

## A comparative study of ground tire rubber devulcanization using twin screw extruder and internal mixer

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**Abstract.** Devulcanization of ground tire rubber (GTR) was done using twin screw extruder (TSE) and internal mixer (IM). Processing parameters were varied to analyze its effect on gel content. Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed as qualitative technique to confirm structural change. The devulcanized rubbers with the least gel content percentage produced in both TSE and IM were then used as filler in natural rubber (NR)/coconut coir (CC) composite preparation. Effects of gel content percentage on NR/CC composite tensile strength and elongation at break were analyzed. The results show that the gel content decreased by 41% for sample processed in TSE and 50% in IM compared to control sample. Overall, the devulcanization is influenced by high energy generated by thermal or thermo-mechanical process. FTIR spectra show chemically structural changes of GTR as C=C, CH<sub>2</sub>, CH<sub>3</sub> with higher intensity for IM sample than its counterpart indicated devulcanization. The replacement of GTR to DGTR on NR/CC/GTR composites provided less network structures and resulted better tensile strength and elongation at break.

### 1. Introduction

Waste tire disposal has been quite a crucial issue worldwide. It was proven that approximately 17 million of waste tire generated each year [1]. Waste tires could be considered as a wealthy material, due to its contain such as natural rubber, and synthetic rubber (generally SBR and BR) [2-4]. Recovery of waste tire can be classified in two ways : material recovery [1, 5] and energy recovery [1] used as source of energy in cement kilns and paper mills. Energy recovery is easier and cheaper than its companion, but it poses dangerous threat to environment and human health for gases produced throughout the process. Hence, material recovery is an alternative to reduce waste tire.

Material recovery could be done with various methods including shredding, grinding that leading to transformation of tire into a powder form [2,6,7], devulcanizing [8-11,4,12] and blending with another polymer [11,4,2]. The key parameter of material recovery was the breakage of three-dimensional cross-linked structure leading to compatibilities improvement with other polymer or filler.

Various methods have been proposed for reclaiming or devulcanizing waste tire, including thermomechanical using twin , and other methods using microwave [15-18], and supercritical CO<sub>2</sub>[10, 11,19]. From the available techniques, twin screw extruder is more attractive due to its ease and



continuity. However, the effect of processing time in extruder cannot be analyzed due to its dependency on screw rotation. On the other hand, the processing time is an independent factor in an internal mixer, so effect of time and the interaction to another variable can be explored.

In order to measure degree of devulcanization, techniques as gel/sol content [2,20-23] and crosslink density [20, 22] were applied. However, gel content is simpler and good measurement and calculation to indicate devulcanization efficiency [21]. Meanwhile, the structural change may be analyzed using FTIR [22], DSC and TGA [21].

In this research, comparative study on the effect of twin screw extruder and internal mixer for ground tire rubber devulcanization was done. Effects of processing temperature on gel content were explored. The structural analysis was observed using FTIR for samples with the lowest gel content. The use of devulcanized rubber as filler on NR composites was compared and analyzed from tensile properties data to that of GTR.

## 2. Experimental

### 2.1. Materials

GTR was donated by PT. Sinar Jaya Rubber (Bandung, Indonesia). It is ground rubber from vehicle car tires. The maximum particle size of GTR was 30 meshes and processed as received. No other chemical or additives were added as promotor agents during devulcanization.

Natural rubber (NR), *Standard Indonesian Rubber (SIR) 20* purchased from Aneka Bumi Pratama Company (Palembang, Indonesia) was used as composite matrix. Coconut coir from Indonesian local producer was used as reinforcement. Maleated Natural Rubber (MNR) produced in our laboratory, used as compatibilizer. The additives used for composite preparation were Butylatedhydroxy toluene (BHT) as antioxidant, zinc oxide (ZnO) as activator, N-cyclohexyl-2-benzothiazole sulphenamide (CBS) as accelerator, and sulphur (S) as vulcanization agent.

### 2.2. Devulcanization of GTR

Devulcanization was carried out using two equipment, intermeshing co-rotating Collins twin-screw extruder ZK 25E x 36D (TSE) and Haake (IM) with Banbury rotors. In IM 80% filling capacity was applied to produce optimum shear. Process parameters were varied according to two-level Full Factorial Design with additional mid-point using Minitab 16, summarized in Table 1. Parameters in TSE and IM have a different variable since time could not be controlled in TSE, and limitation on IM maximum rotor rotation.

**Table 1.** Parameter applied in TSE and IM

Run	TSE		IM		
	T (°C)	SS (rpm)	T(°C)	SS (rpm)	t (min)
1	100	100	100	100	10
2	100	400	100	100	30
3	300	100	100	200	10
4	300	400	100	200	30
5	200	250	300	100	10
6	200	250	300	100	30
7	-	-	300	200	10
8	-	-	300	200	30
9	-	-	200	150	20
10	-	-	200	150	20

### 2.3. Quantitative and Qualitative Analysis of Devulcanized GTR (DGTR)

Devulcanization performance was analyzed quantitatively from crosslink degree by Gel Content determination (GC). It was chosen as a good indicator of devulcanization efficiency [21]. It was performed by soxhlet extraction with toluene as solvent.  $0.050 \pm 0.005$  gr of samples were extracted in 100 mL of toluene at 110 °C for 24 h. The extracted samples were dried in oven at 80 °C for 5 h. Percentage of gel content was calculated as follows:

$$\% \text{ Gel Content} = 100\% - \% \text{ Extracted} \quad (1)$$

$$\% \text{ Extract} = \frac{w_2 - w_3}{w_2 - w_1} \times 100\% \quad (2)$$

Where  $w_1$  is weight of wire net,  $w_2$  is weight of sample in wire net before extraction,  $w_3$  is weight of sample in wire net after extraction.

Qualitative analysis on structural changes of DGTR was analyzed using Bruker Tensor FTIR. Approximately 2 g of samples were individually put in tubes to undergo pyrolysis method. Each prepared tubes were filled with nitrogen gas ( $N_2$ ) and placed above the burner until it reaches pyrolysis term and get the oily polymer of samples. The oil produced were places in natrium chloride glass to analyze the chemical structure in samples.

### 2.4. Composite Preparations

The coconut coir (CC) was soaked in NaOH solution at 5% concentration for 1 h. It was then washed by distilled water and dried at 100 °C for 1 h. The treated coconut coir was then cut and sieved maximum 1 cm long. The composite formulations are summarized in Table 2. The processes were divided into two steps. All formulations in step 1 were done in TSE at screw speed 40 rpm, and temperature 40 °C for zone 1, and 160 – 190 °C for zone 2 – 8. The extruded samples were continued

to step 2 process using Huicai roll mill at 40 °C and 60 rpm for the first 10 min. It was then followed by the addition of ZnO for 10 min and CBS for the next 10 min. Vulcanization of the blend was ended up by mixing the blends and S for 30 min.

**Table 2.** Parameter applied in TSE and IM

Sample	Formulation (phr)							
	Step 1 (TSE)					Step 2 (Roll Mill)		
	GTR	DGTR	CC	MNR	BHT	ZnO	CBS	S
NR Control	0	0	0	0	2	5	2	5
NR/CC composites	0	0	30	6.5	2	5	2	5
NR/CC/GTR composites	10	0	30	6.5	2	5	2	5
NR/CC/DGTR-TSE composites	0	10	30	6.5	2	5	2	5
NR/CC/DGTR-IM composites	0	10	30	6.5	2	5	2	5

Vulcanized compounds were processed in Collins Hot Press P300 P. It was preheated at 150 °C with no pressure for 5 min and pressed at the same temperature, 15 bar for 10 min. The pressed compounds were cooled at 25 °C for 25 min and conditioned for 24 h.

### 2.5. Composite Characterization

Tensile test were carried out according to ASTM 412 type C using universal testing machine Shimadzu AGS10 kNG at 500 mm/min of crosshead rate. Tensile strength and elongation at break of NR, NR/CC composite without GTR, NR/coconut coir composite with GTR as well as DGTR were compared and analyzed. The DGTR added in composites were those produced in TSE or IM with the lowest gel content.

## 3. Results and Discussions

### 3.1. Effect Process on Gel Content Reduction

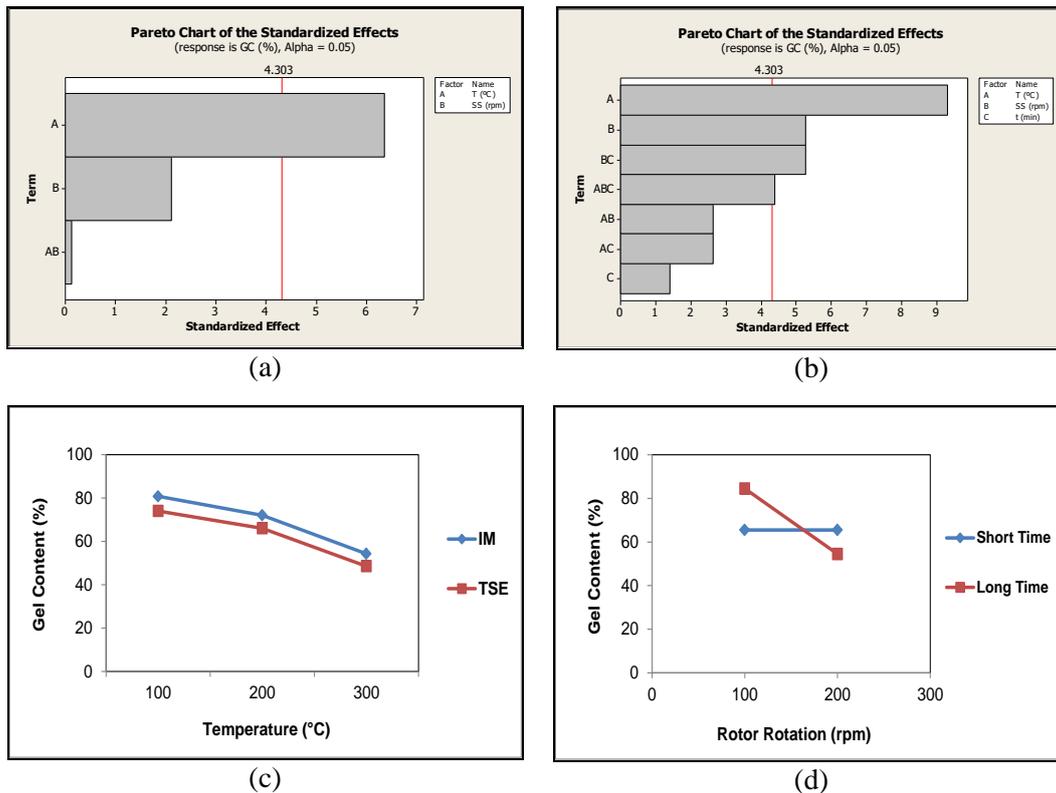
The effect of process conditions on gel content was analyzed because it is potentially break the three dimensional network structures. The lower gel content, the less percentage of crosslink in the rubber compound, the more effective devulcanization process. It may be influenced by thermal, shear or combination between these two mechanisms. Therefore, the analysis on the effect of process conditions on gel content is crucial.

Table 3 shows gel content percentage of samples processed either in TSE or IM. In general, gel content percentages decreased by 41% (from 85% to 44%) for TSE, and 50% (from 85% to 35%) for IM. The decrease on gel content percentage in this research was higher than reported results using two roll mill with additional reclaiming agent [24] and microwave techniques [16, 21]. The better results achieved in this research might be due to generated shear from screw in TSE or rotor in IM. This shear

would function as three dimensional scissors which break crosslink structure in normal, radial and tangential direction [25, 26].

**Table 3.** Gel Content Percentage Samples Processed in TSE or IM

Runs	TSE			IM			
	T (°C)	SS (rpm)	GC (%)	T (°C)	SS (rpm)	t (min)	GC (%)
Untreated	-	-	85	-	-	-	85
1	100	100	78	100	100	10	85
2	100	400	70	100	100	30	84
3	300	100	53	100	200	10	80
4	300	400	44	100	200	30	74
5	200	250	65	300	100	10	46
6	200	250	67	300	100	30	85
7	-	-	-	300	200	10	51
8	-	-	-	300	200	30	35
9	-	-	-	200	150	20	72
10	-	-	-	200	150	20	72



**Figure 1.** Effect Parameters on Gel Content: (a) Pareto Charts of TSE, (b) Pareto Chart of IM, (c) Effect Temperatures in TSE and IM, (d) Effect Factor Interactions in IM

The least gel content was produced at high settings for either in TSE (high temperature, high screw rotation) or IM (high temperature, high rotor rotation, and long processing time) attributed to high energy needed for devulcanization.

Effects of processing parameters were analyzed from Pareto Chart (Figure 1). The charts were generated using Minitab software from collected data. The Pareto charts (Figure 1 (a) and (b)) are useful to analyze the significant parameters applied in process equipment. The significant factors are limited by a vertical red line. All factors on the right side of this line have significant effect on the reduction of gel content percentage. In contrast, variables on the left side may not significantly influence the gel content. Figures 1 (a) and (b) show that temperature is the most significant parameter in either TSE or IM to reduce gel content. The effect on gel content is negative (reducing gel content) (Figure 1 (c)). This finding aligned to previous research using another technique as microwave reported the reduction of gel content due to higher temperature [21]. This also suggests that temperature is the main factor to reduce gel content in devulcanization process.

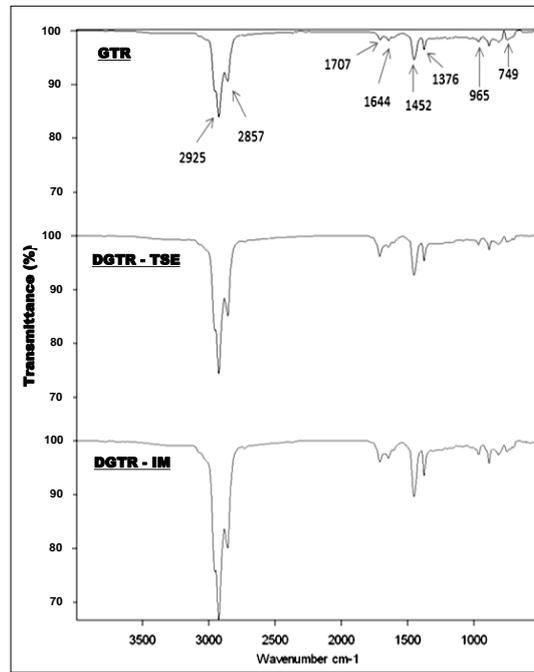
In contrast, Figure 1 (a) and (b) shows different effect of screw rotation in TSE and in IM. The effect was not significant in TSE, but significant in IM. Insignificant effect of screw rotation in TSE may be due to uncontrollable processing time. High screw rotation may cut cross-linked chain [27], however it is also generate short processing time. These would not provide optimum conditions for temperature, as combination with generated shear, to break the network structures maximally. On the other hand, low screw rotation is able to provide longer processing time and facilitate thermal chain scissoring. As a result, the difference effect of screw rotation in TSE was not significant. In contrast, in IM, the variation on rotor rotation shows significant effect on gel content due to interaction to controllable processing time.

The effect of factor interactions on gel content are shown in Figure 1 (d). It is shown that effect rotor rotation is not significant at short processing time. The difference is clearly shown at longer processing time. At this condition, higher gel content on lower rotor rotation suggests that shear generated during process may not enough to perfectly break –S– bond, and produce secondary crosslinking. However, higher rotor rotation produced less gel content, suggested the effect of shear in devulcanization process.

### 3.2. FTIR Analysis

FTIR spectra for untreated GTR as well as the lowest gel content processed in TSE (44%) and IM (35%) are shown in Figure 2. In general, there is no peak difference on FTIR spectra for all samples. However, % transmittances (2925, 2857, 1644, 1452 and 1376  $\text{cm}^{-1}$ ) increased as lower gel content, indicates additional functional group at those peaks. More functional group of C=C (1644  $\text{cm}^{-1}$ ), CH<sub>2</sub>

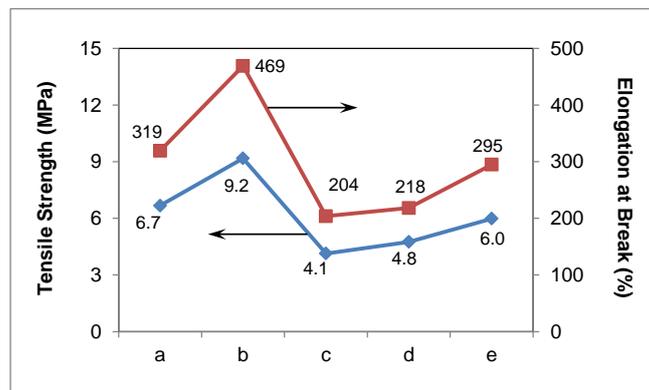
(2857 and 1452  $\text{cm}^{-1}$ ) and  $\text{CH}_3$ (2925 and 1376  $\text{cm}^{-1}$ ) indicated that the devulcanization occurred, while addition  $\text{C}=\text{O}$  (1707  $\text{cm}^{-1}$ ) structure suggested that there was some degradation during process.



**Figure 2.** FTIR Spectra of GTR Processed on TSE and IM

The change on % transmittance may be a good indication of devulcanization, however, there is difficulty to determine the actual structures. So, another technique as Nuclear Magnetic Resonance (NMR) may be needed to be done in future research.

### 3.3. Analysis on Tensile Properties of NR/CC Composites



**Figure 3.** Effect of DGTR on Tensile Properties of NR/CC Composites: (a) NR Control, (b) NR/CC Composites, (c) NR/CC/GTR Composites, (d) NR/CC/GTR-TSE Composites, (e) NR/CC/GTR-IM Composites

Figure 3 shows effect of DGTR on tensile strength and elongation at break of NR/CC composites. DGTR added in composites were those with the least gel content processed in TSE (44%) or IM

(35%). These percentages were chosen to give maximum magnitude of effect DGTR on the NR property recovery. The tensile strength of control NR is 6.7 MPa which is close to previous report using SIR 20 as binder [28]. The strength is also close to another study using different NR [29], but lower than others [30, 31] that may be due to differences on NR type and formulations.

In general, tensile strength and elongation at break of composites with GTR (85% gel content) or DGTR are lower than that of without DGTR attributed to availability of cross-linked structures in GTR or DGTR, indicated by gel content. The higher gel content may produce less interaction between GTR/DGTR and NR chain. This is confirmed by higher mechanical properties of IM sample than TSE's and GTR's

#### 4. Conclusions

A comparative study on the effect of processing equipment on GTR devulcanization using TSE and IM was done. Overall, gel content decreased after processed in TSE or IM. In TSE, devulcanization is only significantly influenced by temperature. In contrast, in IM, temperature, rotor rotation, and rotor rotation-processing time interaction, as well as temperature-rotor rotation-processing time interaction significantly reduce gel content. The least gel content was produced at high settings for either in TSE (high temperature, high screw rotation) or IM (high temperature, high rotor rotation, and long processing time) attributed to high energy needed for devulcanization. Structural changes on DGTR processed in TSE or IM suggested the effect of devulcanization. The use of DGTR providing less crosslink network and improve the mechanical properties of NR/CC/GTR.

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