Performance Improvement of Natural Rubber / Carbon Black Composites by Novel Coupling Agents

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In recent years, various actions for saving resources and energy have been taken and the demand for a contribution by tires to saving energy has become higher. In order to achieve energy savings from tires, the reduction of rolling resistance, which is one of the resistances against driving force, is very important.

In this article, we review the trends in the field of coupling agents and report on the performance of newly-developed carbon black coupling agents for energy-saving tires.

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Introduction

Resource/energy conservation efforts have, in recent years, been made in various fields from the perspective of environmental protection. Thus, improving fuel efficiency (i.e., saving fuel) is very necessary in the automobile industry in order to reduce CO_2 emissions. Each company in the industry has therefore implemented various countermeasures including improving engine efficiency and reducing vehicle weight in order to achieve the fuel-economy standards based on laws regarding the rationalization of energy use. Under such circumstances, contribution to fuel savings is required in the area of tires, which make direct contact with the road surface.

A reduction in the weight of the tire–which can be achieved through a decrease in the tire's thickness by enhancing the rubber's strength or replacing the metal components with polymeric materials–will improve fuel efficiency. However, in order to improve fuel efficiency by way of tires, it is extremely important to reduce the rolling resistance, which is one of the forms of resistance that tires receive from the driving force of the vehicle. For example, when assuming the contribution ratio of tires to fuel efficiency to be 10% and reducing the rolling resistance by 20%, the fuel efficiency will improve by approximately 2% when traveling through a general urban area.1)

Rolling resistance can be caused by the following three forms of energy loss: (1) energy loss due to tire deformation (hysteresis loss); (2) energy loss due to the friction of the tread against the road surface; and (3) energy loss due to air resistance caused by tire rotation. Nearly 90% of rolling resistance originates from tire deformation. Repeated tire deformation increases hysteresis loss, and energy will be lost when part of the kinetic energy required for tire deformation is converted into thermal energy. Therefore, reducing the hysteresis loss means traveling while reducing the kinetic energy consumption, resulting in improving the fuel-saving performance (see **Fig. 1**). It is thought that hysteresis loss is generated due to the following factors: the friction caused by cyclical tire deformation between polymer ends having a high flexibility or between the polymer and the filler; or the friction caused between the fillers when aggregates of the filler repeatedly collapse and re-aggregate.2)

This article reports on the novel carbon-black coupling agent developed by the author, et al. (hereinafter referred to as CC agent), aiming to develop fuel-efficient tires with high performance while at the same time reviewing the technology for coupling polymers and fillers such as silica and carbon black (hereinafter referred to as CB).

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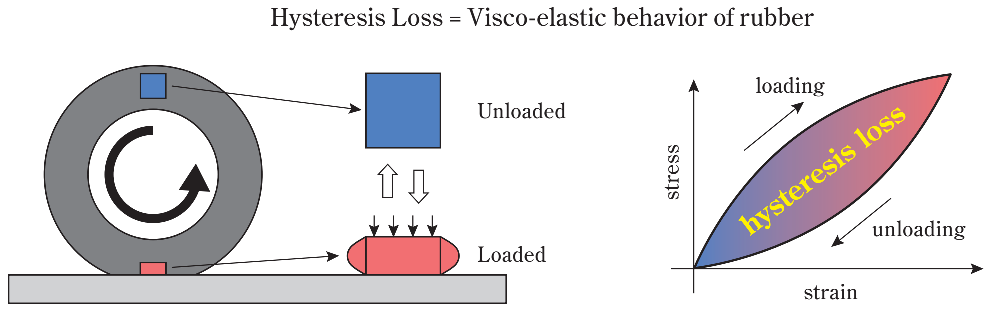


Fig. 1 Hysteresis Loss

Trend in Technology for Energy-Saving Tires

Generally, if the rolling resistance is reduced, the wet grip performance (which indicates the gripping power against wet road surface in the rainy weather) tends to deteriorate. For this reason, each tire manufacturer is engaged in various technological development in order to achieve both performances conflicting with each other. Furthermore, the Japan Automobile Tire Manufacturers Association (JATMA) has been providing information by displaying those two types of performance through the labeling system (domestically implemented since January 2010) (see **Fig. 2**). Europe has implemented a labeling system in which the third item regarding noise level has been added to the aforementioned two types of performance. South Korea also started implementing its labeling system around the same time as Europe. Moreover, the U.S. is also planning to introduce a labeling system. Thus global interest toward fuel-efficient tires with high performance has become heightened.

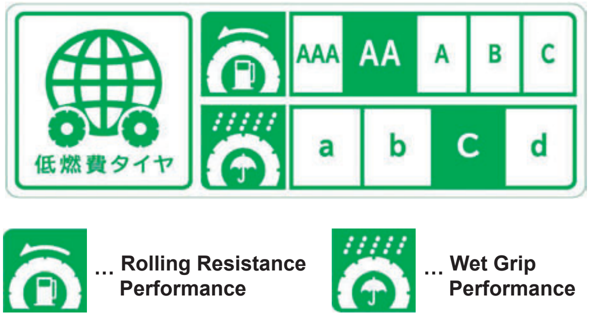


Fig. 2 Tire label[3]

A natural rubber (hereinafter referred to as NR)/CB compounding system had been popularly used for tire treads (areas where the tire comes in contact with the road surface) on passenger vehicles up until approximately a decade ago. However, automobile safety has recently become more of a priority, and now that Europe adopted styrene/butadiene copolymer rubber (hereinafter referred to as SBR) and silica-baced compounding systems, which demonstrates outstanding balance between fuel savings and wet-grip performance, SBR/silica-based compounding systems have become the mainstream globally in tire treads of passenger vehicles. When a SBR/silica-based compounding system was developed anew, it had the shortcoming of poor reinforcement property because silica had poor dispersion and low affinity with hydrocarbon-based polymers. However, partially due to the situation in which the fuel regulation for passenger vehicles was introduced before that for heavy-weight vehicles such as trucks or buses, the technological development for SBR/silica-based compounding systems progressed rapidly. Consequently, silane coupling agents such as TESPT (manufactured by Evonik Degussa GmbH) were developed as a means to improve the dispersion of silica. In silane coupling agents, the alkoxy silane moiety reacts to silica and the sulfide moiety reacts to polymers. The filler then becomes solidified onto the polymers by chemically binding polymers having low affinity and silica particles. Furthermore, a bound rubber that physically adsorbs close to the filler will be formed. Through this solidification and bond rubber formation, the following benefits can be achieved. Thus the dispersion of the filler can be improved, the friction between the fillers can be reduced and the reinforcement property can be improved. Consequently, these improvements will facilitate greater energy-saving performance. **Fig. 3** shows the typical silane coupling agents. Additionally, in regard to silica-based compounding systems, extensive research on silane coupling agents has been conducted thus far. Currently, the combined use of a silane coupling agent has become the mainstream.

Even today, however, NR/CB compounding systems are still used for tire treads used on trucks and buses

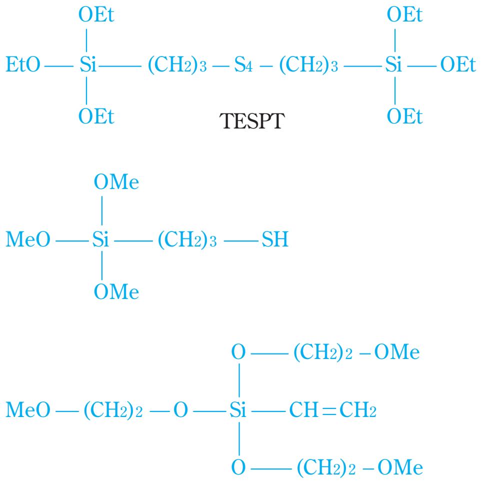


Fig. 3 Various silane coupling agents

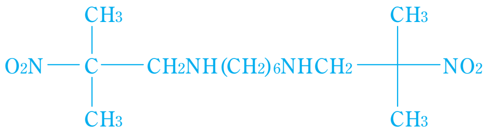
(such usage involving long-distance travel, often on rough road surfaces) due to their high elasticity and durability. Moreover, in addition to treads, the interior parts such as belts and sidewalls are also important components of the tire, and because CB compounding systems that mainly consist of NR are used regardless of the vehicle type, the percentage of NR/CB combined material use is still high in the tire-manufacturing industry.

Although the fuel-consumption regulations and a tire-labeling system for trucks and buses are progressing behind passenger vehicles, it was expected that the need for fuel savings in NR/CB compounding systems would become heightened for the future. Therefore, although measures such as reductions in the weights of vehicles and tires have been undertaken as with passenger vehicles, research has found no coupling agent that is useful for NR/CB compounding systems. For that reason, we believed that new coupling agents would also become highly required by tire manufacturers in the future. Thus, we began developing such agents in order to achieve fuel savings in NR/CB compounding systems by reducing hysteresis loss while traveling in NR/CB compounding systems.

Concept and Molecular Design

The reduction of the number of polymer molecular ends and the suppression of their mobility can be named as a means of reducing hysteresis loss. However, we believed it would be difficult to modify the properties of NR in terms of quality and cost because it is a natural product. Therefore, in reference to the example of silane coupling agents, we began to examine the possibility of improving the dispersion of CB by chemically binding or interacting NR and CB with the coupling agent in order to suppress the friction heat between the fillers.

Research on the CB dispersion technology has been conducted for quite some time. Howland et al. have discovered that N,4-dinitroso-N-methyl-aniline improves the dispersion of CB in NR/CB compounding systems, and that it is useful as a coupling agent that reduces hysteresis loss.4) Furthermore, Walker et al. have found that N-(2-methyl-2-nitropropyle)-4-nitrosoanitline has the effect of reducing hysteresis loss.5) **Fig. 4** shows the typical coupling agents. However, they are all nitroso-based compounds, of which production was discontinued in or around 1975. Although each manufacturer has subsequently worked to develop non-nitroso-based coupling agents, none has exceeded the performance of nitroso-based coupling agents. Under such circumstances, in 1989 Yamaguchi et al. discovered a dinitrodiamine compound (**Fig. 5**) that could significantly reduce hysteresis loss.6) Although it showed extremely high fuel-saving performance, it was not popularly used as a silane-based coupling agent due to its



$$O_2N-C(CH_3)_2-CH_2NH(CH_2)_6NHCH_2-C(CH_3)_2-NO_2$$

Fig. 5 BNAH

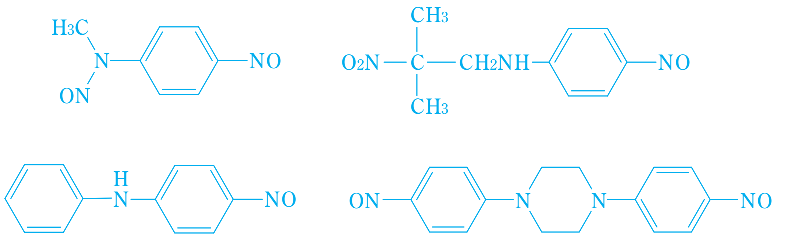
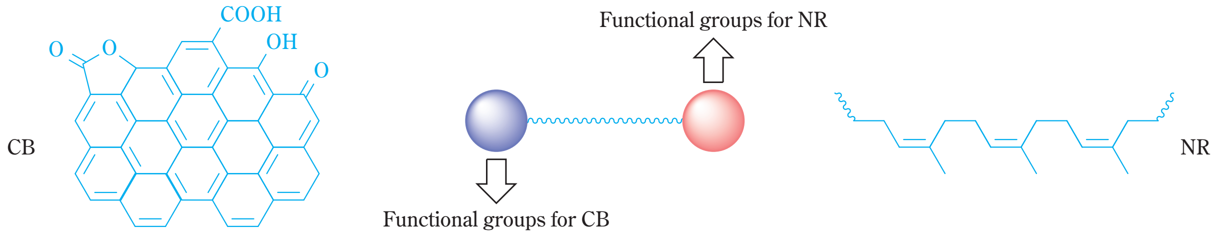
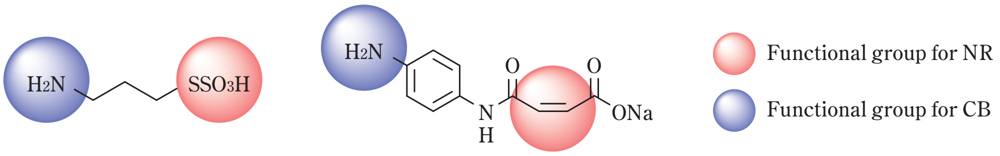


Fig. 4 Various carbon black coupling agents



Functional groups for CB	Spacer	Functional groups for NR
$-NH_2$, NHR, NR_1R_2	$-(CH_2)_n-$	$-S-SO_3M$ (H, Na, K, Li, Ca, etc)
-Ph-OH, $-CH_2OH$	n = 2, 3, 4, 5, 6, 9	$-S-SO_3R_1$ (NH_4^+, NR_4^+, etc)
$-CO_2H$, anhydride	-Cyclic	$-S-SO_2R_2$ (4-Me-Ph, Et, etc)
-Isocyanate	-Aromatic	$-S_x$, ($-S_2$, $-S_4$), SH
-Epoxy	-(Ph)-	-Olefin
-Olefin		-α, β - unsaturated carbonyl
-etc.		-etc.

Fig. 6 Screening of NR/CB coupling agent



SUMILINK®100

SUMILINK®200

Fig. 7 SUMILINK®100/200

workability issue. Since then, no carbon-black coupling agent having high performance has been developed.

Based on the above concept and the bi-functional mechanism[7] of the nitroso-based coupling agents, we began development by selecting a compound having the interacting groups for both CB and NR in a single target molecule. For the interacting group for CB, we chose a functional group that could interact with the phenolic hydroxyl group which is present on the surface of the CB or acid functionality, such as carbonyl group and thereby designed molecules. For the interacting group for NR, we chose either the functional group that could react to the double bond in the NR chain or the functional group that could react to radicals generated when the NR molecular chain is mechanically and oxidatively severed while mixing NR and other compounding agents such as fillers. By following the above strategy, we synthesized a large number of compounds and conducted evaluation screening (**Fig. 6**). As a result, we chose two chemical compounds (SUMILINK®100/200) as developing compounds because they showed particularly high fuel-saving performance during the first evaluation screening (**Fig. 7**).

Results and Discussion

1. Fuel-Saving Effects

(1) Effect of SUMILINK®100/200

Generally, manufacturing rubber products will go through the following processes: Process A, in which polymers, a filler, a vulcanization accelerator, a processing aid and an anti-oxidant are mixed together at a high temperature; Process B, in which a processing aid and a vulcanization accelerator are mixed together at a low temperature; and Process C, in which molding is performed under pressurized conditions at a high temperature using dies and the like (**Fig. 8**). **Table 1** shows the effect of the addition of SUMILINK®100/200 on the rubber properties in terms of fuel-saving performance, which were measured after Process A. (Additionally, the dynamic viscoelastic property (tanδ@60°C) was used as a laboratory evaluation index. The smaller this value is, the better the fuel-saving performance is.) It has been revealed that by adding a small amount of SUMILINK®100/200 under the general compounding conditions (see **Table 2**), the fuel-saving performance will improve significantly (**Table 1**). It is known that although increasing the amount of sulfur (which is a

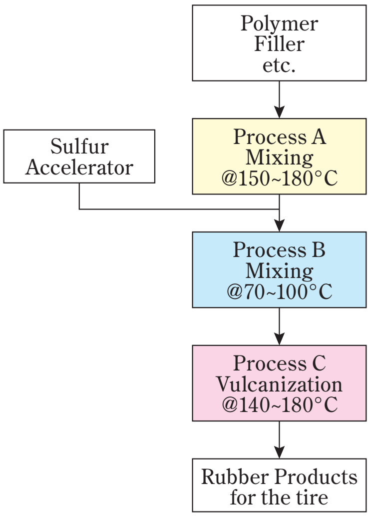


Fig. 8 Processing steps

Table 1 Effect of SUMILINK®100/200

	Control	SUMILINK®100	SUMILINK®200
tanδ@60°C	0.105	0.084	0.078

Table 2 Recipe

		phr
Process A		
NR	polymer	100
CB (N330)	filler	45
Zinc oxide	accelerator activator	5
Stearic acid	accelerator activator	3
6PPD	antioxidant	1
SUMILINK®100/200		1
Process B		
sulfur	vulcanizing agent	2
CBS	vulcanization accelerator	1

cross-linking agent) will improve the fuel-saving performance, the flexibility will decline because the number of cross-linking points will increase, thereby increasing the rigidity.

Declined flexibility hinders the tires from following the irregularity of the road surface due to its deformation, resulting in the deterioration of road gripping power. Furthermore, because impact toward the tires will not be absorbed but will directly affect the vehicle body, the ride will become more uncomfortable. However, unlike an increase in sulfur amount, an outstanding feature of the addition of SUMILINK®100/200 is that it can improve the fuel-saving performance without affecting other physical properties of rubber compounds such as rigidity (see **Fig. 9**).

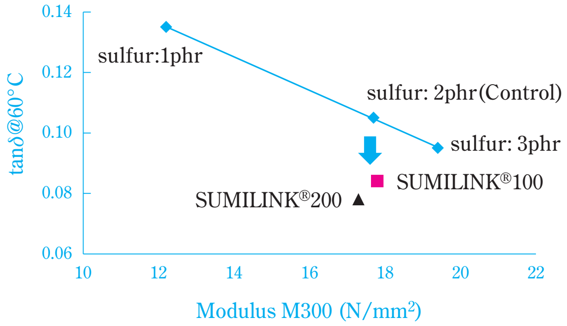
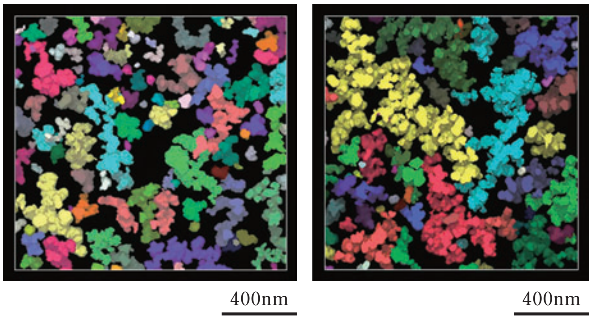


Fig. 9 Comparison with sulfur variate

In order to verify whether or not the improvement in fuel-saving performance was due to the dispersion of CB by using SUMILINK®100/200, as in the concept, we measured the 3D-TEM of the group, into which SUMILINK®200 had been added. In **Fig. 10**, the same color indicates a single CB aggregate and different colors mean different aggregates. Different colors also mean the different aggregates are separated from each other by a certain distance. It has been discovered that while aggregates are relatively large in a control group, each aggregate in the SUMILINK® 200-added group is smaller than that of the control group. This result suggests that adding SUMILINK® 200 will cause CB aggregates to collapse and disperse.



SUMILINK®200 Control

Fig. 10 3D-TEM

To further confirm the concept, we measured and analyzed the volume resistivity value and the Payne effect on the SUMILINK®100/200-added group (the Payne effect is a phenomenon in which, when distortion is given to the rubber, filler-to-filler interaction is destroyed. If this value is large, it means the bonding between the fillers is strong, indicating poor dispersion.) Consequently, the increase in the volume resistivity value was confirmed, suggesting the improvement in the dispersion of the CB, which serves as an electric conductor in the vulcanized rubber. Regarding the Payne effect, its decrease was confirmed, suggesting that the interaction between the CB aggregates (mainly intermolecular force) decreased and CB dispersion was thereby improved.

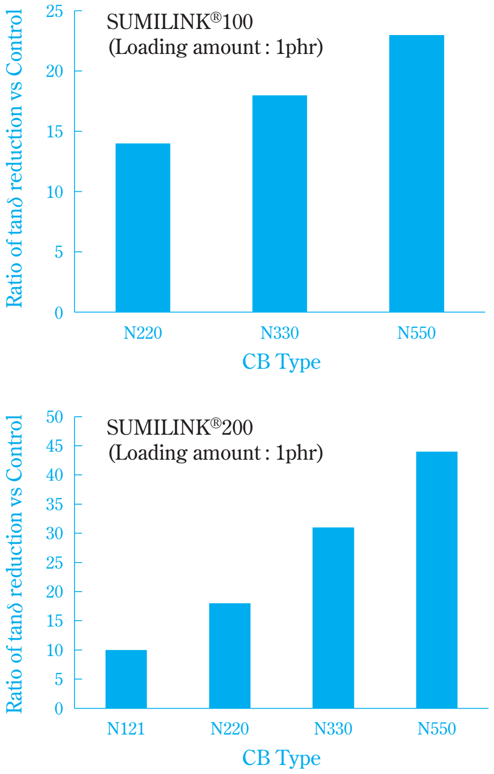
(2) Effect of CB Type

There are various types of CBs, and they are used for different purposes (see **Table 3**). For example, CBs having a small particle size and high reinforcement (N121 and N220) are used for treads. CBs having large particle sizes and low pyrogenetic properties (N550) are used for sidewalls, which do not directly come in contact with the road surface. We therefore confirmed the effects of SUMILINK®100/200 on each CB type. **Fig. 11** shows the results. Generally, due to the processing conditions during the CB manufacturing, the amount of acid functional groups differs depending on the CB type. The smaller the CB particle size is, the greater the amount of acid functional groups is. Contrary to this, it is known that CBs having a large particle size have less acid functional groups.[8] In the comparison of CBs containing the same amount of SUMILINK®100/200, CBs with a smaller particle size and a larger amount of acid functional groups showed less improvement in fuel-saving performance than in CBs with a larger particle sizes but smaller amount of acid functional groups. Although the reaction to the acid functional groups on the CB surface was expected, no correlation was observed with the amount of acid functional groups.

Table 3 CB type used in tire components

	Tread	Belt	Sidewall
CB type	N121(20), N220(22)	N330(28)	N550(45)

( ) : CB mean particle size (nm)



Ratio of tanδ reduction vs Control

$$= 100 - \frac{\tan\delta@60°\text{C (SUMILINK®)}}{\tan\delta@60°\text{C (Control)}} \times 100$$

Fig. 11 Effect of SUMILINK®100/200 in CB type

(3) Action Mechanism

To reveal the action mechanism of CB dispersion, we have confirmed the behavior of the bound rubber quantity and the Payne effect during each rubber mixing process. **Table 4** shows the results. Bound rubber is a polymer ingredient that adheres to CB, and it is insoluble in toluene, in which raw rubber dissolves (see **Fig. 12**). Although the magnitude of the effect varies depend-

Table 4 Behavior of bound rubber and Payne effect

	SUMILINK®100	SUMILINK®200
Bound rubber	increased	increased significantly
Payne effect of unvulcanized rubber	decreased slightly	decreased significantly
Payne effect of vulcanizates	decreased	decreased significantly

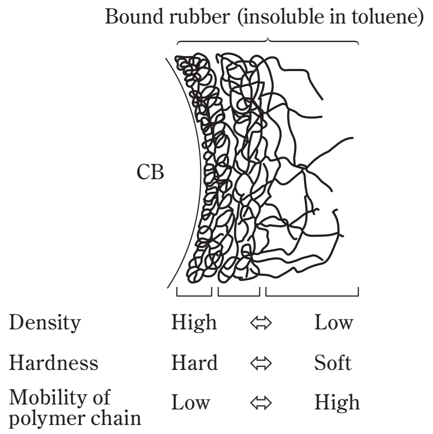


Fig. 12 Model of bound rubber

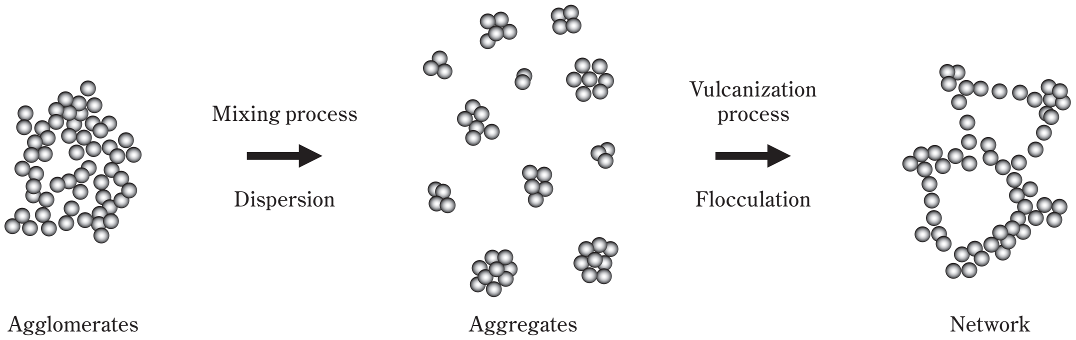


Fig. 13 Hypothesis of CB network

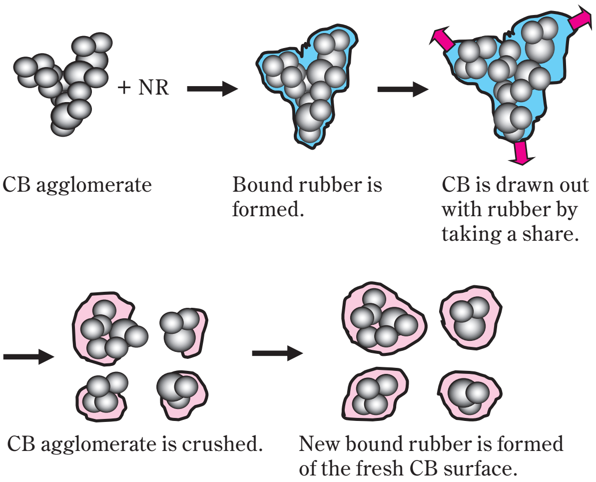


Fig. 14 Hypothesis of CB dispersion effect by SUMILINK®

ing on the type of CC agent during the CC agent-mixing process (see **Fig. 8**, Process A), the decrease of the Payne effect and the increase in bound rubber were observed, suggesting the possibility that bound rubber may contribute to CB dispersion.

As shown in **Fig. 13**, although CB is in the dispersion state during the mixing process, we have assumed the following action mechanism for SUMILINK®200, considering the fact that it has been reported that it re-aggregates upon vulcanization and forms a network.[9] The results are shown in **Table 4** (see **Fig. 14**):

(i) During the mixing process (see **Fig. 8**, Process A), SUMILINK®200, NR and CB are chemically bonded or interacted with each other and the formation of bound rubber becomes accelerated and its quantity increases;

(ii) When polymers and bound rubber become increasingly intertwined and thereby cause the shearing of the rubber compound, the destruction of CB aggregates tends to advance, as they are pulled by polymers;

(iii) New bound rubber is formed on the surface of the collapsed CB aggregates and it maintains the CB dispersion status; and

(iv) When increased bound rubber suppresses the re-aggregation of CB during the mixing process (see **Fig. 8**, Process C), the CB dispersion status will be maintained even after vulcanization, thereby producing a rubber compound that has fuel-saving performance.

Additionally, reviewing the results for each CB type described in (2) based on the above assumed action mechanism, because CBs with large particle sizes have a poor cohesive force between themselves, the dispersion status formed before vulcanization is maintained even after vulcanization. On the contrary, it is assumed that CBs with a small particle size having strong cohesive force form a network among CBs in the areas where bound rubber was not formed during vulcanization, and therefore the CB dispersion effect could be small.

Contrastingly, SUMILINK®100 shows a significant CB dispersion effect after vulcanization, although it shows a small increase in the amount of bound rubber and a small decrease in the Payne effect in the unvulcanized rubber. Based on this fact, we assume that SUMILINK®100 suppresses the formation of a CB network and demonstrates the CB dispersion effect through a mechanism that is different from SUMILINK®200. Furthermore, we surmise that SUMILINK®100 demonstrates the effect via a composite with sulfur (or a vulcanization accelerator) because the interacting group for NR is a radical-generator type on the sulfur atom.

2. Low Dynamic Magnification Effect

NR/CB compounding systems are widely used, not only for tires but for anti-vibration rubber. The requirements for anti-vibration rubber include low dynamic magnification and high attenuation (high hysteresis loss). The dynamic magnification is a ratio between the kinetic spring constant (Kd) and the static spring constant (Ks). In formula (1), when the dynamic magnification approaches 1–in other words, when the frequency dependency becomes smaller–the anti-vibration property becomes better. The previous techniques for improving the dynamic magnification include decrease in the CB amount and increase in the sulfur amount. However, because each method has shortcomings, such as decreases in rigidity and heat resistance, a new approach has been in demand.

$$\text{Dynamic-to-static modulus ratio} = \frac{\begin{array}{c}\text{Dynamic elastic modulus}\\ \text{(High frequency)}\end{array}}{\begin{array}{c}\text{Static elastic modulus}\\ \text{(Low frequency)}\end{array}} \quad (1)$$

We then evaluated the anti-vibration rubber property of SUMILINK®100/200, from which we had obtained satisfactory results from the previous evaluation using the NR/CB compounding systems **Table 5** shows the results of this new evaluation. Although it shows low hysteresis loss, it demonstrates a high dynamic magnification improvement effect. Unlike previous techniques, no adverse effect against rigidity or heat resistance can be observed. We therefore believe it is a promising measure for achieving low dynamic magnification.

Table 5 Effect on dynamic-to-static modulus ratio of SUMILINK®

sulfur/accelerator	Control	SUMILINK®100	SUMILINK®200
2/1	1.36	1.29	1.34
0.3/2	1.44	1.43	1.39

Furthermore, we have examined the use of SUMILINK®100/200 for each different purpose, depending on the combination of vulcanized materials. As shown in **Table 5**, SUMILINK®100 demonstrates a high degree of CB dispersion when sulfur is present, and, when using a material that contains a large amount of sulfur, SUMILINK® 100 brings out a greater effect. Contrastingly, in the material containing less sulfur, SUMILINK®200 shows a greater effect in lowering dynamic magnification.

It has thus been discovered that the low dynamic magnification effect can be achieved by selecting SUMILINK®100/200 for different purposes in accordance with the combination of vulcanized materials.

Conclusion

As described in this paper, it can be expected that SUMILINK®100/200 will have functionality as a novel CC agent for NR/CB compounding systems. Therefore, from this point forward SUMILINK®100/200 will contribute to improving the performance of rubber products, mainly for tires for trucks and buses but also for anti-vibration rubber. Furthermore, we hope to expand their applications to other areas in which CBs are used and to replace the existing techniques with new methods by using the combination of CBs and CC agents.

The performance level demanded in tires has become higher in recent years. This means even more advanced technology has become in demand. Accordingly, we believe that, after developing SUMILINK®100/200, it is necessary to keep developing not only additives that can provide a higher CB dispersion effect but to also develop a novel technology for greater fuel savings and higher performance. In order to respond to the need for improved performance in rubber products, we will continue to engage in development with our full effort.

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