

Hardness

Hardness was measured using an indentation hardness tester according to ASTM D2240. The test method is based on the penetration of a specific type of indenter when forced into the material under specified conditions. The indentation hardness is inversely related to the penetration and dependent on the elastic modulus and visco-elastic behavior of the material.

Resilience

Wallace Dunlop Tripsometer was initially set at an angle of 45° . The sample was placed in the sample holder and the tripsometer was released. The 'indenter' rebounds after impacting the sample and the maximum angle of rebound was noted. Rebound resilience is calculated according to the equation (eq.2):

$$\text{Percentage resilience} = \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \times 100\% \quad (\text{Equation 2})$$

where θ_1 = initial angle = 45° , θ_2 = maximum rebound angle

Results and Discussion

Table 2 shows the Mooney viscosity of SVR 3L and SMR CV60 that relates to the NR average molecular weight [5]. From Table 2, SVR 3L exhibits final Mooney viscosity higher than SMR CV60 which is contributed from the longer polymer chains. The molecular weight of gum natural rubber is very high which leads to strong elastic properties and difficulty in processing. Mastication is one of the basic steps for natural rubber processing which during mastication step, long chains of gum natural rubber are cut into shorter chains to rapidly decrease the viscosity of the rubber [17]. Figure 1 showed that shear force due to mastication process reduced the molecular weight of SMR CV60 faster than SVR 3L. Results indicated that SVR 3L contributes to longer time of processing compared to SMR CV60.

Table 2. Mooney Viscosity for Raw Rubber

Types of NR	Initial Mooney Viscosity [MU]	Final Mooney Viscosity [MU]
SVR 3L	179.80	91.40
SMR CV60	129.00	71.00

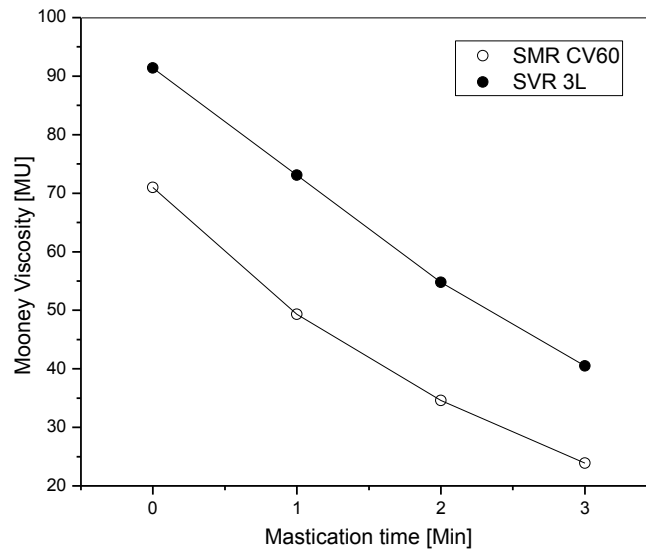


Figure 1. Effect of mastication time on Mooney viscosity

Table 3 shows cure characteristics of different origins of gum NR compounds and NR filled with 30phr CB loading with efficient curing system (EV system) and conventional curing system (CV system). For each curing system, both NR compounds showed almost similar scorch time, t_{s2} , and cured time, t_{90} . However, SVR 3L showed slightly shorter scorch time which may attributed from slightly longer polymer chains and better heat transfer. For cured characteristics of NR compounds with 30phr CB loading, each compound showed faster scorch time and cured time after addition of CB. The addition of CB increased the reinforcing potential of a physically bonded flexible filler network and strong polymer filler couplings [13].

From Table 3, cure rate index (CRI) in SVR 3L gum compound with EV system was higher compare to SMR CV60 gum compound. While the CRI of both NR compounds in CV system showed similar value. The longer polymer chains need higher amount of accelerator which can speed up the vulcanization process. The polymerization reaction took place at the rubber particle surface, and it has been proven that rubber transferees is an integral membrane protein or protein complex [7]. At optimum CB loading, there was an increase in CRI of NR compounds in EV system, where CRI of SVR 3L were higher than SMR CV60. However, CV system showed decreases in CRI for both compounds. This may be the effect of CB content that reduced the speed of CRI. In CV system, CB may act as filler and interrupt dispersion of accelerator [8] which slowed the speed of vulcanization process.

The torque difference (torque maximum – torque minimum) which is correlated to hardness and modulus [14] from both NR compounds showed similar stiffness for each cure system, in which SVR 3L compounds showed slightly higher value while there was significant increase with addition of CB. The origins of NR did not affect the stiffness of compounds while CB improved the mechanical and physical properties due to its high surface activity and specific surface of CB particles [13].

Table 3. Cure Characteristics of NR Compounds

NR	EV System				CV System			
	0 phr		30 phr		0 phr		30 phr	
	SMR CV60	SVR 3L	SMR CV60	SVR 3L	SMR CV60	SVR 3L	SMR CV60	SVR 3L
t _{s2} [mn]	3.20	2.99	1.41	1.49	2.39	2.13	1.47	1.32
t ₉₀ [mn]	6.43	5.75	3.85	3.86	5.85	5.67	5.89	5.96
CRI [%]	30.96	36.23	40.98	42.19	28.90	28.25	22.62	21.55
MH – ML [dNm]	5.53	5.69	9.94	10.31	7.15	7.18	12.28	12.78

Figure 2 showed similar swelling ratio of SMR CV60 and SVR 3L compounds in CV and EV systems. With addition of CB loading, swelling ratio decreased remarkably. It might be attributed to increase in crosslink density, agglomeration, voids of CB and bound rubber [10] which make solvent difficult to diffuse into the compound. Mostafa et al. [9] observed the effect of CB loading on swelling of NBR and SBR in which crosslink density of rubber compounds increased with the increasing of CB loading. The crosslink restricted the expansion of rubber compounds which made it difficult for solvent to diffuse into the gap between molecules hence decreased the swelling ratio. Different origin does not contribute in swelling ratio because both rubbers have a similar rubber molecule which is polyisoprene.

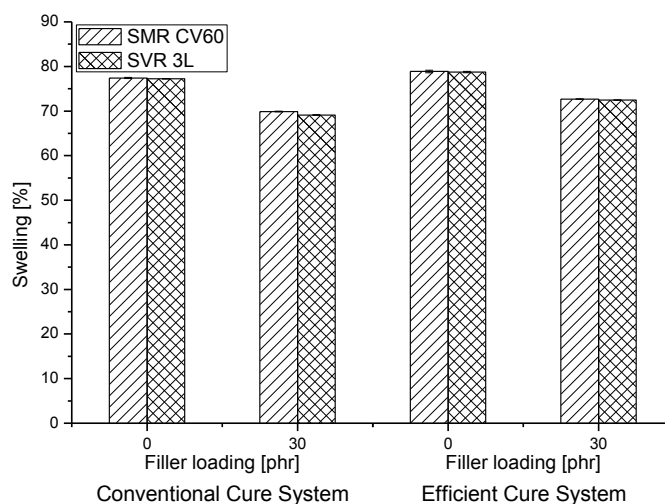
**Figure 2. Swelling ratio of NR compounds without and with 30phr of CB**

Table 4 showed tensile, hardness and tear properties of gum NR and NR with 30 phr of CB loading with CV and EV cure systems. SVR 3L showed slightly better tensile strength compared to SMR CV60 supported by similar swelling ratio in Figure 2. Ngolemasango et al.[10] showed that the tensile strength of CB filled NR compound increased to a certain CB loading and it decreased at higher loading due to CB dispersion effect. It is explained that at higher CB loading, the agglomeration in large cluster due to higher filler-filler interaction than filler-matrix interaction may occur which leads to failure hence reducing the strength. Polymer chains which contain higher functionality (number of bonds a unit can crosslink with other units in a reaction) [4], SVR 3L might have higher filler-matrix interaction and cross-links than SMR CV60.

Considering elongation at break (EB) of both NR compounds, gum compounds of SVR 3L showed higher percentage of EB for both cure systems while at optimum CB loading, the ratio of EB became comparable due to addition of CB in NR compounds which increased the cross-link density, agglomeration and bound rubber, supported by less swelling ratio, which can be accounted by the reduction of EB [10,11]. Tensile modulus M100 and M300 for both compounds for each system showed very similar values. At low elongation, polymers have good ability to significantly alter their size and shapes by adjusting their conformations through backbone bond rotations [15].

The hardness of compounds increased with addition of CB as it increased the surface resistance. The Shore A hardness of SMR CV60 and SVR 3L are similar in Table 4. This is consistent with torque difference in Table 3 which correlated with hardness with different origin of NR not giving significant effect on hardness. Tear strength is the force per unit thickness used to initiate a rupture or tear of the materials. In a tear test the force is not applied evenly but concentrated on a deliberate flaw or sharp discontinuity and the force to continuously produce a new surface is measured [16]. The observation in both cure systems, compounds of SVR 3L showed similar tear strength to SMR CV60 and it increased with addition of CB due to strong filler-rubber interaction [13]. The similar tear strength of both compounds might be attributed to similar conformation of the composites supported by same bond energy of mono- and poly-sulfidic crosslinks in EV and CV systems and fracture mechanics of rubber.

Table 4. Physical Properties of NR Compounds

NR	EV System				CV System			
	0 phr		30 phr		0 phr		30 phr	
	SMR CV60	SVR 3L	SMR CV60	SVR 3L	SMR CV60	SVR 3L	SMR CV60	SVR 3L
M100 [MPa]	0.51 (±0.01)	0.44 (±0.04)	1.42 (±0.03)	1.42 (±0.02)	0.71 (±0.02)	0.70 (±0.02)	2.12 (±0.01)	1.98 (±0.05)
M300 [MPa]	1.43 (±0.01)	1.35 (±0.06)	6.12 (±0.17)	6.34 (±0.11)	2.33 (±0.06)	2.26 (±0.03)	9.17 (±0.14)	9.11 (±0.27)
TS [MPa]	10.11 (±0.09)	11.20 (±0.80)	20.60 (±0.21)	22.55 (±0.27)	11.91 (±0.85)	12.40 (±0.57)	23.18 (±0.25)	23.52 (±0.26)
EB [%]	699.49 (±13.01)	743.33 (±12.58)	636.10 (±12.73)	612.93 (±46.42)	615.40 (±34.21)	638.87 (±14.19)	572.80 (±1.91)	572.80 (±10.18)
Hardness [ShoreA]	39.83 (±0.29)	40.83 (±29)	55.00 (±0.00)	54.50 (±0.50)	45.83 (±0.29)	46.50 (±0.00)	58.00 (±0.00)	58.00 (±0.00)
Tear strength [MPa]	5.60 (±0.50)	5.93 (±0.30)	20.51 (±0.45)	20.68 (±0.90)	4.63 (±0.16)	4.64 (±0.26)	11.14 (±0.40)	11.15 (±0.13)

There was a significant decrease in rebound resilience with 30phr CB loading contributed from reduction of strain energy due to decrease in molecule mobility of NR [12]. In Figure 3, SVR 3L showed higher resilience compared to SMR CV60 which can be associated to better recovery from loading force of SVR 3L. With higher Mooney viscosity, SVR 3L possesses higher molecular weight which allows SVR 3L composites to have faster internal response than SMR CV60 composites [15].

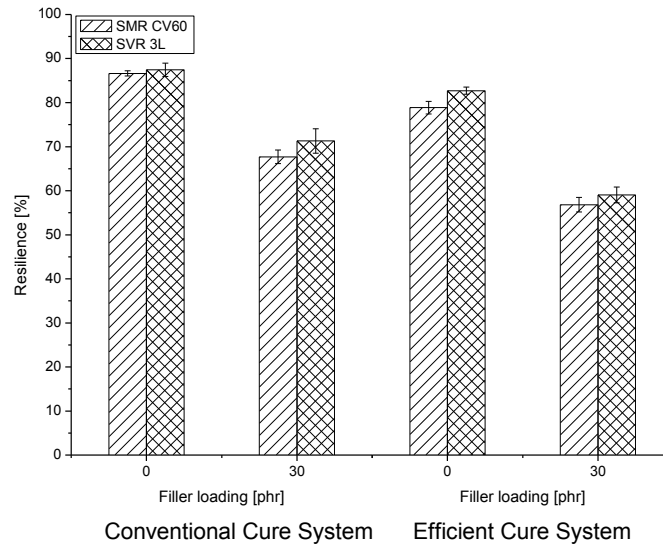


Figure 3. Rebound resilience of NR compounds with 0 and 30phr of CB

Conclusions

Different origin of NR showed difference Mooney viscosity. SVR 3L showed higher Mooney viscosity than SMR CV60 which is related to presence of longer polymer chains. Different origins of NR influenced the cure characteristics with no influence on mechanical and physical properties. With higher Mooney viscosity, SVR 3L exhibits shorter scorch time and cure time while vulcanization speed was faster than SMR CV60. However, mechanical and physical properties depended on addition of CB. SVR 3L composites exhibited better tensile strength and recovery from loading force than SMR CV60 supported by similar swelling ratio and higher molecular weight of SVR 3L. Hardness and tear strength of both compounds were similar which are consistent with torque difference and the conformations of the composites.

Acknowledgements

This work was supported under AUN/SEED-net Research Grant (Grant no – 304 / PBAHAN / 6050218). The authors gratefully acknowledge the support and research facilities provided by Universiti Sains Malaysia.

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