

운동화 겔창용 BR/CIIR 고무 복합체의 마찰특성 향상에 대한 연구

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Improvement of Frictional Property of BR/CIIR Composite Rubber for Shoes Outsole

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초록: 본 논문은 신발 아웃솔용 재료로 사용하기 위하여 마찰특성은 낮으나 내마모성이 우수한 부타디엔고무(BR)에 내마모성은 약하지만 마찰특성이 우수한 염화이소부틸고무(CIIR)를 블렌딩하는 경우 고무복합체의 마찰특성이 저하되는 현상을 방지하기 위한 제조방법에 대한 연구이다. BR/CIIR 복합체에서 마찰특성이 저하되지 않도록 하기 위하여 CIIR을 예비가교한 후 BR에 혼합하여 고무복합체로 제조한 경우, 복합체의 마찰특성이 현저히 향상되었다. 예비 가교한 CIIR을 40% 혼합하여 제조한 복합체의 내마모성과 마찰특성은 신발 아웃솔용으로 사용하기에 만족할 만한 값을 나타내었다.

Abstract: This paper introduced a new preparation method of a composite rubber by mixing BR (butadiene rubber) and CIIR (chloro-isobutyl rubber) for the purpose of improving frictional property of BR. Since BR has high abrasion and low frictional properties, its frictional property needs to be enhanced in order to be used as an outsole of a sport shoe. Such enhancement was difficult to achieve by simple blending of CIIR. In here, CIIR was added into BR matrix after CIIR was pre-crosslinked for a time period, and both high frictional and high abrasion resistance properties were achieved. Our experiments showed that the composite rubber blend of 60% of BR and 40% of pre-crosslinked CIIR had desired BR's frictional and abrasion resistance properties for sport shoes.

Keywords: blend, friction, abrasion, chloro-isobutyl rubber, butadiene rubber.

Introduction

Footwear is composed of three general components; upper, midsole, and outsole. The outsole makes contact with the ground and generates propulsion which pushes the ground backward and moves a body forward. When walking or running, the heel of the footwear touches the ground before its entire sole does. Then the heel starts to be lifted until the toe leaves the ground. During this contact process, friction force is generated and abrasion takes place as well. Lack of the friction force can cause slipping, which in turn results losing one's posture control. Low friction force also decreases mobility due to

low propulsion. However, high friction force also causes high shear stress on the outsole surface of a shoe, which results in abrasion of its outsole material. It can be concluded that the outsole needs to keep both high friction coefficient and high abrasion resistance in order to be better athletic footwear.

Chloro-isobutyl rubber (CIIR) and butadiene rubber (BR) are very common rubber materials used in the shoe industry. CIIR provides higher frictional property compared to BR. On the other hand, BR has higher abrasion resistance than CIIR does. Various researches have tried to synthesize a rubber containing both desirable properties in friction and abrasion by blending two materials, but such rubber has not yet been found. Other approaches are blending various materials with various treatments, where each material has its own desirable property, such as friction, abrasion and other properties.¹⁻⁵

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Among various researches, Choi and *et al.*^{6,7} reported that those properties were affected by styrene content after researching stress relaxation and recovery behavior of BR. Kim *et al.* reported that plasma treatment to a natural rubber decreased its friction coefficient significantly depending on its processing time.⁸ Park investigated a reason why uniform blend of BR and CIIR failed to pertain both the desired properties.⁹

In the previous research, when BR is simply blended with CIIR, it is well known that the blend rubber can't keep BR's high abrasion resistance while keeping CIIR's high frictional property.⁹ The abrasion resistances of the pure CIIR and the pure BR were reported as 14% and 600%, which was the lowest value and the highest value among all blended rubbers, respectively. When CIIR was blended with BR, its abrasion resistance located in between those of the two pure rubbers. On the other hand, a trend of friction coefficients of those composite rubbers seemed to be opposite to their abrasion resistances. The friction coefficients of the pure CIIR and the pure BR were reported 3.73 and 1.35, respectively. By blending more BR with less CIIR, its friction coefficient tended to decrease because BR's crystallization is hindered by CIIR.^{9,10}

This study was then intended to find a new method by which CIIR does not interfere in crystalline of BR in mixing two materials so that the composite rubber could pertain both high abrasion resistance and high frictional properties. The new method suggested that BR is mixed with a pre-crosslinked CIIR, which was prepared in a pre-process. By using a pre-crosslinked CIIR in mixing two materials, an intrinsic mechanical property of CIIR could be sustained in the mixture, which was considered as a composite rubber. The composite rubber could also be produced by various combinations according to a mixing ratio and a pre-curing time of CIIR. Hence, this study introduced the best method for guaranteeing both high friction and high abrasion resistance through mechanical property tests with various combinations of composite rubbers.

Experimental

Materials. Among the raw materials used in this study, CIIR was the 1066 model supplied from Exxon Mobil Corporation, and BR was the KOSYN 01 from Kumho Petrochemical. Sulfur, ZnO and denzothiazole disulfide (DM) produced by Hanil Chemical were selected for crosslinking agent and crosslinking activator. For lubricants, PEG-4000 from KPX Chemical and

W-1500 from Michang Oil were used. Butylated hydroxytoluene (BHT) for anti-oxide and Zeosil 175G for filler were supplied from Sumitomo Chemical and Raudia, respectively.

Specimen Preparation. In order to prepare the specimens used in this study, four steps are required. The first mixing step is proceeded by feeding 100 g of CIIR into a closed kneader of 500 mL capacity with 30 rpm at 80 °C for 2 min. It is continued by adding 10 g of stearic acid, 30 g of zeosil-75, 2 g of Si-69, 3 g of white oil, 1 g of BHT and 1 g of PEG 4000 for 15 min. In the second mixing step, an open roll with 15 cm diameter is used in adding and mixing 5 g of ZnO, 1.5 g of sulfur, 0.5 g of tetramethyl thiuram monosulfide (TS) and 1.0 g of DM into the outcome of the first step at 40 °C for 5 min. The outcome of the second step is then normalized for 24 h at room temperature. Up to these two steps, BR is also required to go through the same process.

In the third step, particles in the CIIR outcome from the previous step need to be crosslinked by being pressed in a prepared mold with the 155 °C temperature for a certain time, which is called the pre-curing process. This step is the most important process in the study, in which each specimen can be differentiated by selecting each pre-curing time described in the Figure 1. The torques in the y-axis of the Figure 1 are measured by using Rheometer (Mansanto ODR 2000) in accordance with ASTM D 208416 standard. T_{10} here is the elapsed time for the torque of the material to reach 10 units out of total 100 units between the maximum torque and the minimum torque as shown in Figure 1. The specific curing times are listed in the Table 1 and their outcomes are classified as PCIIR10, PCIIR20, and etc., where PCIIR10 means the pre-crosslinked CIIR by curing the outcome for the T_{10} period time and PCIIRxx is also corresponded to T_{xx} as shown in Figure 1 and Table 1.

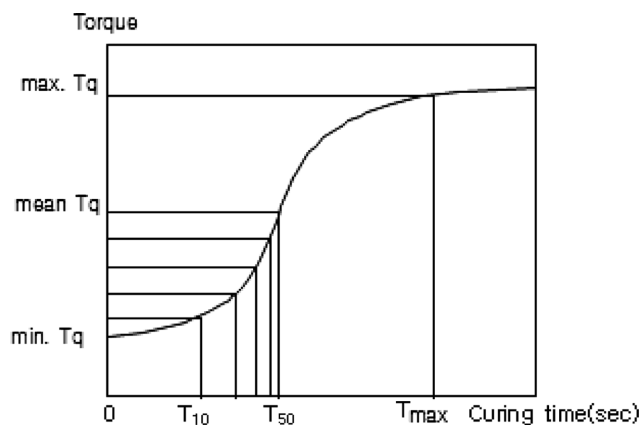


Figure 1. Torque versus curing time of CIIR.

The final step is then proceeded by blending BR with the pre-crosslinked CIIR outcomes after being shaped by a cube (3×3×3 mm). After making the cubic shape of the pre-crosslinked PCIIR_{xx}, CIIR domains can be separated from BR matrix except the surface of the cube when mixing them together. In order to investigate the effect of the pre-curing time of CIIR, various PCIIR's as listed in Table 1 are prepared and mixed with BR by different weight ratios. According to a mixing ratio of two materials, BR and each PCIIR, the spec-

Table 1. Precuring and Second Curing Times of CIIR

Code	Curing time(sec)			
	Pre-curing		Second curing ^a	
CIIR	-	-	T_{max}	2638
PCIIR10	T_{10}	520	$T_{max}-T_{10}$	2118
PCIIR20	T_{20}	720	$T_{max}-T_{20}$	1918
PCIIR30	T_{30}	912	$T_{max}-T_{30}$	1726
PCIIR40	T_{40}	1078	$T_{max}-T_{40}$	1560
PCIIR50	T_{50}	1265	$T_{max}-T_{50}$	1373

^aSecond curing time is a time duration for mixing CIIR (or PCIIR_{xx}) with BR.

Table 2. Basic Formulations of All Specimens with CIIR and BR

Class	Name	Ratio of rubber compounds				
		BR	CIIR	PCIIR20	PCIIR30	PCIIR40
a	BR	100	-	-	-	-
b	CIIR	-	100	-	-	-
c	BR/CIIR (90/10)	90	10	-	-	-
d	BR/PCIIR20(90/10)	90	-	10	-	-
e	BR/PCIIR30(90/10)	90	-	-	10	-
f	BR/PCIIR40(90/10)	90	-	-	-	10
g	BR/CIIR(80/20)	80	20	-	-	-
h	BR/PCIIR20(80/20)	80	-	20	-	-
i	BR/PCIIR30(80/20)	80	-	-	20	-
j	BR/PCIIR40(80/20)	80	-	-	-	20
k	BR/CIIR(70/30)	70	30	-	-	-
l	BR/PCIIR20(70/30)	70	-	30	-	-
m	BR/PCIIR30(70/30)	70	-	-	30	-
n	BR/PCIIR40(70/30)	70	-	-	-	30
o	BR/CIIR(60/40)	60	40	-	-	-
p	BR/PCIIR20(60/40)	60	-	40	-	-
q	BR/PCIIR30(60/40)	60	-	-	40	-
r	BR/PCIIR40(60/40)	60	-	-	-	40

imens are also classified as listed in Table 2. Each mixture is then mixed in the kneader for 5 min and it is pressed in a prepared mold at the 155 °C temperature during the second curing time as shown in Table 1 to produce the final specimens. Finally, all the specimens prepared for this study are listed at the Table 2. The specimens BR/CIIR(90/10), BR/CIIR(80/20), BR/CIIR(70/30) and BR/CIIR(60/40) as listed in Table 2 are produced by simply blending BR and CIIR by each different ratio, where BR/CIIR(90/10) represents the mixture of 90% weight of BR and 10% weight of pure CIIR. The specimen BR/PCIIR20(90/10) is also made by mixing 90% weight of BR and 10% weight of PCIIR20 and the others are also made by mixing all different ratios of BR and PCIIR_{xx}.

Mechanical Property. At first, tensile stress and strain of the specimens were measured by using Instron's model 4466 tension tester with an extension speed of 500±25 mm/min. These data are also decided by averaging 5 time measurements. For this test, specimen needs to be shaped as a dumb-bell No. 3 specified in the KSM 6518. For abrasion test, the specimen is shaped as a rectangle with length of 25.4 mm and thickness of 6.3 mm as specified in the NBS abrasion standard(ASTM 1630). The specimen is then bonded to a holder and placed on a drum with an abrasive paper. Then the drum is rotated with 45 rpm and the number of rotation for the specimen worn by 2.54 mm is counted. The anti-abrasion rate is then calculated through the following,

$$\text{Anti-abrasion rate(\%)} = (R_1/R_2) \times 100 \quad (1)$$

where, R_1 is a number of rotation for the specimen worn by 2.54 mm and R_2 is an average number of rotation for a reference specimen worn by 2.54 mm.

In order to measure friction coefficient of each specimen, it was shaped as a rectangle of 55 mm by 100 mm. It is then placed on a plate, and one end of the plate is raised until the specimen starts to slip. The inclined angle of the plate at the moment is measured as the coefficient of friction of the specimen according to the law of Coulomb's dry friction. For measuring a $\tan\delta$ of a specimen, it was also shaped as a sheet of 1.2 mm thickness and 6.5 mm width and a dynamic visco-elastic measuring instrument (DMA, TA Instrument's 2980) is used at 1 Hz. The range of temperature for measurement was set from -60 to 80 °C and the heating rate was set to 5 °C/min. X-ray diffraction pattern of all specimens were obtained by using a X-ray diffract-meter (D/max-III-A type, Rigaku Co., Japan), where X-ray was diffracted by 2 θ (=5~40°) with

respect to the horizontal plane after CuK_α ray was filtered through a Ni filter.

Results and Discussion

To become better athletic shoes, their outsole material must have excellent properties in both anti-slip and abrasion resistances for safety and durability. Figure 2 shows abrasion resistances and friction coefficients of various BR/CIIR blended rubbers, where we can see that CIIR has a high coefficient of friction 3.75, but it has a low anti-abrasion rate of 14% measured by the NBS abrasion tester. On the other hand, BR has a great anti-abrasion rate of 600%, but its coefficient of friction is 1.35, which is too low to prevent a person from slipping when walking or running. In order to enhance the slip resistance while keeping the high abrasion resistance, various specimens were produced as listed in Table 2. All specimens were then investigated to find the most enhanced ratio throughout several experiments.

The experiment performed at first is the tensile strength test as described in Experimental section. According to the Figure 3, it is found that the tensile strengths of all specimens tend to decrease as the weight percentage of CIIR content in a rubber composite increases up to 20%. The associated specimens are CIIR, BR/CIIR(90/10) up to BR/PCIIR40(80/20). After 20% of content of CIIR, the tensile strengths of the specimens BR/CIIR(70/30), BR/PCIIR20(70/30), up to BR/PCIIR40(60/40) are limited in a small range. For cases of the composite rubbers composed of PCIIR20 and BR, a trend of their tensile strengths is similar to those of the simple blending composite rubber, BR/CIIR(70/30) and BR/CIIR(60/40). However, for

cases of composite rubbers with PCIIR30, their tensile strengths are dropped much more when comparing with the previous cases. Such decreased tensile strength of blended rubbers with CIIR and BR is due to low interaction between CIIR and BR matrix. It is typical phenomena of heterogeneous polymer blend.¹¹⁻¹³

Since the friction between an outsole of a shoe and the ground provides its user posture control and propulsion while walking and running, it is considered friction coefficient of a outsole material of shoes is the most important design factor of sports and hiking shoes. In order to complement low traction property of BR (while keeping high abrasion resistance), various PCIIRs which have high traction property are mixed with BR by various ratio. Results from frictional tests of various specimens are plotted at Figure 4. For the two extreme specimens, 0% of CIIR (100% BR) and 100% of CIIR, their friction coefficients are 3.75 and 1.35, respectively. For the specimens blended with BR and no crosslinked CIIR, their friction coefficients increase as the weight percentage of the CIIR content increases. Furthermore, when the specimens are mixed with BR and PCIIRxx, such as BR/PCIIR20(90/10), BR/PCIIR30(90/10), etc, their friction coefficients increase even more as the weight percentage of the PCIIRxx content increases. It can be explained that since the pre-crosslinked CIIR exist as macro-size domains in BR matrix, it has more chances to be directly exposed to a contact surface, their frictional property can be pertained. Especially, the specimens, BR/PCIIR30(70/30), BR/PCIIR40(70/30), BR/PCIIR30(60/40), and BR/PCIIR40(60/40), have friction coefficients higher than 2.0 which is the frictional criteria well known in the sports

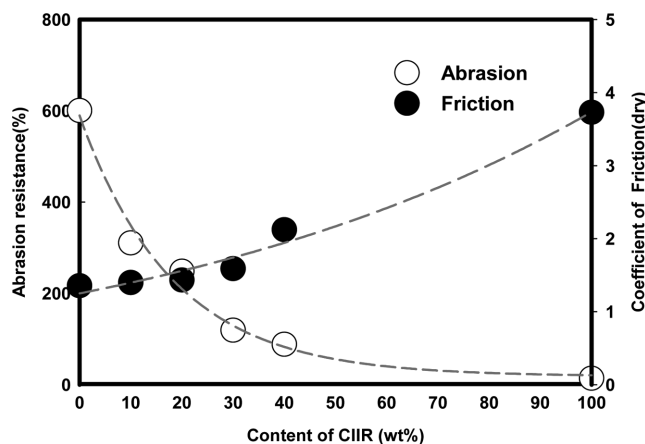


Figure 2. Friction coefficient and abrasion resistance of BR/CIIR blended rubbers.

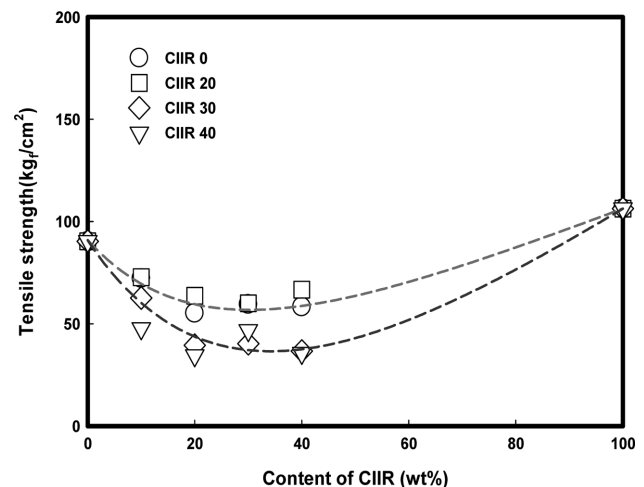


Figure 3. Tensile strengths of blends and composites with BR and CIIR.

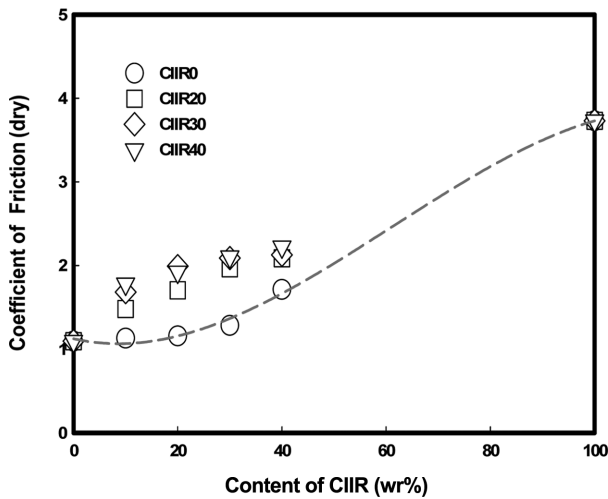


Figure 4. Friction coefficients of blends and composites with BR and CIIR.

shoes' industry. Therefore, it can be concluded that lack of frictional property of BR can be compromised by adding PCIIR in BR matrix more than 30% only after pre-cured for longer than the pre-curing time period, T_{30} .

When BR is blended with CIIR for the purpose of improving its abrasion resistance while keeping its frictional property, CIIR is distributed as micro size domains in the BR matrix so that it interferes in crystallization of BR particles and lead to deterioration of its abrasion property. To minimize such undesirable results, CIIR needs to be pre-cured before mixed with BR as suggested in this study. According to the various pre-curing times and mixing ratios, various specimens are prepared and performed for the abrasion test. The results are plotted in Figure 5. The abrasion resistance of the specimen of BR is 600%, as high as expected. On the other hand, that of the specimen of CIIR is 14% which seems to have no abrasion resistance property. For the specimens of simple mixture of BR and CIIR with various mixing ratios, their abrasion resistances decrease dramatically as the content ratio CIIR increases. However, such sharp drops of abrasion resistances appeared in the specimens seem to be alleviated by mixing BR with pre-cured CIIRs (referred to PCIIR). The most effective alleviation in this test is achieved by using PCIIR40 as shown in Figure 5. For the specimens of PCIIR40 and BR, their abrasion resistances seem to be proportional to the content of PCIIR40.

When BR is mixed with CIIR and when BR is mixed with 40% content ratio of PCIIRxx, a tendency of their abrasion resistances was investigated through the $\tan\delta$ test. Their results

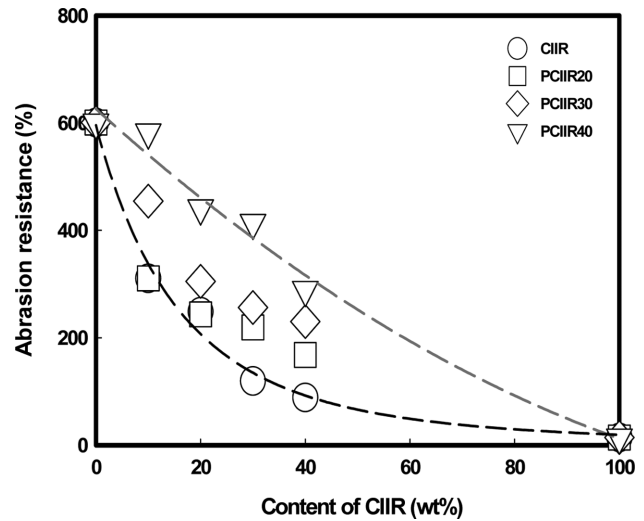


Figure 5. Abrasion resistance of blends and composites with BR and CIIR.

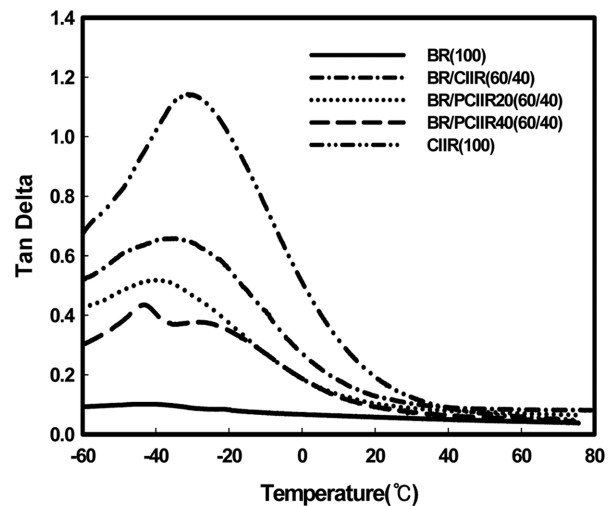


Figure 6. $\tan\delta$ curves of rubber blends and composites.

are plotted in Figure 6, where the test temperature is ranged from -60 up to 70 °C. A peak of the curve of the specimen of CIIR(100) appears around -30 °C, which is here called the CIIR peak. As also for the specimen BR(100), a peak appears slightly at 40 °C so that it is called the BR peak. Now, when two materials are blended as BR/CIIR(60/40) and mixed as BR/PCIIR20(60/40), it is observed that the two peaks are combined into one peak. But for the specimen BR/PCIIR40(60/40) the two peaks are pertained as shown in Figure 6, where CIIR is mixed after pre-cured for the T_{40} time period which is relatively longer time period than T_{20} . Hence, we can conclude when the pre-crosslinked CIIR pre-cured for enough time period (T_{40}) is mixed with BR, the intrinsic property of BR

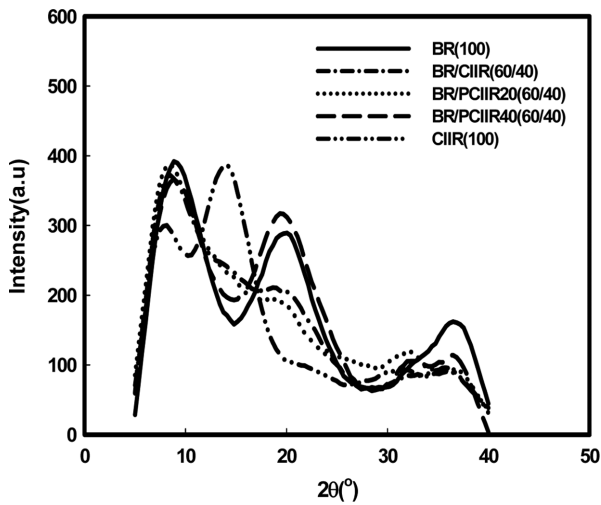


Figure 7. X-ray diffraction patterns of rubber composites of BR and CIIR.

known as the high abrasion resistance does not disappear.

Generally, crystallinity of a material is an important physical property which determines its abrasion resistance. The BR material referred in this study belongs to a high crystalline rubber. When CIIR is blended into BR matrix, then it can be explained that micro-size CIIR domains scattered inside BR matrix disturb crystallization of BR. However, when PCIIR40 (referring to pre-cured CIIR) is mixed into BR matrix, the pre-curing process for a relatively long time period makes macro-size CIIR domains so that they can not affect on crystallization of BR. Therefore, it is expected that a possible drop in abrasion resistance of BR due to CIIR can be prevented by using pre-crosslinked CIIR (PCIIR) when making a composite rubber of BR and CIIR.

From x-ray diffraction tests, we hope to discover a composite rubber sustaining the crystalline peak of BR. In order to obtain intrinsic patterns of two pure rubbers, BR and CIIR are tested and plotted in Figure 7. For the specimen of BR(100) which is a pure BR rubber, the second peak of its x-ray diffraction pattern appears at around 20° of 2θ . Hence, existence of the second peak in a composite rubber can be represented that the intrinsic crystalline character of BR materials pertained. The x-ray diffraction patterns of various composite rubbers, such as the specimens BR/CIIR(60/40), BR/PCIIR20(60/40), and BR/PCIIR40(60/40) are also obtained and plotted in Figure 7. For the specimens BR/CIIR(60/40) and BR/PCIIR20(60/40), their second peaks disappears at 20° of 2θ , which means losing the intrinsic character of BR. However, for the specimen BR/PCIIR40(60/40), of which CIIR is pre-crosslinked

for the T_{40} curing time period, its second peak appears at 20° of 2θ exactly same as BR's, which means it still sustains the crystalline character of BR. These overall tendency coincides with the tendency explained in the previous section that domains of CIIR distributed in the BR matrix hinder crystallization of BR matrix and lead to deterioration of its abrasion property. However, when PCIIR40 is mixed with BR, it does not interfere in crystallization of BR matrix so that the composite rubber can still keep the abrasion resistance and the high frictional property as well. Therefore, it can be concluded that when CIIR is pre-cured for longer than T_{40} , the composite rubber of BR and CIIR can possess both desirable mechanical properties, such as high friction and high abrasion resistance.

Conclusions

The goal of this paper is to enhance slip resistance of a composite rubber of BR and CIIR while keeping BR's high abrasion resistance property. CIIR is here strongly recommended to be pre-crosslinked (pre-cured) before mixing with BR matrix. At first, through tensile strength test, it was found that the composite rubber mixed with PCIIR which is pre-cured for a longer time have lower tensile strengths due to a phase separation of the pre-cured CIIR against BR matrix. Lack of frictional property of BR was compromised by adding PCIIR in BR matrix more than 30% only after pre-cured for longer than the pre-curing time period, T_{30} . Furthermore, when the pre-crosslinked CIIR pre-cured for an enough time period (T_{40}) is mixed with BR matrix, the intrinsic property of BR known as high abrasion resistance does not disappear. It is confirmed through the X-ray diffraction test. From the test, we can see that domains of CIIR distributed in the BR matrix hinder cohesion of BR matrix and lead to deterioration of its abrasion property. However, when PCIIR40 is mixed with BR, the composite rubber can still keep abrasion resistance and high frictional property as well. Therefore, it can be concluded that when CIIR is pre-cured for longer than T_{40} , the composite rubber of BR and CIIR can retain both desirable mechanical properties, such as high friction and abrasion resistance.

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