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Influence of filler network on thermo-chemical de-vulcanization efficiency of carbon black filled natural rubber

Anuwat WORLEE[1], Sitisaiyidah SAIWARI[1,*], Wilma DIERKES[2], Siti Salina SARKAWI[3], Charoen NAKASON[4]

[1] Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, 94000, Thailand.
[2] Department of Elastomer Technology and Engineering, University of Twente, 7500AE Enschede, The Netherlands
[3] Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
[4] Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, Surat Thani 84000, Thailand

[*]**Corresponding author e-mail:** sitisaiyidah.s@psu.ac.th

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Abstract

Carbon black is often used as the reinforcing filler in tires since it plays an important role in improvement of tires mechanical properties such as abrasion, stiffness, modulus and fatigue life. In this study, natural rubber (NR) filled with various loadings of carbon black was prepared. Then, the NR vulcanizates were de-vulcanized via thermo-chemical method using diphenyl disulfide as de-vulcanization aid. The de-vulcanization efficiency was analyzed by relationship between sol fraction and crosslink density of the de-vulcanizates. It is found that the de-vulcanization efficiency is influenced by filler loading. This is attributed to the degree of filler network formation in a rubber matrix which is depended on the filler loadings. In the unfilled de-vulcanizates the results showed that almost 100% of sol fraction and the crosslink density reduced to almost zero are observed. Adding carbon black results in a decrease of sol fraction and increase of crosslink densities. This is due to during de-vulcanization some occurred reactive radicals reacted with active site of carbon black surfaces in filler network to form gels of complex compound. Hence, the de-vulcanization efficiency is lower with increasing carbon black loadings.

1. Introduction

Tire rubber is a very durable material and do not decompose easily since it is made up of complex components including several rubbers, fibers, inorganic substances, fillers and other chemicals [1]. Natural Rubber (NR) is one of the most general elastomers used in sidewall and carcass of tire processing, especially in large tires like truck and airplane tires because of its strength, tactility and low heat buildup [2-3]. In Addition, reinforcing filler such as carbon black and silica are added to the tire formulation to strengthen properties like dynamic mechanical, abrasion, stiffness, modulus, fatigue resistance, wear resistance, tear and tensile properties of vulcanized rubbers [4-8].

Recycling of used tires is practically complicated since there are various aspects to be considered. The main factors involve the presence of several types of elastomers in the different tire parts, various types of fillers and, as a consequence, different interactions between elastomers and fillers. Therefore, used tires are still discarded in environment and generate a lot of challenges for tire recycling.

This study aims to transform used tires into a useful rubber material by thermochemical de-vulcanization process using diphenyldisulphide as de-vulcanization aids. As tires usually contain carbon black in the compounding formulations, influence of carbon black contained in tires on de-vulcanization efficiency is of interest issue. However, tires are composed of several parts with using several specific rubbers for each part. Study of de-vulcanization mechanisms of individual rubber is occasioned in order to simplify their phenomena. NR is selected to study as it is one of the most general elastomers used in several tire parts. Therefore, influence of carbon black loading on devulcanization efficiency of NR is focused in this work. The de-vulcanization efficiency was investigated concerning the relationship between soluble fraction and crosslink density of the de-vulcanizates. Moreover, the balance of rubber network breakdown via crosslink versus main-chain scission is also analysed. Finally, the mechanisms of rubber network breakdown in carbon black filled NR and are discussed.

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2. Experimental

2.1 Materials

Natural Rubber (RSS#3) obtained from Yang Thai PakTai Company, Thailand was used as the rubber material. Treated distillate aromatic extract or TDAE oil (Vivatec 500) was supplied by Hansen & Rosenthal KG (Hamburg, Germany). The compounding ingredients for preparing rubber compounds were cure activators (ZnO (Global Chemical, Thailand)), and stearic acid (Imperial Chemical, Thailand)), accelerator (N-tert-butyl-2-benzothiazyl sulfonamide, TBBS (Flexsys, Belgium)), and curing agent (sulfur (Siam Chemical, Thailand)). The carbon black (N550) as filler was supplied by Polychem chemicals, Thailand.

2.2 Preparation of de-vulcanizated NR

Mixing and vulcanization: Filled NR was first compounded using the laboratory Banbury mixer with a mixing chamber volume of 500 cm^3. The compounding formulations are shown in Table 1. The mixer was operated at a rotor speed of 60 rpm; a fill factor of 0.75 and an initial temperature of 50°C. The recipes are simplified from tire part formulations in order to facilitate analysis of the materials. The influence of filler loading on de-vulcanization efficiency was studied. The compound was tested for its cure characteristics using a RPA 2000 dynamic mechanical cure meter from Alpha Technologies at 170°C, 0.833 Hz and 0.279 degree strain, according to ISO 6502. The filler network formation in terms of Payne effect of rubber vulcanizates was measured at 100°C, 1.00 Hz and strain sweep from 0.28% to 100% also using RPA machine. The vulcanized rubber was prepared using a compression molding machine, operated at 170°C and 100 bar, producing 2 mm thick sheets.

Table 1. Formulations of the rubber compounds.

Ingredients	Amount (phr.)
NR	100
Zinc oxide	5
Stearic acid	1
Carbon black N550	Varied: 0, 30, 60 and 90 phr
TDAE oil	Varied*
TBBS	1
Sulfur	2.5

*Varied based on amount of carbon black (14.6% by weight of carbon black).

Grinding: The vulcanized rubber sheets were subsequently ground in a Fritsch Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen at room temperature.

De-vulcanization: Thermo-chemical de-vulcanization was performed batch wise in an internal mixer with a fill factor of 0.7 and a constant rotor speed of 50 rpm. The de-vulcanization of ground rubbers was carried out using the process conditions given in Table 2. Firstly, DPDS (30 mmol/100 g rubber) and 5 phr of TDAE oil were mixed with ground rubber and later heated in an oven at 60 °C for 30 min before adding into the mixer chamber. The de-vulcanization was then carried out at 220°C for 6 min. After de-vulcanization, the material was taken out of the internal mixer and directly quenched in liquid nitrogen, and subsequently stored in a refrigerator to avoid oxidation.

Table 2. De-vulcanization condition.

Factors	Conditions
De-vulcanization aid	DPDS 30 mmol/100 g rubber
De-vulcanization oil	TDAE 5 phr.
De-vulcanization temperature	220°C
De-vulcanization atmosphere	With nitrogen gas purging
Dumping condition	In liquid nitrogen

2.3 Characterization of the de-vulcanization efficiency

The soluble (Sol) and insoluble (Gel) fractions of the vulcanized and de-vulcanized materials were determined by Soxhlet extraction by acetone for 48 hr and THF for 72 hr, respectively. After extraction, the samples were dried in a vacuum oven at 40°C and then the weight loss to constant weight was determined. The extracted rubber samples were allowed to swell in toluene for 72 h at room temperature. The weight of the swollen gel was measured after removal of excess surface liquid with tissue paper. The crosslink density was calculated based on the Flory-Rehner equation [9] using the Kraus-correction [10]. To estimate the de-vulcanization efficiency of de-vulcanized rubber using the method developed by Horikx and Verbruggen [11-12]: the correlation between the soluble phase generated after rupture of polymer chains and the relative decrease in crosslink density in the remaining gel, as a result of either main chain rupture or crosslink scission. The method is applicable in the context of rubber reclamation, in which the main chains as well as the sulfur bonds will break. When main chain scission takes place, the relative decrease in crosslink density is given by:

$$1-\frac{v_f}{v_i}=1-\left[\frac{\left(1-S_f^{1/2}\right)^2}{\left(1-S_i^{1/2}\right)^2}\right] \qquad (1)$$

Here the parameter S$_i$ is the soluble phase of the polymer network before de-vulcanization or degradation, S$_f$ is the soluble phase of the rubber after degradation, v_i is the crosslink density of the network before treatment and v_f is the crosslink density of the rubber after degradation. When only crosslink scission takes place, the sol fraction is related to the relative decrease in crosslink density by:

$$1-\frac{v_f}{v_i}=1-\left[\frac{\gamma_f\left(1-S_f^{1/2}\right)^2}{\gamma_f\left(1-S_i^{1/2}\right)^2}\right] \tag{2}$$

Here γ_i and γ_f are the average numbers of crosslinks per chain in the insoluble network before and after degradation, respectively. The γ_i and γ_f are calculated as described by Verbuggen [12].

3. Results and discussion

3.1 Influence of carbon black loading on Payne effect

Filler network is usually determined by the so-called Payne effect: the drop in storage modulus ($\Delta G'$) in a dynamic mechanical test when the strain is increased from low (0.28%) to a high value (100%) at constant frequency and temperature. The influence of the carbon black loading on the storage modulus (G') of the NR vulcanizates is shown in Figure 1. The G' of unfilled NR vulcanizates are not considerably changed with increasing strains. However, after adding carbon black, the storage modulus drastically decreased with increase of strain, as can be seen in Figure 1(a). This is due to the breakage of filler aggregates or agglomerates. Moreover, it is noticed that the change of the Payne effect has a tendency to increase as a function of carbon black loading as can be seen in Figure 1 (b). This indicates an increase of the filler network formation in rubber matrix with increasing carbon black loading. This is due to a decrease of inter-aggregate distance with an increase of carbon black loading [13].

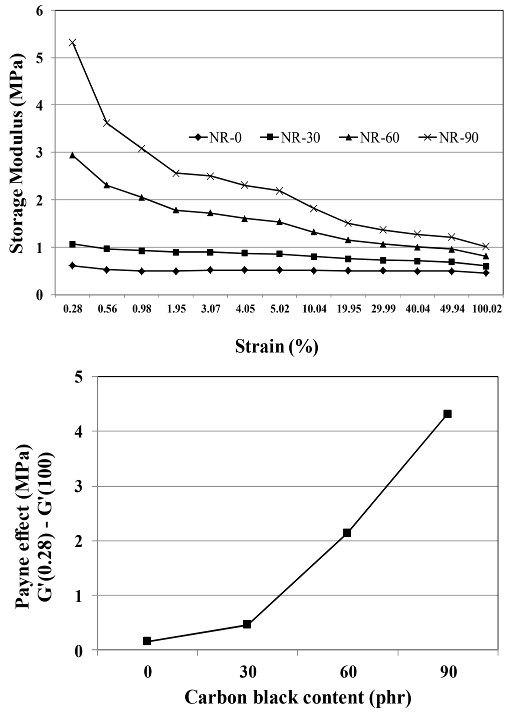

Figure 1. Payne effect of carbon black filled NR at various carbon black loadings.

3.2 Influence of amount of carbon black on de-vulcanization efficiency

Sol fraction and crosslink density*:* Basically, the rubber sol fraction after de-vulcanization indicates the destruction of the rubber network either by crosslink scission, polymer breakdown or both of them. Figure 2 showed the sol fraction and crosslink density of remaining gels of filled natural rubber de-vulcanizates as a function of carbon black loading. The results showed that almost 100% of sol fraction is observed in unfilled de-vulcanized NR. It is found that increases of carbon black loading tend to a decrease of the sol fraction. Moreover, the crosslink densities of the de-vulcanizates are corresponds well with the sol fraction. That is the crosslink density of NR de-vulcanizates is marginal increased with increasing carbon black loading.

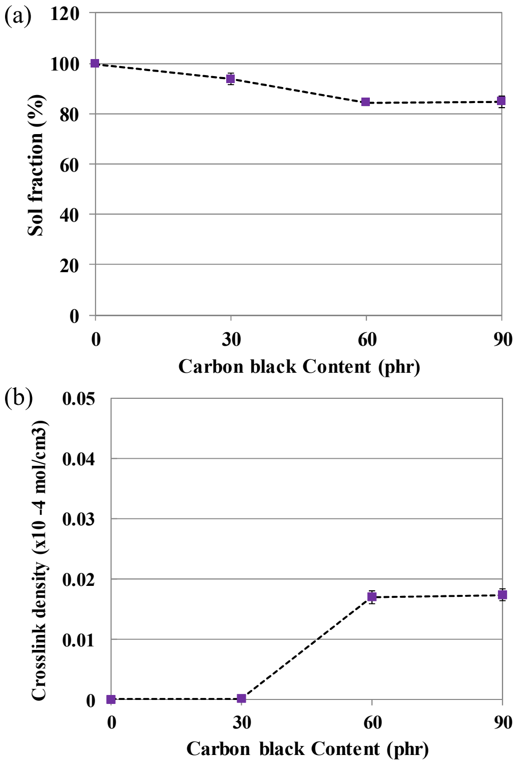

Figure 2. Influence of carbon black loadings on the sol fraction (a) and crosslink density (b) of carbon black filled NR de-vulcanizates.

The decrease of sol fraction and increase of crosslink density with increasing carbon black content can be attributed to a generated complex compound as the proposed reaction scheme in Figure 3. In addition, it is well known that the addition of reinforcing filler such as carbon black in rubber will cause the forming of the existence of tightly bound rubber. Therefore, decreasing the sol fraction and increasing the crosslink density de-vulcanized rubber may be due to the arising of bound rubber. In Figure 3, the opening of crosslinks or the rubber main chains scission by heat and shearing forces occurred as seen in sub-reaction A [14]. Further, reaction B can be followed as many active free radicals are formed and consequently further react with oxygen to form hydro-peroxide during de-vulcanization [15-16]. A variety of hydro-peroxides are formed from oxidized sulfur vulcanized network of the various mono-, di-, polysulfide groups with oxygen. The hydroxyl group of sulfenic acids (RSOH) and thiosulfoxylic acids (RSSOH) would be expected to react with active functional groups of filler-network such as carboxyl group (-COOH) which original located on carbon black surfaces via esterification reaction mechanism to form gels of complex ester compounds in reaction C. These compounds are regularly insoluble in solvent resulting in a decrease of sol fraction and an increase of crosslink density of the de-vulcanizates.These functional groups in the DR could react via hydrogen bonding or by other means with the COPE molecules during and after the dynamic vulcanization. It is clear that

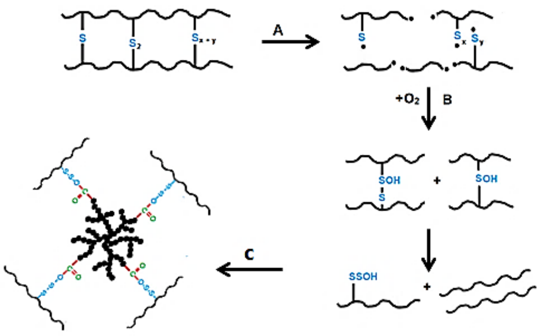

Figure 3. Simplified reaction scheme proposed for reaction of carbon black surface with hydro-peroxide groups which formed from oxidized sulfur vulcanized networks with oxygen and generated during de-vulcanization.

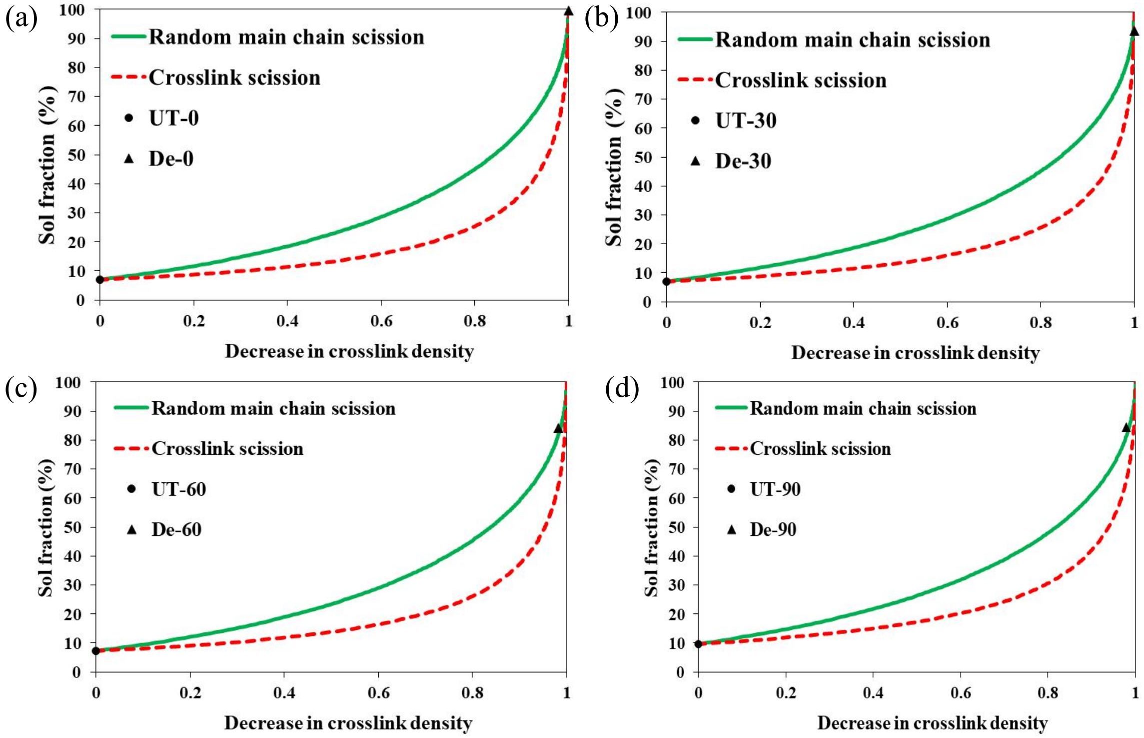

Figure 4. Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of (a) unfilled NR de-vulcanizates, and carbon black filled NR de-vulcanizates with 30 phr of carbon black (b), 60 phr of carbon black (c) and 90 phr of carbon black (d): UT = Untreated rubber and De = De-vulcanized rubber.

Consideration of de-vulcanization efficiency: The de-vulcanization efficiency of de-vulcanized NR is estimated using the method developed by Horikx and Verbruggen [11-12]: the sol fraction of de-vulcanizates and the decrease in crosslink density of remaining gels after swollen in toluene are correlated. The rubber sol fractions of NR de-vulcanizates at various amounts of carbon black as a function of the relative decrease in crosslink densities are shown in Figure 4. Figure 4(a), 4(b), 4(c) and 4(d) show the sol fraction as a function of the relative decrease in crosslink density of unfilled de-vulcanizate and the devulcanizates filled with carbon black at 30, 60 and 90 phr, respectively. It is known that the molecular chains of NR have low thermal resistance and are destroyed easily at high temperature (220°C). Therefore, an almost 100% sol fraction and the crosslink densities reduced to almost zero are observed in unfilled NR de-vulcanizates as can see in Figure 4(a). This indicates that the NR networks are completely broken down during de-vulcanization. The addition of 30 phr of carbon black resulted in decrease in sol fraction as the data point shift to the position that below of the unfilled data as shown in Figure 4(b). Moreover, at higher carbon black loading such as 60 phr (Figure 4(c)) and 90 phr (Figure 4(d)), the data point are even more shifted to below and the left hand side of graph. These lower sol fraction and higher crosslink density of carbon black filled NR compared to unfilled NR indicate the decrease of de-vulcanization efficiency.

4. Conclusions

As NR has low thermal resistance, high temperature is able to damage the NR molecules easily. In unfilled NR de-vulcanization, almost 100% of sol fraction and the crosslink density reduced to almost zero are observed. The addition of carbon black into NR caused the formation of filler network. Additionally, the functional groups on carbon black surfaces can react with a variety of hydro-peroxides which occurred during de-vulcanization to form gels of complex compounds. These compounds are regularly insoluble in a good solvent like toluene resulting in a decrease of sol fraction and an increase of crosslink density of the carbon black filled NR de-vulcanizates. Considering the de-vulcanization efficiency of both unfilled and carbon black filled NR, it is observed that the de-vulcanization efficiency is lower with increasing carbon black loadings.

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