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The curing characteristics and tear properties of phenolic resin on chloroprene rubber vulcanizate

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Abstract. Chloroprene rubber (CR) is synthetic rubber widely used for seal, joint, and also adhesive. For making rubber product, additives are needed and it can influence the properties of vulcanizates. This study aims to determine the curing characteristics and mechanical properties of chloroprene vulcanizate. The chloroprene vulcanizates were prepared by compounding with the two-roll mill and vulcanizing with the hydraulic press. Phenolic resin used as additives were varies i.e: 0, 10, 20, and 30 phr. The curing characteristics of the CR vulcanizates were studied by rheometer at 140 ºC, 150 ºC, and 160 ºC. The tear properties of the CR vulcanizates were studied by tensile strength tester. The phenolic resin improves the mooney viscosity, scorch time and optimum curing time. The compound without phenolic resin gives the highest mooney viscosity and optimum curing time. The 10 phr phenolic resin give the best mooney viscosity, optimum curing time, constant rate, activation energy and also tear strength. The suitable curing temperature for CR compound is at 150 ºC and the proper additive for CR vulcanizate is 10 phr phenolic resin.

1. Introduction

Rubber is widely used in industry because of its excellent properties. Chloroprene rubber (CR) is a synthetic rubber that has excellent oil and ozone resistance [1]. CR is polar and has good resistance to alcohols, hydraulic fluids, gasoline, organic acids, alkalis, oils and fats [2-4]. Chloroprene is widely used to make seal, joint, and also as an adhesive.

Before used as rubber product, the CR must be added with several additives. One of the additives is the phenolic resin. Phenolic resin is one of the resin-based additives. There are some types of resins based on its structure, phenolic resin, hydrocarbon (petroleum) resin, terpene resin, and rosin resin [5,6]. Phenolic resin is one of the most common types of resin materials that has a low price and good resistance to temperature [7]. Resin has some function in making rubber product such as processing aids, tackifier, reinforcing agent, and bonding agent. Resin also commonly used as adhesive that needs the tackifier agent.

There is some previous study about phenolic resin that had been done by the previous researcher. Ming *et al.* found that phenolic resin give the best improvement on the physical properties of the styrene-butadiene rubber modified asphalt [7]. Wang *et al.* found that phenolic resin with chlorinated butyl rubber could be potential damping materials [8]. Masa *et al.* proved that phenolic resin could improve the strain-induced crystallization of NR vulcanizate [9]. Mirabedini *et al.* found that phenolic resin can increase the crosslink density and swelling resistance of NBR [10]. Jose *et al.* investigated that phenolic

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resin improves the mechanical and thermal properties of EPDM/CIIR [11]. However, the compound characteristics of CR with phenolic resin have not been well studied. This study aimed to determine the curing characteristics and tear properties of CR vulcanizates using phenolic resin as additive. The information of this research can be used to find out the best formulation and processing for chloroprene vulcanizates.

2. Experimental method

2.1. Materials

Chloroprene (CR) Baypren 220 was used in this study. Paraffin wax (Antilux 654 A) and 6PPD as antioxidants, paraffinic oil (Indrasari, Semarang) as softener, Zinc Oxide (ZnO, Indoxide) and Magnesium oxide (MgO, Multi Citra), and stearic acid (Aflux 42M) as activators, sulfur (Miwon) as a vulcanizing agent, phenolic resin as tackifier, MBTS (Shandong Sianxian) and TMTD (Starchem) as accelerators.

2.2. Methods

CR and additives in Table 1 were weighed and were mixed using a two-roll mill. The CR compounds were conditioned for 24 hours at room temperature. Then, the compounds were tested with a rheometer MDR Gotech 3000 A to determine the curing time of the compound and it was vulcanized by hydraulic press according to the time of the test results from the rheometer. The phenolic resin was varied by 0, 10, 20, and 30 phr. The compounds then were pressed by the hydraulic press (Toyoseiki A-652 200 500) at a certain temperature and a certain time based on rheometer result.

Table 1. Formulation of CR compound.

Materials	phr			
	CP0	CP10	CP20	CP30
CR	100	100	100	100
6PPD	4	4	4	4
Paraffin wax	2	2	2	2
ZnO	5	5	5	5
MgO	3	3	3	3
Phenolic resin	0	10	20	30
Sulfur	2	2	2	2
MBTS	1	1	1	1
TMTD	1	1	1	1
Stearic acid	2	2	2	2
Paraffinic oil	10	10	10	10

*phr: part per hundred resin

2.3. Mooney viscosity

Mooney viscosity ML (1+4) was measured by MonTech Mooney Viscometer MV3000 at 100 ºC with velocity 2 rpm (0.21 rad/second). ML (1+4) means 1 second is preheating time and 4 minutes for testing.

2.4. Curing characteristics

The curing characteristics of the compounds were calculated from the data taken from the rheometer performed at 140 °C, 150 °C, and 160 °C. Cure rate index (CRI) can be calculated from the test results from the rheometer with the following equation (1):

$$CRI = \frac{1}{(tc_{90} - ts_2)} \tag{1}$$

The curing kinetics can be calculated by equation (2) as previous study [12].

$$ln\frac{(M_H-M_{L)}}{(M_H-M_t)} = kt \quad (2)$$

Rearrangement equation

$$ln(M_H - M_t) = \ln(M_H - M_{L)} - kt \quad (3)$$

The constant rate, k, is obtained from the plot $\ln(M_H - M_t)$ versus *t.* Where M_H is the maximum torque and M_L is the minimum torque and M_t is the torque at certain time, t. The M value is the 25% until 45% torque change [13]. From the rate constant, we can determine the activation energy with the equation (4).

$$k = A\ x\ exp\ (-\frac{Ea}{RT}) \quad (4)$$

Or

$$ln\ k = ln\ A - \frac{Ea}{R}\ x\frac{1}{T} \quad (5)$$

The activation energy was calculated from the slope of plotting the constant rate versus $\frac{1}{T}$. A is the pre-exponential factor, R is the gas constant, T is the vulcanization temperature and Ea is the activation energy for the curing process.

2.5. Tear properties

The tear strength of the CR vulcanizates was studied using the tensile strength tester Kao Tieh according to ISO 34.

3. Result and discussion

3.1. Mooney viscosity

The mooney viscosity shows the processability of the compound and also related to the compound flow. The higher mooney viscosity shows that the flowability is not good so that it is more difficult for a compound to be processed. However, the compound with high mooney viscosity has better mechanical properties than compounds with low mooney viscosity.

Figure 1 shows that CR vulcanizate without phenolic resin results in the highest mooney viscosity. Vulcanizates with phenolic resin produce lower mooney viscosity. It means that phenolic resin is a good additive for CR because it can improve the flowability of the compound. The low viscosity shows that the compound is easy to process and doesn't need high energy in the vulcanizing process. So that the electricity is lower and this is preferable in the production process. 10 phr phenolic resin give the best mooney viscosity, but not significantly different with 20 phr phenolic resin.

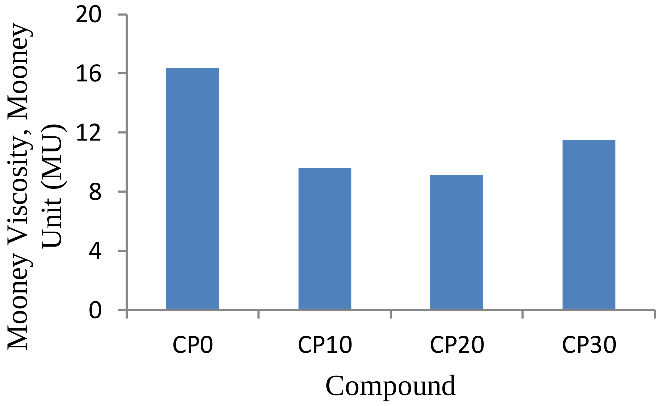

Figure 1. Mooney viscosity of CR compound.

3.2. Curing characteristics

The curing process was studied by rheometer. It is an important stage in making rubber product. The heat is transferred to the rubber from its surface at a certain time according to the rheometer result [14]. Rheometer provides the data of curing characteristics. The scorch time (ts_2) and the optimum time (t_{90}) of curing compound shows in figure 2. The CR compound without phenolic resin gives the highest scorch time. Scorch time is a safe time when the rubber still can be processed. The highest scorch time is preferable because the safe time is longer. Phenolic resin gives the shorter scorch time, and also the lower optimum time. The 10 phr phenolic resin give the fastest optimum time. The optimum curing time is the time needed to cure the compound. Faster optimum time means lower energy so that the production process is more efficient. The higher curing temperature provides the higher the scorch time and optimum time. The suitable curing temperature for the CR compound is 150 ºC.

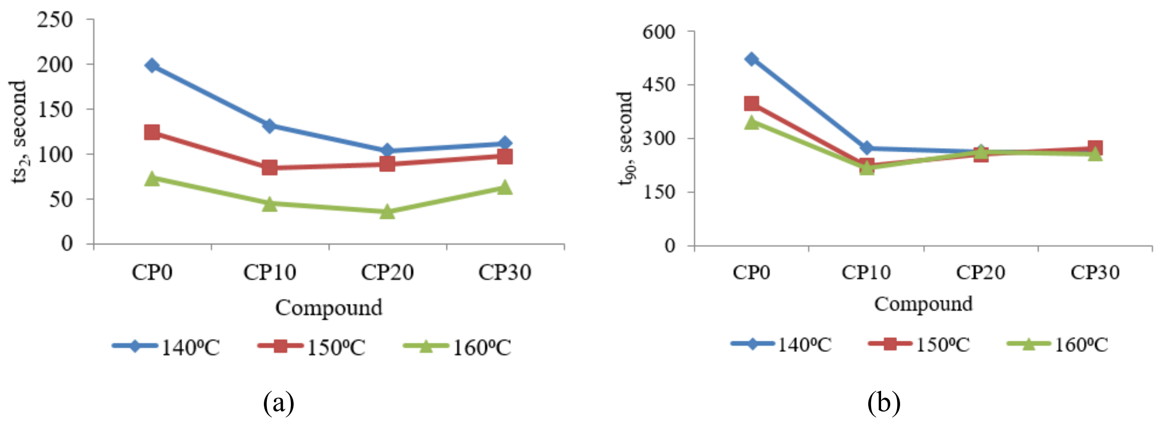

Figure 2. Scorch time (a) and optimum curing time (b) of CR compound.

The curing kinetics of CR compound can be known from the torque-time data from rheometer. The constant rate (k) shows the speed of reaction on rubber curing. The result from plotting equation (2) shows in Table 2. The constant rate can be calculated from the slope. The constant rate (k) is shown in Table 3.

Table 2. The plotting results from equation (2).

Temperature	Compound	y=mx+c	slope	R^2
140°C	CP0	y= -0.0042x+3.0903	-0.0042	0.9924
	CP10	y= -0.0044x+2.3772	-0.0044	0.9960
	CP20	y=-0.0041x+2.2973	-0.0041	0.9927
	CP30	y=-0.0030x+2.6729	-0.0030	0.9881
150°C	CP0	y=-0.0064x+3.3035	-0.0064	0.9997
	CP10	y=-0.0076x+2.5843	-0.0076	0.9892
	CP20	y=-0.0077x+2.4316	-0.9943	0.9943
	CP30	y=-0.0056x+3.2226	-0.0056	0.9964
160°C	CP0	y=-0.0113x+3.3713	-0.0113	0.9990
	CP10	y=-0.0196x+3.1515	-0.0196	0.9900
	CP20	y=-0.0117x+2.1954	-0.0117	0.9857
	CP30	y=-0.0078x+3.4322	-0.0078	0.9995

Table 3. The constant rate (k) and activation energy of CR compound.

Vulcanizate	Constant rate, k (sec^{-1})			Ea (kJ/mol)
	140 °C	150 °C	160 °C	
CP0	0.0042	0.0064	0.0113	9172.00
CP10	0.0044	0.0076	0.0196	13807.89
CP20	0.0041	0.0077	0.0117	9793.89
CP30	0.0030	0.0056	0.0078	8945.03

After plotting the equation (2), the activation energy can be calculated by plotting the k versus $\frac{1}{T}$ as shown in Figure 3. Activation energy presents the energy needed for curing process.

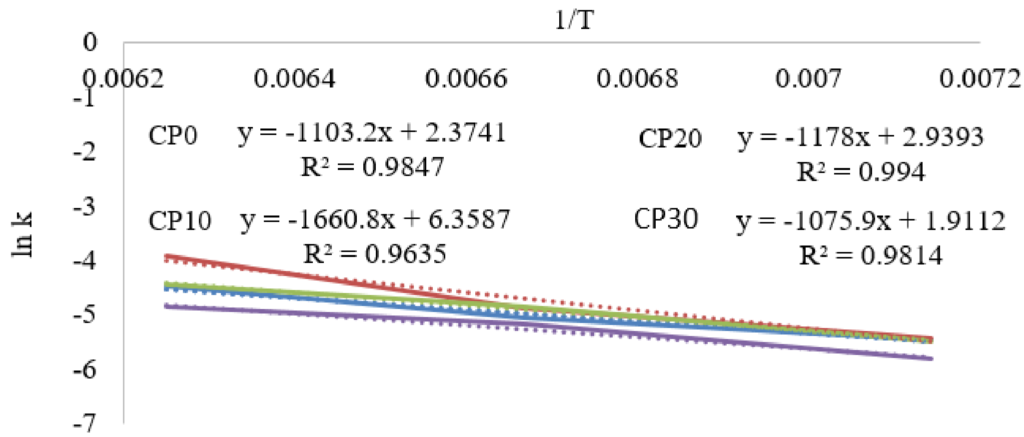

Figure 3. Plotting graph of constant rate, k.

The constant rate of the CR compound increases with the increasing of temperature. The high temperature makes the interaction of the molecule become faster so that the reaction also becomes faster. Phenolic resin 10 phr gives the highest constant rate and the highest energy activation. The CR compound without phenolic resin results in low constant rate and activation energy. But, the highest phenolic resin (30 phr) gives the lowest constant rate and activation energy. The information of a suitable amount of phenolic resin is important to get the best CR vulcanizate.

3.3. Tear properties
The CR compounds that were vulcanized by the hydraulic press at 150 ºC are called CR vulcanizate. The CR vulcanizate then tested by tensile strength tester to study its tear strength. Tear strength shows the resistance of vulcanizate to stress. The tear strength of CR vulcanizate is shown in Figure 4. The CR vulcanizate with 10 phr phenolic resin gives the highest tear strength. But 20 phr and 30 phr phenolic resin don't give the good tear strength. The tear strength reduction of CR vulcanizates was due to the incompatibility between the additives and rubber [15]. The incompatibility of materials can cause agglomeration so that the mechanical properties can decrease. The right amount of phenolic resin results in good compatibility between the phenolic resin and the rubber. The 10 phr is the optimum amount of phenolic resin for CR vulcanizate.

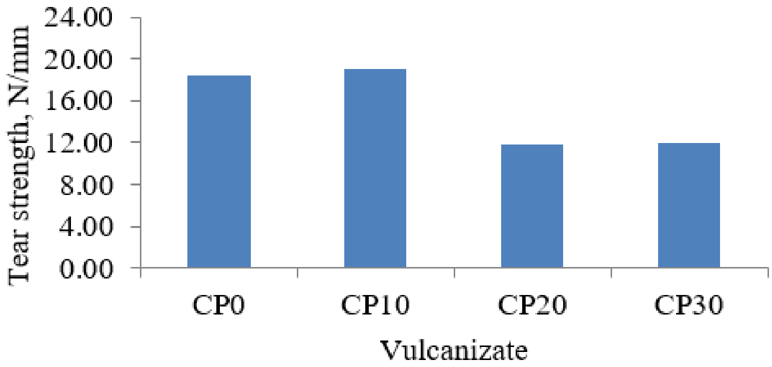

Figure 4. The tear strength of CR vulcanizates.

4. Conclusion
The vulcanizate with phenolic resin give the higher properties than vulcanizate without phenolic resin. Compound without phenolic resin results in the highest mooney viscosity (16 MU) and optimum curing time (524 s at 140 ºC, 397 s at 150 ºC, 347 s at 160 ºC). The 10 phr phenolic resin give the best mooney viscosity (10 MU), optimum curing time (274 s at 140ºC, 225 s at 150 ºC, 218 s at 160 ºC), constant rate (0.0044 sec^{-1} at 140 ºC, 0.0076 sec^{-1} at 150 ºC, 0.0196 sec^{-1}at 160 ºC), activation energy (13807.89 kJ/mol) and also tear strength (19.07 N/mm). The higher curing temperature results in the higher constant rate. The phenolic resin improves the curing characteristics and mechanical properties of CR vulcanizate. The suitable curing temperature for the CR compound is 150 ºC. The 10 phr phenolic resin is the proper additive for the CR vulcanizate.

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