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Vinyl *Cis* Rubber superior polymer for future trends

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Abstract. Vinyl *Cis* Rubber (VCR) is *cis*-1,4-polybutadiene reinforced by highly crystalline fibrous syndiotactic-1,2-polybutadiene (SPB). It has been developed and commercialized by Ube Industries Co.,Ltd. The highly crystalline syndiotactic-1,2-polybutadiene having melting point (M.p.) up to 473K is obtained by using cobalt catalyst system. Fibrous crystalline domains in VCR are effective for the stress-induced crystallization of the rubber matrix. VCR has various improved properties such as high green strength, good processing, large modulus, good flex-crack resistance, etc. The improvement of physical and dynamic mechanical properties depends on the content of syndiotactic-1,2-polybutadiene dispersion in *cis*-1,4-polybutadiene matrix and rubber compound recipe. For examples; with the same compound recipe, VCR vulcanized significantly improve in modulus up to 80%, increase hardness up to 10%, and improve in flex-crack resistance. With the same hardness of vulcanized recipe, filler can be reduced down to 10-20 part per hundred rubbers consequently energy loss performance can be improved up to 10-18%. This polymer is widely used in eco-friendly tires, high performance tires, out sole of shoe, conveyor belts and other rubber goods.

1. Introduction

Regarding to tire labeling regulation have been started since 2012 that must specify fuel consumption, wet grip and noise classification of every tire sold in market. This regulation designed to improve the energy performance of tires, buildings and services to reduce energy consumption by 20% until 2020 [1].

Polybutadiene rubber is one important component of tire both of passenger car tires and truck bus tires. The design of polymer structure of polybutadiene, for example, linearity, molecular weight or molecular weight distribution is importance for producing suitable rubber with lowers energy loss and higher abrasion resistance. Furthermore, the composite polybutadiene rubber is one of technology that can provide satisfying properties of rubber composition for eco-friendly and high-performance tires. Such a composite polybutadiene is commercially available under registered trade mark UBEPOL VCR[®] from composite technology of Ube Industries Co., Ltd. This polymer in the form of a composite composed of an elastomer which is a part of *cis*-1,4-polybutadiene and fibrous crystals which is a part of syndiotactic-1,2- polybutadiene uniformly dispersed in elastomer matrix with desired amount [2]. UBEPOL VCR412, its composition includes *cis*-1,4-polybutadiene 88% and syndiotactic-1,2-polybutadiene 12%. UBEPOL VCR617, its composition includes *cis*-1,4-polybutadiene 83% and syndiotactic-1,2-polybutadiene 17%, respectively.



The present study, the suitable rubber compositions comprises a butadiene rubber containing syndiotactic crystal will be provided for using in standard typical sidewall formulation of pneumatic tires, which is having not only high reinforcement, high durability, and excellent in processability but also having satisfy energy loss performance.

2. Experimental

In this study, two cases were investigated; same formulation and same hardness of vulcanizate formulation.

2.1. Materials

2.1.1 Natural Rubber

2.1.2 *Polybutadiene rubber.* Polybutadiene rubber containing syndiotactic crystal; UBEPOL VCR412, UBEPOL VCR617, Neodymium polybutadiene rubber (NdBR)

2.1.3 High Abrasion Furnace carbon black (HAF, N330), other standard rubber compounding ingredients such as stearic acid, zinc oxide, processing oil, accelerator and sulfur are commercial grades.

2.2 Mixing and curing

To prepare the compounds, rubber compounds were mixed in small banbury mixer with different compound formulation as shown in Table 1. Preparation of sheets for testing was done on a two roll mill.

Ingredients (phr)	S-1	S-2	S-3	S-4	S-5	S-6
UBEPOL VCR412	50					
UBEPOL VCR412		50				
UBEPOL VCR617			50			
UBEPOL VCR617				50		
NdBR-1					50	
NdBR-2						50
STR5L	50	50	50	50	50	50
CB N330	30	50	30	50	50	50
Process oil	10	10	10	10	10	10
ZnO	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2
Antioxidant	2	2	2	2	2	2
TBBS	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
Total	149.3	189.3	149.3	189.3	169.3	169.3

Table 1 Rubber compound formulation

For each type of rubber compounds, the vulcanization process was performed by compression molding process. The optimal curing time (t_{90}) obtained from RPA2000 Rheometer (Alpha Technologies) measurements according to ASTM D5289

3. Results and discussion

3.1 Rubber compound properties

It was found that the Mooney viscosity of rubber compounds containing same amount of carbon black were increased related with the Mooney viscosity of polybutadiene rubber as shown in Table 2. Both of rubber compounds containing SPB showed lower Mooney viscosity than NdBR. The results were inherently related to the processability test which rubber compounds included UBEPOL VCR showed better workability, smoother surface of extrudate, and smaller die swell than NdBR as shown in Figure 1. This phenomenon is corresponding to reinforcement effect of syndiotactic crystal in rubber compounds.

The carbon black content was adjusted in order to keep same hardness level of vulcanizates at 60 Shore A in this study. It was found that Mooney viscosity of rubber compound containing SPB were spontaneously decreased with decreasing amount of carbon black as shown in Table 2. Lower filler contents showed lower compound viscosity that inherently related to better workability. Rubber compounds containing UBEPOL VCR

still showed better processability than NdBR compounds as shown in Figure 1. This phenomenon is corresponding to reinforcement effect of syndiotactic crystal in rubber compounds as discussion above.

Table 2 Raw polymer properties of each polybutadiene rubber

Property	UBEPOL VCR412	UBEPOL VCR412	UBEPOL VCR617	UBEPOL VCR617	NdBR-1	NdBR-2	
Carbon Black (phr)	30	50	30	50	50	50	
Raw Polymer ML1+4 (373K)	44	44	64	64	66	49	
Syndiotactic-1,2-polybutadiene (%)	12	12	17	17	-	-	
Rubber compound ML1+4 (373K)	40	56	43	62	69	61	
Cure characteristic, 423K	t10 (min)	8.1	7.0	8.1	6.3	6.9	7.0
	t90 (min)	15.0	13.5	14.7	12.9	13.4	13.6
Extrusion Die Swell	2.61	2.31	2.20	2.14	3.00	2.94	

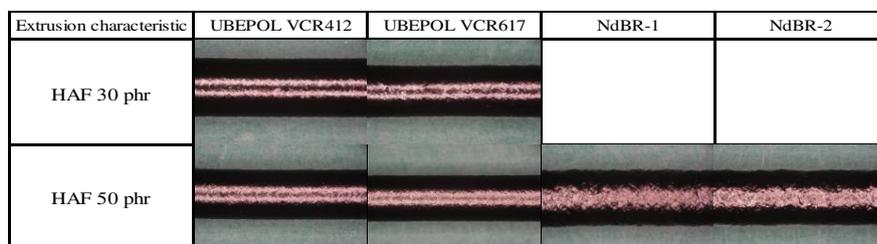


Figure 1 Extrusion characteristic of each rubber compound at shear rate 2,000 (1/sec)

3.2 Vulcanizate properties

We observed that rubber compounds containing SPB showed higher modulus than NdBR compounds around 19%-85% as shown in Table 3. This behavior is related to reinforcement effect of syndiotactic crystal in rubber compound. The effect is more evident in the case of higher syndiotactic crystal content. Furthermore, syndiotactic crystal containing compounds showed better Picro abrasion resistance and crack growth resistance than NdBR compounds. This behavior can be explained that syndiotactic crystal act as fibrous filler well dispersed and interact with polymer, consequence of higher hardness and Picro abrasion resistance. In addition, syndiotactic crystal can be also seen as rigid polymer-filler interface which leads to accumulation of stress and crack can change direction of growth, which may lead to crack stopping [3].

It was also observed that carbon black content could be reduced 10-20 phr for rubber compounds containing SPB in order to keep the same hardness level as NdBR compounds. However, they showed same modulus level as NdBR compounds even lower carbon black content, especially UBEPOL VCR617. This behavior is related to reinforcement effect of syndiotactic crystal as mention above. The decreasing filler content leads to increase the mobility of rubber chains, consequently, induce elasticity in lower filled compounds [4]. Therefore, elasticity of rubber compounds containing SPB was improved. Their rebound resilience was same level as NdBR compounds. In addition, heat generations of low filled UBEPOL VCR compounds were better than NdBR compounds. Furthermore, these compounds still kept better performance of crack growth resistance than NdBR rubber compounds, especially, in low stoke area. These behaviors of syndiotactic crystal containing compounds will be suitable for sidewall application of future eco-friendly and high performance tires.

The dynamic viscoelastic properties for the low filler filled rubber containing syndiotactic crystal compounds are shown in Table 3. It was observed that syndiotactic crystal containing compounds with lower filler content still showed higher $\tan\delta$ in low temperature corresponds to better wet skid resistance compared to NdBR compounds. In addition, their rolling resistance performance which related to $\tan\delta$ in the temperature range of 333K was better than NdBR compounds. It can be explained that rubber compounds containing SPB will dissipate and lose more energy in the low temperatures range. Therefore, these rubber compounds have better

wet skid resistance. However, filler loading decreases the filler-filler interaction decreases, consequently, reduce energy loss from filler-filler friction in the compounds.

Table 3 Mechanical properties of each vulcanizates

Testing items	UBEPOL VCR412	UBEPOL VCR412	UBEPOL VCR617	UBEPOL VCR617	NdBR-1	NdBR-2
<u>Mechanical properties</u>						
Carbon black (phr)	30	50	30	50	50	50
Specific Gravity (g/cm ³)	1.046	1.099	1.047	1.100	1.098	1.097
Hardness (Shore A)	55	63	61	68	60	60
100% Modulus (MPa)	1.7	2.5	2.5	3.9	2.1	2.1
200% Modulus (MPa)	4.0	7.0	5.5	9.5	5.6	5.5
300% Modulus (MPa)	7.5	12.6	9.4	15.3	11.1	10.7
Tensile at Break (MPa)	22.1	21.9	19.4	22.3	22.9	23.9
Elongation at Break (MPa)	608	494	516	462	515	545
Tear Resistance (kN/m)	65	73	68	72	72	71
Rebound (%)	65	58	64	57	67	65
Compression set (%)	28.8	29.8	31.7	40.1	27.4	28.8
Heat Build Up : ΔT (K)	13.5	21.8	15.0	24.5	16.8	18.0
Picro Abrasion (Index)	97	152	102	167	140	142
Crack growth resistance (mm/cycles)						
Stroke 30 mm ($\times 10^{-6}$)	0.61	1.20	1.10	1.24	4.47	5.41
Stroke 56 mm ($\times 10^{-4}$)	3.59	4.15	3.43	0.10	2.94	1.07
<u>Viscoelastic properties</u>						
Carbon black (phr)	30	50	30	50	50	50
tan δ @ 253 K	0.237	0.267	0.241	0.260	0.214	0.222
tan δ @ 273 K	0.132	0.173	0.142	0.185	0.125	0.139
tan δ @ 333 K	0.095	0.148	0.105	0.131	0.109	0.115

4. Conclusion

UBEPOL VCR is polymer composite include mixture of *cis*-1,4-polybutadiene and a short fiber of crystalline syndiotactic-1,2-polybutadiene. Syndiotactic crystal containing compounds showed better workability, higher modulus up to 80%, higher hardness, better Picro abrasion resistance, better crack growth resistance and better wet skid resistance performance than non-containing rubber compounds in same compound formulation. In order to keep the same hardness level of vulcanizates, filler contents could be reduced 10 to 20 phr in syndiotactic crystal containing compounds formulation. Low filled rubber compound of syndiotactic crystal showed better workability, better heat generation, better wet skid resistance performance and better rolling resistance performance up to 10% to 18% than non-containing rubber compounds. These behaviors of syndiotactic crystal containing compounds are useful for sidewall application of eco-friendly and high performance tires as future trends.

5. References

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