A Study on the Characteristics of IR/CR Rubber Blends by Surface Treatment with Chlorine

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Abstract: In this study, blend materials were prepared according to the blending ratios of IR and CR. Physical and chemical properties of the blend materials were investigated before and after the surface of blend materials were chlorinated. In addition, the effect of surface treatment with chlorine on the friction coefficient was investigated through friction test. For the physical properties, with increasing contents of CR, the cross linking rate became slower and the mechanical properties including tensile strength and elongation were decreased. The change of physical properties was decreased before and after aging, when the contents of CR were increased and the blend materials were chlorinated. For chemical properties, with increasing contents of CR, the surface distribution was improved. The surface of samples was uniformly treated in a constant direction and their smoothness and gloss were improved. With increasing the contents of CR, the friction coefficient was decreased sharply at the initial stage of the surface treatment but the decrease in the friction coefficient slowed down when the concentration of chloride in the treatment solution was increased. In conclusion, physical, chemical and friction properties suggest that the optimal ratio of CR to IR/CR blend materials is 30 phr.

Keywords: Warpage, Injection Molding, Rib, PC, ABS, PP, PA66, Packing Time.

1. INTRODUCTION

As natural rubber supply was short after the breakout of World War II, the U.S. government initiated a massive R&D project with the industries to improve and mass-produce styrene butadiene rubber. Among the various types, IR (Isoprene Rubber) is a monomer that was synthesized by the scientists who intended to make synthetic rubber that is identical to natural rubber in terms of chemical structure. CR (Chloroprene Rubber) is the monomer of chloroprene and has the longest history among the different types of synthetic rubber. It offers good weather-resistance, Ozone-resistance, heat-resistance, grease-resistance, and chemical-resistance with low gas permeability and strong adhesion [1, 2].

As one type of rubber cannot generally satisfy all physical, chemical, and mechanical properties required, two or more rubbers are blended to improve the weaknesses and enhance value. As IR has low cis-1,4 content, it shows low crystallization under tension to show lower tensile strength and internal tearing strength. To improve this property, it can be blended with CR to improve low-temperature, wear-resistant, and heat-aging properties. As a way to have a low friction factor, the technology to treat the surface of rubber with chlorine was studied and is most widely used today [3, 4].

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In this study, IR and CR blends, the rubber materials selected to improve heat-resistance, cold-resistance, and weather-resistance which are the performances required from rubber materials used for wiper blades on cars, in various ratios to examine the physical properties of the blended materials and the surfaces of IR/CR mixtures were treated with chlorine to improve friction- resistance.

In terms of the chemical structures of IR and NR, NR shows slightly lower cis-1,4 content than IR, but has improved 3,4-bonding. However, there is no significant difference in the physical properties of vulcanizate. IR is different from NR in that IR is a synthetic material and contains even gel powder with no impurities to make it easier to make patterns. The major characteristic of IR is that it can be worked very simply for mastication. It sometimes does not even need mastication, but mastication for 3-5 minutes generally improves the results in terms of dispersion. The physical properties of IR are almost identical to those of NR, but in the same ratio of mixture IR has slightly lower modulus and hardness and greater elongation. It is also most elastic and generates less heat, but the difference is not very significant [5-7].

IR shows lower strength and adhesion than NR before vulcanization. Because the blended IR shows higher elongation at break and lower modulus compared to the blended NR with a same composition, its crystallization under tension at a high deformation speed is less significant than NR. In addition, it yields even quality, less gel powder, no impurities such as

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dust, easier mastication, good flow, outstanding absorption and electrical properties, good coloring property, and less smell [8, 9].

Neoprene, a synthetic rubber, is often called Chloroprene (CR). It is generally called Neoprene rubber in the industries and written as CR in abbreviation. Dupont USA has an advanced research and production facility for Neoprene to supply Neoprene across the world. Neoprene rubber is generally used for wires, cables, hoses, and some mechanical products. CR rubber is mainly made for heat- resistance and produced as alkaline rubber. It shows excellent chemical-resistance and weather-resistance. CR rubber shows improved swelling-resistance against hydrocarbon as the chlorine atoms that attract electrons deactivate double-bonding against the attack of Ozone or oxygen and polarize the rubber. Compared to regular rubber, CR shows good combustion-resistance and adhesion to polar materials such as metal [10].

IR's low cs-1,4 content contributes to low crystallization under tension for lower tensile and internal tearing strengths. Such data provide useful technical resources when considering the use of IR for a blend and prove the need for a blend with CR. Blending with IR improves breaking strength and cold-resistance. The use of CR and IR blends improves low-temperature properties, wear-resistance, and heat-aging properties. These blends do not easily attach to the mill roll or soften and have few calendering process issues for fast extrusion molding and good workability [11].

The technology to treat the surface of rubber with chlorine for low friction factor has been studied since the 1950s. Rho *et al*. treated rubber for wiper blades with chlorine solution in various concentration level to measure the contact angle and used the reciprocating friction tester to study the friction characteristics. The contact angle decreased radically when treated with chlorine for about 10 min, whereas the friction factor mostly decreased when treated with chlorine for about 2 min. Therefore, it is believed that additional study would be needed to decrease the friction angle radically at an early stage of chlorine treatment [12-14].

The process of chlorination on the surface of rubber using regular chlorine and sodium hypochlorite involves substitution, addition, and circulation. The mechanism of chlorination of rubber that began at a part of polyisoprene chain composed of two C5 groups by Troussier is as follows. The chlorine fixed on the surface of rubber at the early stage of chlorination takes the allylic form and comes after a very strongly substituted carbon atom.

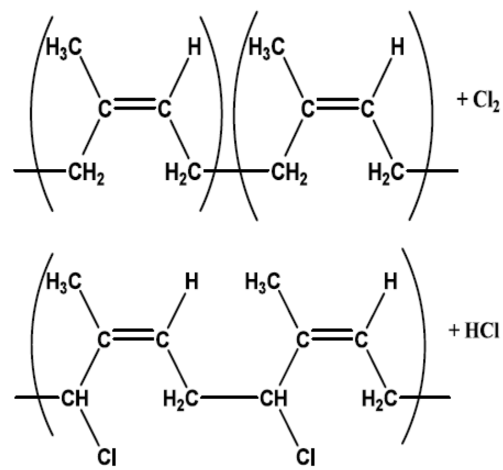

Figure 1: Allylic form of rubber before chlorination.

The CHCl-C(CH_3)=CH- group shows strong reaction and affinity with the cyclic structure. The H atom of CHCl moves in this cyclic structure to eliminate one of

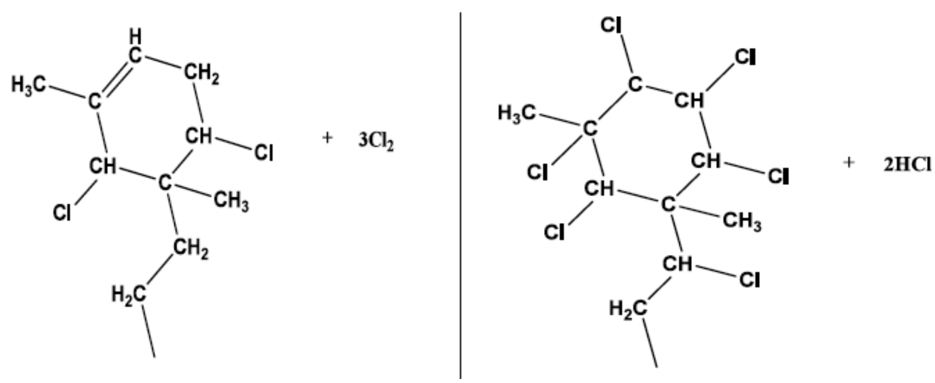

Figure 2: Addition reaction of chlorine to rubber.

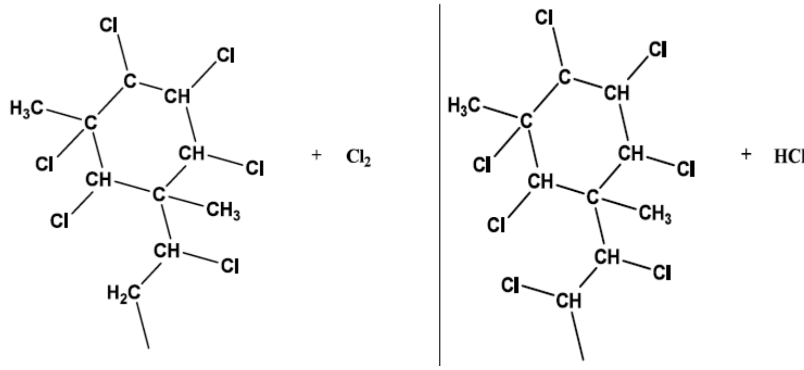

Figure 3: Substitution reaction of chlorine to rubber.

the C=C double-bonding. The following reaction is triggered with the addition of chlorine.

The C=C double-bonding is completely eliminated by this reaction that includes 57% chlorine. The last step of chlorination is the substitution reaction of 65% chlorine shown below.

This study treated IR/CR blends with chlorination to improve the friction property and studied the morphology, status property, and aging property of surface according to the duration of treatment. Then chlorine residue on the surface of rubber sample and the friction factor were measured to examine the condition of surface treatment suitable for wiper blades.

2. EXPERIMENTAL

2.1. Materials

The raw material for IR (cis-Polyisoprene Rubber) used in this study was IR 2200 of Nippon Zeol (Japan) and the raw material for CR (Chloroprene Rubber) used was Neoprene WRT of Dupont Dow (Germany) in room temperature. The fillers used Carbon Black N-770 Grade of HANKUK Carbon and the anti-aging agent used Uniroyal's Octimine, Rhein Chemical's Antilux, and Daeil Polychem's ST-S. The vulcanizing catalyst used Rhein Chemical's Sulfenamides, CBS-80 and TMTD-80. Cross-linking agents used Rhein Chemical's S-80 and Hanil Chemical's ZnO. Surface-treating chemicals used Duksan Chemical's EP, HCl and NaOCl.

2.2. Specimen Preparation

The mixing ratio of materials used to produce the IR/CR blends for this study applied the suggested ratio of each blend. The raw materials and additives were mixed in the CMB (Carbon Master Batch) stage and the vulcanizing catalyst and cross-linking agents were mixed for mechanical blending in the FMB (Final Master Batch) stage. The ratio of IR/CR blends is as shown in Table **1** below:

The specimen used for this study applied mechanical blending and the agitator used Φ12 × 36“L Mixing Mill manufactured by Bongshin-sa. The raw IR and the raw CR were masterbated for 3 minutes at 35℃. After blending masterbated raw IR and raw CR for 3 minutes at 40℃, each additive was added for mixing

Table 1: Ratio of IR/CR Blends

Recipe No	#1	#2	#3	#4	#5	#6
IR/CR [IR2200/WRT]	(100/0)	(90/10)	(80/20)	(70/30)	(60/40)	(50/50)
Carbon Black [N-770]	70	70	70	70	70	70
Anti-Oxidants [Octimine, Antilux, ST-S]	6.5	6.5	6.5	6.5	6.5	6.5
Accelerators [TMTD, CBS]	4.9	4.9	4.9	4.9	4.9	4.9
Curatives [S/ZnO]	7.15	7.15	7.15	7.15	7.15	7.15
TOTAL	**188.55**	**188.55**	**188.55**	**188.55**	**188.55**	**188.55**

for 10 minutes at 50℃. Then, the mixture was poured onto a sheet. Pressure molding (auto vacuum molding machine, 120ton, Woosung, Korea) was used to produce the flat sample (dumbbell-type #3) and the compressed sample with completely blended FMB (final master batch) for measuring various material properties. As shown in Figure **4**, 140Kg/cm^2 pressure was applied at 160℃ to make the samples [15].

2.3. Surface Treatment

The method of surface treatment used in this study was the chemical treatment method using the chlorine treatment system fabricated by KCW and underwent degreasing, washing, chlorine-treating, washing, and drying processes. Three chlorine solutions were produced by adding 40㎖ and 80㎖ (A), 120㎖ and 160㎖ (B), or 200㎖ and 240㎖ (C) 35.0% hydrochloric acid (HCl) and 5.25% sodium hypochlorite (NaOCl) to 4L water in the chlorination agitator. Chlorination was done in each of solutions A, B, or C for 3 minutes, 6 minutes, 9 minutes, 12 minutes, 15 minutes, or 18 minutes. NaOCl takes much time to dissolve in water, but this study mixed HCl and NaOCl to make the chlorine solution as it increases the efficiency of chlorine treatment within a short period of time. Table **2** shows the condition for adding HCl and NaOCl used for the chlorination of IR/CR blend compound. The above 4 liters of water was converted to a unit of 1 liter.

IR/CR rubber blends' chlorination process underwent 5-minute degreasing, 2-minute washing, and 10-minute drying in hot air. The chlorination process was performed with a certain interval at 30℃ as shown in Table **3**.

2.4. Test and Analysis method

To study the vulcanizing characteristics of blending samples, Rheometer ODR 2000 (oscillating disk rheometer, Labtech, Korea) was used at the vulcanization temperature of 160 °C. The basic properties and heat resistance were evaluated by KS M 6518. Morphology was analyzed by looking at the surface at 1,200x magnification with an optical microscope (Video Microscope IT System, SV 32, Korea). The contents of chlorine were analyzed by using EPMA (Electron Probe X-ray Micro Analyzer, JXA-8100, JEOL, Japan). In addition, the friction coefficient of the specimen whose surface was treated or not done according to ASTM 1894 was measured using a friction coefficient tester [DAVENPORT 772-A 189, UK].

3. RESULTS AND DISCUSSION

3.1. Vulcanizing Properties

This study measured the vulcanizing properties of samples that changed the ratio of CR to IR from 0 to 50 phr and these data were arranged in Table **4**. It was found that vulcanizing and scorching speed slowed down with greater CR content to slow down the vulcanizing speed. Also, the scorch time delayed with greater CR blend ratio probably because IR affects the stability of CR as CR with strong reaction to heat is mixed with IR.

Table 2: Condition for Chlorination of IR/CR Blend

Treatment Solution of Chlorination	Concentration			Treatment Temperature (℃)
	H_2O	35.0% HCl	5.25% NaOCl	
A	1ℓ	10 ㎖	20 ㎖	Room temp.
B	1ℓ	30 ㎖	40 ㎖	Room temp.
C	1ℓ	50 ㎖	60 ㎖	Room temp.

Table 3: Process Condition for Chlorination of IR/CR Blend

	Degreasing	Washing	Chlorine	Washing	Drying
Time (min.)	5	2	3, 6, 9, 12, 15, 18	3	10
Temp. (℃)	80	35	30	25	60

Table 4: Cure Characteristics of IR/CR Rubber Blends

Content		#1 (100/0)	#2 (90/10)	#3 (80/20)	#4 (70/30)	#5 (60/40)	#6 (50/50)
ODR (160℃*6min)	T_{max}	37.1	37	37.3	37.7	37.3	38.1
	T_{min}	7.8	8.2	8.2	8.3	6.3	7.0
	tc90(sec)	283	209	218	242	269	289
	ts2(sec)	80	80	84	92	99	143

Tmax: maximum torque; Tmin: minimum torque; Tc90: 90% curing time; ts2: Scorch Time.

3.2. Basic Material Properties

In this study, IR/CR blends with different ratios have been prepared as specimen of wiper blades. CR is a good polymer matrix which is superior to IR in terms of heat resistance and weatherability, but has disadvantage of not being able to be treated with chlorine due to its saturated bonding. Whereas, IR having double bonds can be treated by chlorine, which result in enhancement of tribological property. Both untreated sample and treated samples showed slightly increased hardness, tensile strength, and modulus with greater ratio of IR/CR blend. However, elongation increased up to 10 phr CR content and slightly decreased after 20 phr for both untreated and treated samples. This is because CR content affects the material properties of IR/CR blend and becomes the indicator of appropriate ratio of CR blend. It is determined that the CR content of IR/CR blend should not exceed 30% in order to control elongation. Treated samples tended to show higher hardness and modulus, but lower tensile strength and elongation, meaning that surface treatment with chlorine affects the basic material properties of IR/CR blends. Also, chlorine treatment increased the hardness of rubber surface to make it stiff probably because chlorine was carburized on the surface of rubber to affect its hardness.

3.3. Heat-Resistance

The rate of change of aging properties decreased as CR content increased. Comparing the rate of change of aging properties before/after surface treatment, treated samples showed less change probably because chlorination slowed down the change to a certain degree. C-H and C=C bonds were decreased and C-Cl bond was increased in chlorinated rubber in comparison with not treated rubber. Therefore, it suggests that the changes in physical properties were decreased by heat.

3.4. Morphology

Figure **4** shows the sectional views of samples with different IR/CR contents to observe the amount of chlorine on the surface through EPMA. As CR content increased, the intensity level of chlorine increased [16].

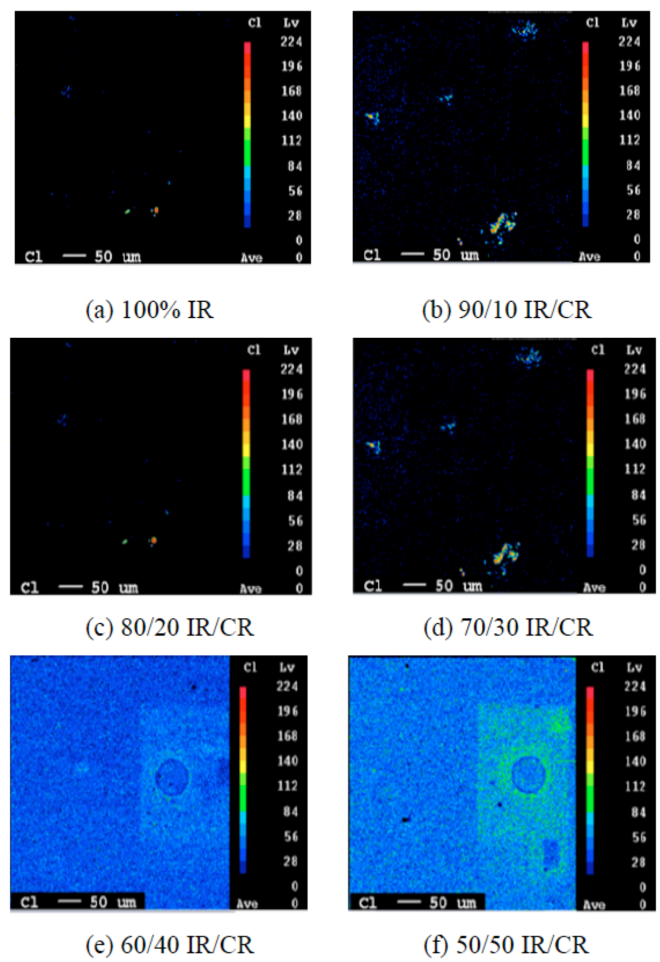

Figure 4: Images of EPMA with the various IR/CR contents.

The condition of surface of samples was observed before/after surface treatment by magnifying the surface by 1,200 times with an optical microscope. The surface of samples showed increased dispersion as

CR content increased to even out illumination and the surface treatment made the grain of rubber clearer to make the surface smoother and glossier.

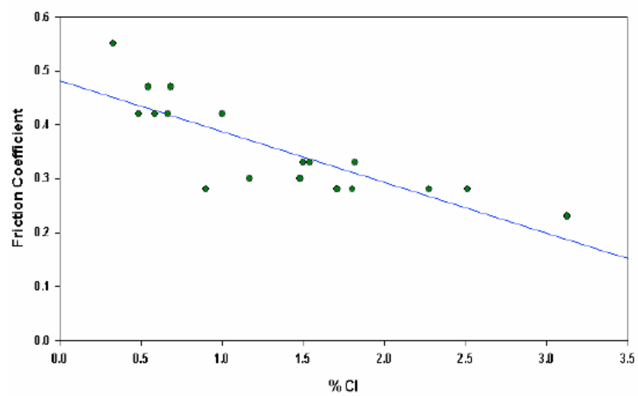

Figure 5: Friction factor according to chlorine treatment condition and time.

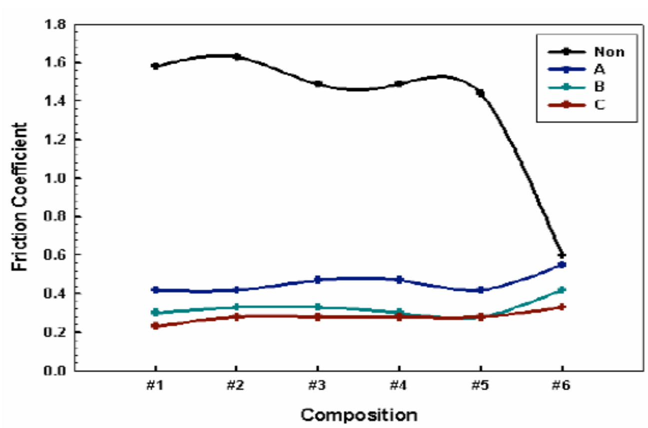

Figure 6: Friction factor of untreated and chlorine-treated samples.

3.5. Chlorine Concentration and Friction Factor

In order to examine the impact of chlorination on the friction behavior of IR/CR blend rubber, the friction factor according to chlorination condition and time was examined and shown in Figure **5**. As shown here, the friction factor decreased as the chlorine residue of blended rubber increased. Also, Figure **6** shows the results of friction factor of an IR/CR blended rubber sample not treated and the samples treated with chlorine. The samples treated with type C chlorine showed decreased friction factor overall, but the change in friction factor according to the composition of blends was minimal. However, the friction factor decreased significantly for the sample with 50 phr CR content when the surface was not treated, meaning that it was affected by both adhesive friction and hysteresis friction.

CONCLUSIONS

This study applied mechanical blending to produce the samples according to the radio of IR and CR blends and measured the physical properties (tensile strength, elongation, hardness, modulus, etc) and chemical properties (EPMA, XRF, etc) before/after surface chlorination of blended rubber to acquire the following findings.

For the testing result of vulcanizing properties, cross-linking speed was delayed as CR content increased, but the density was consistent. Also, scorching time increased as CR content increased, meaning that it improves stability.

For the testing result of physical properties, with increasing the contents of CR, the hardness and modulus were increased, and tensile strength and elongation were decreased in not treated specimen. It was closely associated with changes in volcanic characteristics. The crystallization may be affected by activation of vulcanization reaction.

For the surface treatment of chlorine, untreated samples showed increased hardness and modulus with greater CR content, meaning that these properties are closely related to the change in cross-linking properties and crystallization due to cross-linking reaction increases the mechanical strength.

The change in material properties decreased as CR content increased also after the aging test. This is because the IR/CR blends improved the weaknesses in mechanical properties to decrease the change in material properties caused by aging. This is why the change in material properties of samples treated with chlorine before/after aging.

For the results of EPMA and video microscope, it was found that surface dispersion increased as CR content increased. The surface gloss was dark before chlorination due to the uneven surface of rubber, but the chlorination process expose the compound grain to improve surface gloss.

For the result of measuring XRF, the improvement of rubber surface could be examined by observing chlorine residues on the surface and the friction factor was depending on the amount of chlorine that combined with rubber on the surface. The friction factor quickly decreased in the early stage of surface treatment up to 10-40 phr CR content, but the decrease slowed down as the chlorine concentration of the solution increased. There was a proportionate relationship between chlorine concentration and friction factor.

As a result, with increasing ratio of CR, mechanical properties and changes in physical properties before and after chlorination suggest that the optimal ratio of CR to IR/CR blend materials turned out to be 30 phr.

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