Development and Foresight of Solution SBR for Energy-Saving Tires

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The market for solution styrene-butadiene rubber (S-SBR) which is mainly used for the treads of the energy-saving tires for automobiles has continued to expand rapidly while the fuel efficiency requirements for automobiles have been tightened worldwide. It is estimated that the annual S-SBR demand for 2011 will be between 400 and 350 thousands tons.

We have supplied special S-SBR with controlled molecular weight, molecular weight distribution and quantitative end-functionality to both domestic and international tire manufacturing companies and our S-SBR has been highly regarded.

This review first describes an overview of the recent situation for high performance energy-saving tires, then gives some details of our technology for both polymer design and synthesis and of the latest general analysis technologies.

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Introduction

In recent years, the awareness of the conservation of resources and energy has increased globally with a focus on countermeasures for global warming and environmental protection.

If we look at the transportation sector, which makes up 20% of the carbon dioxide emissions in Japan, approximately 90% of that is from automobiles. With this background, the Ministry of Land, Infrastructure, Transport and Tourism established the FY 2015 fuel economy standards based on the Act on the Rational Use of Energy. According to these standards, in FY 2015, improvements on an average of 23.5% over actual performance in FY 2004 are required for the fuel economy of passenger cars (**Fig. 1**). In the automobile industry, various measures related to energy conservation are being attempted in addition to this. For example, the Ministry of Land, Infrastructure, Transport and Tourism has decided to require measures for evaluation and publication of automobile fuel economy performance to promote the dissemination of automobiles with high-level fuel economy performance, and the performance for each automobile will be published

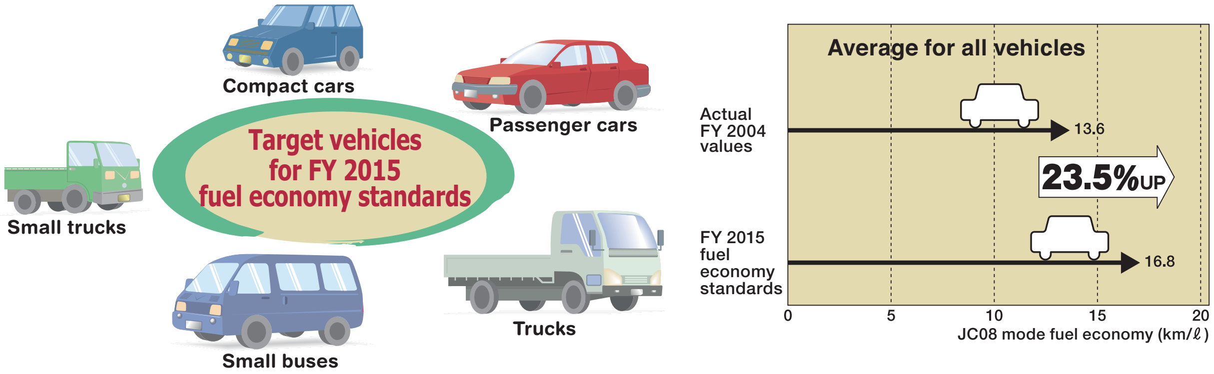

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Fig. 1 Target of fuel economy in 2015[1)] annually by manufacturer and model in a vehicle fuel economy list. Furthermore, the "ecocar" tax reduction policy (reduction of vehicle weight taxes, etc., for automobiles with superior environmentally friendly performance) that was in force last year is still fresh in our memories.

Tires are the only components of automobiles that make contact with the ground, and they make possible the fundamental automotive operations of driving, rolling and stopping by transferring the drive force of the engine to the surface of the ground. It is not too much to say that responding to the demands for greater performance in fuel economy without losing these fundamental performance properties has been the most important problem for tire manufacturers recently. With the dissemination of energy-saving tires, terms such as "low fuel consumption" and "rolling resistance," which were technical terms, have come to be recognized by the general public. In addition, there have been requirements for energy-saving performance in tires not only for passenger cars, but also for large vehicles such as trucks and buses in recent years.

Energy-saving performance is achieved through a variety of improvements and innovations from the fundamental structure of the tire to various types of materials, but among these the role played by the tread, which is the part coming into contact with the surface of the ground, is particularly important. This means providing polymer materials that give energy-saving performance and road surface grip, which is related to safety, in the trade-off between these two properties, and this is an area where the most is expected of the manufacturers of polymers for tires.

Sumitomo Chemical began solution polymerized styrene-butadiene rubber (SBR), which is mainly used in the tread part of tires, in 1983, and our SBR, with its well-designed and controlled structure has been supplied to tire manufacturers not only in Japan but also overseas and has received high marks from them. On the other hand, the demand for SBR for energy-saving tires has expanded rapidly with the strengthening of automotive fuel economy regulations worldwide, and an annual market of 350,000 to 400,000 tons is expected for 2011. In particular, tire manufacturers have designed new facilities one after another in Asian countries starting with China, India and Thailand; therefore, there are expectations for a quick expansion of SBR supply capacity. Under these circumstances, Sumitomo Chemical has decided to construct a new plant on Jurong Island in Singapore. The newly constructed plant will have an annual capacity for producing 40,000 tons, and the plan is to start commercial operations in the fourth quarter of 2013.

After giving an overview of the recent situation surrounding high performance energy-saving tires in this article, the authors would like to give an introduction to the design and synthesis technology for polymers and finally touch upon the latest analytical techniques.

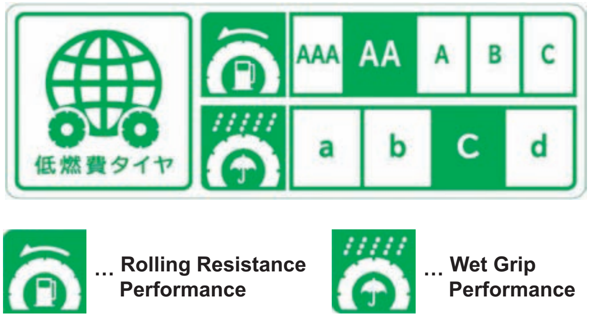
High Performance Energy-Saving Tires

1. Labeling system

In Japan, the Japan Automobile Tyre Manufactures Association (JATMA) has established labeling guidelines for promoting the dissemination of fuel-efficient tires (labeling system), and were put into effect in January 2010. The target of the guidelines is summer tires for passenger cars purchased by consumers at tire retail stores as replacements, and it creates a display (labeling) showing their performance. This system, where each tire manufacturer displays labeling that gives the performance for each tire in its catalogs and other documents, is implemented through voluntary standards in a form that general consumers can see directly. The labeling system shows two types of performance, fuel efficiency performance (rolling resistance coefficient (performance)) and wet grip performance (braking performance on the wet road surfaces), and each of these are displayed on the label. Fuel efficiency performance is divided into five grades, with the top being AAA, followed by AA, A, B and C, and wet grip performance is divided into four grades a through d (**Fig. 2**). If the coefficient of rolling resistance is 9.0 or less, A or higher, tires with wet grip performance a through d are defined as fuel efficient tires.

At present, as of March 2011, eight tire manufacturers are participating in the voluntary standards, and 24 products are classified as fuel efficient tires. Currently there are three tires among these with the top fuel efficiency performance of AAA.

This kind of labeling system has started with Japan, but South Korea and Europe plan to introduce such systems. In Europe, in particular, there is a plan to require rolling noise (road noise) labeling in addition to fuel efficiency performance and wet grip performance. In addition, the introduction of a labeling system in the United States is being investigated.



Unit (N/kN)

RRC	Grade
RRC≦6.5	AAA
6.6≦RRC≦7.7	AA
7.8≦RRC≦9.0	A
9.1≦RRC≦10.5	B
10.6≦RRC≦12.0	C

Unit (%)

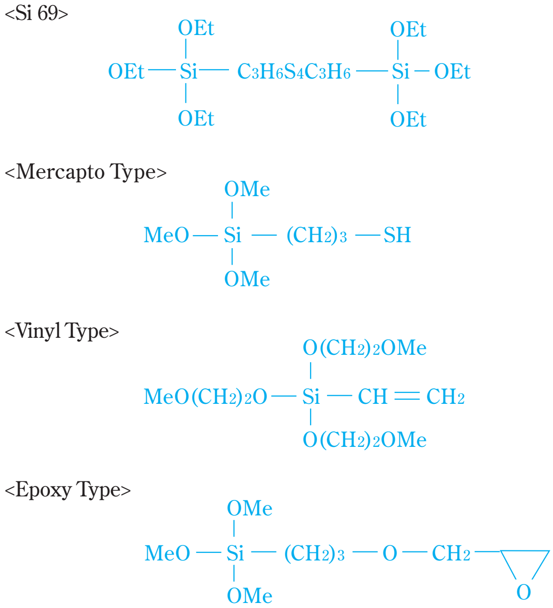
Wet Grip performance (G)	Grade
155≦G	a
140≦G≦154	b
125≦G≦139	c
110≦G≦124	d

Fig. 2 Labeling for "Fuel Efficient Tires" by JATMA[2)]

2. Silica-compound rubber

To maintain strength in tires, the raw rubber starting material must first of all be vulcanized, and it must be compounded with a filler (reinforcing filler) to improve strength. The designs for compounding in passenger car tire treads have been greatly transfigured in the last 20 years or so. Silica is used frequently instead of the carbon black that has been known for a long time as a filler. From the standpoint of fuel efficiency performance and wet grip performance, using silica as a filler, in other words, silica compounding, is an indispensable technology for high-performance fuel efficient tires that started in Europe and has spread to the rest of the world.

Since the surface of silica is coated with hydrophilic silanol groups, its affinity for hydrocarbon polymers is typically lower than carbon black, and there are difficulties in that good dispersion is difficult and without modification the reinforcing properties are inferior. Silane coupling agents, typified by Evonik Degussa GmbH Si 69, have appeared as a means for resolving these difficulties (**Fig. 3**). A silane coupling agent is typically a polysulfide compound having a combination of six alkoxysilyl groups and (S)n bonds, and the alkoxysilyl group parts form an intermediary that chemically bonds the low affinity SBR and silica particles by cleaving the (S)n bonds and reacting the silica surface with the double bond parts in the SBR. With the use of silane coupling agents, silica compound rubber has made it possible to achieve advanced physical properties that could not be obtained with carbon compound rubber. Furthermore, there is now an inexpensive and stable supply of silane coupling agents, which were extremely expensive at the beginning of development, because of the development of an innovative synthesis method using sodium oligosulfides as the starting materials[3)] and breakthroughs in synthesis techniques. Silica-compound rubber has disseminated widely centering on the field of high-performance fuel efficient tires.



<Si 69>

$\mathrm{OEt-Si(OEt)(OEt)-C_3H_6S_4C_3H_6-Si(OEt)(OEt)-OEt}$

<Mercapto Type>

$\mathrm{MeO-Si(OMe)(OMe)-(CH_2)_3-SH}$

<Vinyl Type>

$\mathrm{MeO(CH_2)_2O-Si(O(CH_2)_2OMe)(O(CH_2)_2OMe)-CH=CH_2}$

<Epoxy Type>

$\mathrm{MeO-Si(OMe)(OMe)-(CH_2)_3-O-CH_2-}$

Fig. 3 Various silane coupling agents

In addition, development of new silane coupling agents has accelerated with the increase in the demand for high-performance fuel efficient tires. For example, a variety of silane coupling agents for rubber have been developed, including mercapto based ones such as gamma-mercapto-propyl trimethoxysilane, vinyl based ones such as vinyl tris (2-methoxy ethoxy) silane and epoxy-based ones such as gamma-glycidoxy-propyltrimethoxysilane. For all of the silane coupling agents, the point of bonding with silica because of the alkoxysilyl groups is the same as for the conventional polysulfide-based ones, but a variety of innovations have been made in the bonding scheme for SBR. The development of silane coupling agents that further increase the dispersibility of silica and allow free control of the bonding with the polymer is anticipated.

Solution Polymerized SBR for Silica Compounding

At Sumitomo Chemical, we are aiming at establishing both grip performance and fuel efficiency performance for silica compound SBR from the standpoint of controlling the polymer structure. Solution polymerization SBR is synthesized by living anionic polymerization; therefore, the basic backbone of the polymer (styrene or butadiene composition, glass transition temperature, molecular weight, molecular weight distribution, microstructure, etc.) can be controlled precisely.4) Furthermore, we are examining basic polymer backbones and the introduction of polar functional groups in the polymer aimed at developing new silica compound grades. By introducing polar functional groups and increasing the polarization of the polymer itself, we can expect to have a good direct effect on the affinity for the hydrophilic silica. With silica compounding, we cannot expect physical binding as is seen between carbon and rubber components; therefore, the introduction of polar functional groups to the polymer chain is even more important, as are silane coupling agents.

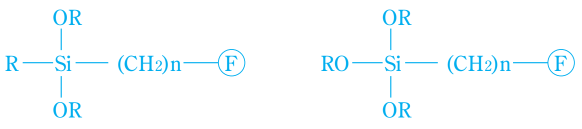
The introduction of polar functional groups to polymer chain terminals can be achieved comparatively easily by reacting growing terminal polymer anions having high nucleophilic properties with a terminal modifier that is an electrophilic reagent.5) In this method, the functional groups are introduced to terminal groups for which polymerization has stopped. Besides amino groups and hydroxyl groups, which are typical polar groups, there have been reports of the introduction of siloxane compounds, epoxy compounds, tin compounds, etc., and it is clear that they contribute to improvements in fuel efficiency performance.6), 7)

Recently, there have been attempts at using alkoxysilane compounds in modifiers as an application of the concept for silane coupling agents, and this is attracting attention.8), 9) There have been reports of SBR with polymer chain terminals modified by gamma-glycidoxypropyltrimethoxysilane, which was described earlier as a new silane coupling agent.

Sumitomo Chemical is investigating the use of its own alkoxysilane compound. Here we will introduce its interesting synthetic strategies.

1. Alkoxysilyl group modified SBR

It is known that in the reaction of living polymers of SBR and alkoxysilyl groups, the nucleophilic addition reaction of the polymer anions occurs rapidly, and the alkoxy groups are detached. Therefore, the special reaction system should be designed in order to introduce the alkoxy groups into the polymer chain terminals. Using di-alkoxysilane compounds and tri-alkoxysilane compounds (**Fig. 4**) having functional group F, we made it possible to design various polymer molecules through ingenuity with the reaction conditions, and specifically, addition conditions and reaction conditions.



$$R-\overset{OR}{\underset{OR}{Si}}-(CH_2)_n-\textcircled{F} \qquad RO-\overset{OR}{\underset{OR}{Si}}-(CH_2)_n-\textcircled{F}$$

Fig. 4 Di-alkoxysilane and tri-alkoxysilane with functional group Ⓕ

We will describe this (**Fig. 5**) using a tri-alkoxysilane compound as an example. If one alkoxy group of the tri-alkoxysilane compound reacts with the living polymer SBR, SBR (1) with two alkoxy groups and functional group F introduced to the chain terminal is obtained. If two alkoxy groups of the tri-alkoxysilane compound react with the living polymer SBR, two SBR chains are bonded, and a coupled polymer (2) with one remaining alkoxy group and functional group F introduced at the bonding site is produced. In addition, if three alkoxy groups of the tri-alkoxysilane compound react identically with the living polymer SBR, only functional group F is introduced, and a three branch star polymer (3) having no alkoxy groups is produced. It becomes important to increase the proportion of production of SBR (1)

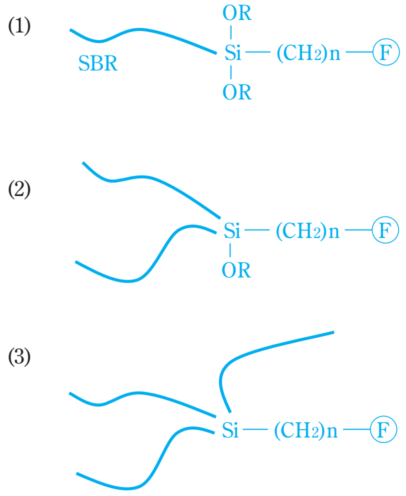


Fig. 5 Resulting SBR structures (1) – (3)

with many alkoxysilyl groups introduced to express fuel efficiency performance in silica compounding systems.

We changed the adding time of active terminals and equal amounts of the tri-alkoxysilane compound to SBR living polymer that was synthesized in an autoclave. In this instance, the rate of addition for the tri-alkoxysilane compound was slow, and the smaller the amount of each addition, the greater the insufficiency of the alkoxy groups. Therefore, it is preferable for the addition rate to be as fast as possible. As predicted, the results showed that there was a reduction in coupled polymer when the addition rate was made faster (**Fig. 6**). The rate of production of coupled polymers was also clearly affected by the strength of the stirring and the molecular weight of the SBR living polymer.

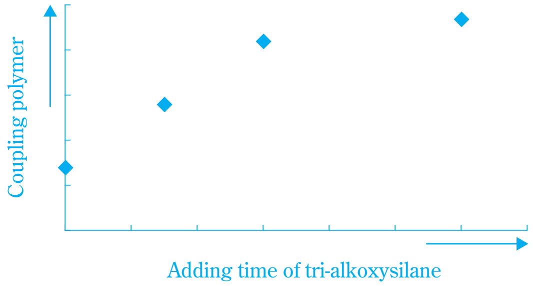


Fig. 6 Coupling polymer against adding time of tri-alkoxysilane

Since there is either one alkoxy group that can bond with the silica surface or none present in the coupled polymers, the contribution to establishing both a targeted fuel efficiency performance and grip performance is low. On the other hand, strength is increased by increasing the molecular weight, and improvements in processability, etc., can be expected by expanding the molecular weight distribution. At Sumitomo Chemical, we have discovered SBR design techniques with a variety of characteristics by controlling various synthesis conditions. For example, even when the same tri-alkoxysilane compound was used, we were successful in freely and simply synthesizing polymers with the various molecular weight distributions shown in **Fig. 7** by changing the design technique. In the synthesis of polymers having this kind of multifarious molecular weight distribution, coupling agents corresponding to each of the molecular weights had to be selected conventionally, and reactions corresponding to the several stages or polymer blending were required. It might be that by using tri-alkoxysilane, it will be possible to more simply and precisely control molecular weight distribution, and we can expect an improvement in SBR performance.

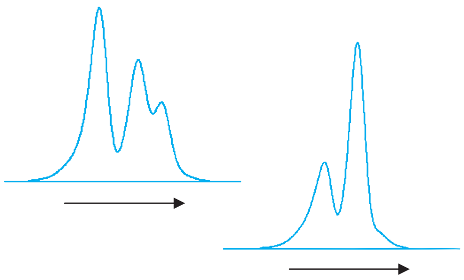


Fig. 7 GPC curves of various functionalized SBR with tri-alkoxysilane

2. Next generation multifunctional SBR

At Sumitomo Chemical we have not only introduced multiple functional groups at the chain terminals but also along the chain at multiple sites, and we have developed multifunctional polymers ahead of other companies. Multifunctional polymers can have unlimited types of designs (**Fig. 8**) through the selection of the types and number (length between functional groups) of multifunctional groups, and there are great expectations for their performance and possibilities. However, there are a vast number of factors that must be controlled for achieving molecular designs for each multifunctional polymer. Therefore, in the field of polymer synthesis, it has conventionally been extremely difficult to introduce functional groups of a specific number to specific sites, and even looking at the very few reports of examples, most of them have required multiple vexatious synthesis procedures. However, at Sumitomo Chemical we have developed several innovative synthesis methods for multifunctional polymers,

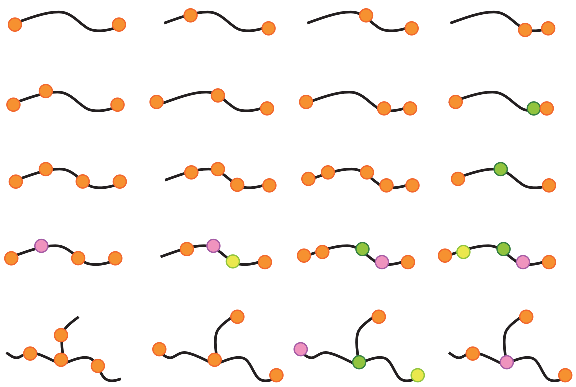


Fig. 8 Various multi-functional polymers

and it is truly possible to achieve order-made polymers. One example of this is our gaining a high level of recognition in industry and academia with development of a simple synthesis method for multifunctional polymers using 1,1-diphenylethylene (DPE) derivatives.[10), 11)]

Here we will introduce the design and performance of Sumitomo Chemical multifunctional SBR.

We synthesized polymers with the same type of functional group introduced in different numbers and sites (**Fig. 9**). Specifically, we synthesized ones with the functional groups introduced on both ends of the polymer chain and ones with the functional groups introduced in the middle and at the end of the chain of the polymer for polymers where to functional groups were introduced, and for polymers where three functional groups were introduced, we synthesized ones where the functional groups were introduced at substantially even intervals along the chain. The structures and performance evaluation results for the polymers obtained are summarized in **Table 1**. A value measured using a Lubke resilience tester at 60°C according to JIS K–6255 was used for the resilience, which is one index of fuel efficiency performance. The larger the value for resilience is the more superior fuel efficiency performance is indicated.

Fig. 9 Multi-functional polymers synthesized

Table 1 Evaluation results of multi-functional polymers

	Mw	ML$_{1+4}$ 100°C	Resilience
	35.7	56	57
	34.8	51	64
	37.7	63	62
	29.5	53	65

While there was always a functional group introduced on one end of the polymer in both of the polymers where two groups were introduced, the polymers with three groups introduced all introduced the functional groups along the chain. In the case of the functional groups used this time, the resilience value gave better results in all cases than for the polymers with one modified terminal. The more the number of functional groups is increased, the higher the resilience is, and in comparing two types of polymers with two functional groups introduced, the polymers with functional groups introduced at both terminals gave better results than the polymers with functional groups in the middle and chain terminal. It is predicted that these results will vary greatly according to the type of functional group introduced, and it is possible that performance not possible up to now will be expressed through molecular design that makes use of the characteristics of functional groups.

Study on Elucidating the Relationship between Morphology and Mechanical Properties

With the silica compounding that is necessary for high performance fuel-efficient tires, it is possible to improve the balance between fuel efficiency performance and wet grip performance at a high level in comparison with the carbon black used up to now as was described previously. Since the silica particles have a hydrophilic surface, the wet grip during rain is better than that with carbon black compounding. On the other hand, the hydrophilicity of the silica particles reduces the compatibility with the hydrophobic polymer, and since this prevents the dispersion of the silica, there is concern about energy loss due to friction among the filler particles in parts where the filler has clumped and a lowering of the abrasion resistance because of clumping of the filler particles.

However, with the use of silane coupling agents and the improvement in dispersibility of the silica particles by modifying the parts of the molecular chain of the polymer, superior fuel efficiency performance has been achieved.

On the other hand, various tire manufacturing companies have started optimizing tire grooves using computer simulations and other tools, and development aimed at improving tire performance is moving forward through total tire design.

In addition, there have been attempts to elucidate the correlation between structure and physical properties in various studies focusing on the silica dispersibility and the rubber characteristics in the vicinity of the silica particles. In this section, we will describe the recent trends in this structural analysis and the outlook for the future.

1. Relationship between viscoelastic properties and tire characteristics

The expression of fuel efficiency performance and grip performance functions may be thought of as being determined by the size of the hysteresis loss (= tan δ) for the material in the mode of movement that impacts the tire from the road surface. Hysteresis loss is the energy lost by the material when impacted mechanically by periodic motion. **Fig. 10** shows a schematic diagram of hysteresis loss. The reduction of hysteresis loss means driving a vehicle without wasteful consumption of energy of motion, and is connected to improving fuel efficiency performance. Conversely, if hysteresis loss is increased, the energy of motion is converted into heat energy, and the grip performance can be improved.

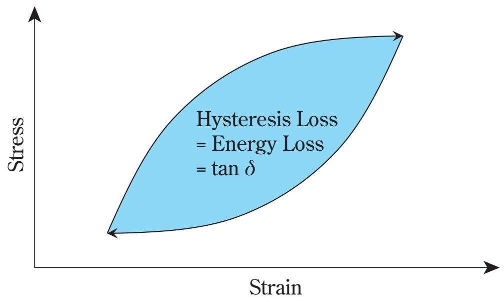


Fig. 10 Schematic image of hysteresis loss

At a glance, the two of these can be seen as types of performance that absolutely cannot be established together, but as is shown in **Fig. 11**, it is known that the movement mode (frequency) is different for each of fuel efficiency performance and grip performance. By designing suitable materials, balance at a high level is possible.12)

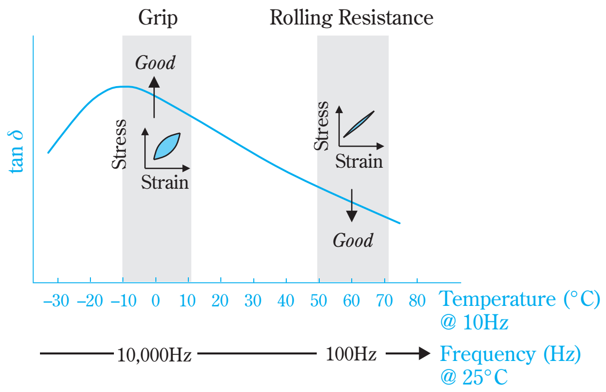


Fig. 11 Relationship between tan δ and performance of tire

2. Relationship between dispersion structure of silica and tire characteristics

The primary particles of silica compound in tires have a size of approximately 20 to 30 nm, and as was discussed previously, they have the property of clumping easily due to hydrogen bonds. Therefore, the silica in the rubber is known to have a clumpy structure to a greater or lesser extent. The significance is that smaller the size of these clumps is the greater the dispersion of the silica particles, and we can assume that it will improve the fuel efficiency performance and grip performance. For example, as a result of observations using a transmission electron microscope of the silica dispersed in various polymers (SBR A, SBR B and SBR C) that have been modified, **Fig. 12** shows a comparison of superiority and inferiority of fuel efficiency performance and grip performance.

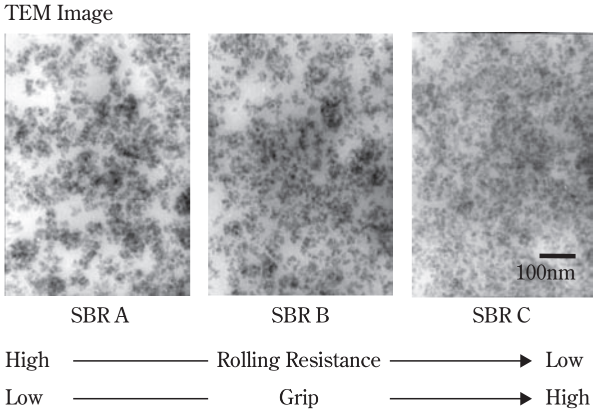


Fig. 12 Relationship between dispersibility of silica and performance of tire

To balance the two properties of fuel efficiency performance and grip performance and a high level, it is important to disperse the silica by carrying out effective modifications to the polymer as described previously. The dispersion state of the silica in the rubber can be observed using a transmission electron microscope. However, two-dimensional information is obtained by this method, and it is difficult to obtain information on the clumping structure of the particles, which spreads out over three dimensions.

The recently developed three-dimensional transmission electron microscopes solve this problem. Using this method, three-dimensional information on the clumping structure of the silica can be obtained from the beginning.13) Since it has become possible to "directly" observe the position and size of the silica, the specific size of the clumping structure, there have been reports of simulations of the effect of the silica clumping structure in the rubber using the finite element method.14)

However, even though three-dimensional transmission electron microscopes are an extremely effective means for obtaining three-dimensional information visually, the range of observation is small, on the other hand, and the statistical information is somewhat poor. From the standpoint of compensating for this, attempts are being made at ultra small angle to small angle X-ray scattering tests. In addition, research is being done to elucidate the relationship between hysteresis loss and dispersion state by simultaneously making axially extended tensile measurements using radiant light and x-ray scattering measurements to clarify the process by which hysteresis loss occurs due to the clumping of silica particles.15)

Furthermore, attempts are being made at tracing the changes in silica dispersion arrangements using a method called reverse Monte Carlo method from the two dimensional X-ray scattering images obtained through these experiments,16) and there have been reports of simulations using these results on the effects of the silica clumping structure in rubber on mechanical properties using the Earth Simulator.17)

If the clumping of silica particles can be controlled by combining three-dimensional electron microscope and ultra small angle to small angle X ray scattering techniques with simulation techniques as described above, local distortion can be controlled, so it becomes possible to make the mechanism for reducing hysteresis loss visible.

3. Role of rubber bound to silica

Up to this point we have described the role of the silica dispersed in silica-compound rubber. On the other hand, it has long been known that when rubber has been kneaded with fillers such as carbon black and silica, there is rubber that is bound around the filler.

Using the property of rubber that has strongly bound to silica not being soluble in organic solvents such as toluene, it is possible to measure the amount of absorbed rubber in the mixture of the silica and rubber before vulcanization. For example, the amounts of bound rubber given for the polymers that we have developed are given in **Table 2**. Comparing this with **Fig. 12**, we can qualitatively see that tire characteristics are more superior the greater the amount of bound rubber is.

Table 2 Amount of bound rubber after mixing rubber, silica and curing reagents

	SBR A	SBR B	SBR C
Bound Rubber (wt%)	50 – 60	60 – 70	80 – 90

In addition, the polymer molecule chains of the rubber that is bound to the filler are more confined then the rubber that is not bound, so it can be said that the glass transition point is higher. The various proportions of rubber that is bound to the filler and rubber that is not bound that are present influence the temperature range corresponding to various modes of movement and the viscoelastic properties of frequency. As a result, the fuel efficiency performance and grip performance are affected. The correlation between the state of binding of the polymer molecular chain on the solid surface and the glass transition temperature is being investigated using molecular dynamics calculations. Here, it has been reported that in ones where a loop shape is formed by binding both terminals, the glass transition temperature is higher than in cases of binding at one terminal.18) It is possible to control the morphology of the binding to the filler by modifying the polymer, and there have been reports suggesting that the viscoelastic behavior can be controlled by the morphology of the molecular chain that is bound to the silica.

In addition, tests of methods for measuring the how the molecular chains of bound rubber are confined by the silica particle surface using pulse NMR have been conducted, and attempts have been made at verifying the state of confinement of the bound rubber phase at the silica surface from the relaxation time.19) The result is that the rubber component bound to the silica is more confined within that which is not bound.

On the other hand, neutron scattering has recently been proposed as a method for measuring the size of the silica clumping structure and the thickness of the bound rubber, and the specifics of the thickness of the bound rubber are becoming clearer.20), 21) In this investigation by Takenaka et al., results of a bound rubber phase thickness of 5.3 nm have been reported for a primary silica particle size of 13.6 nm and a clump size of 65.4 nm.

By also incorporating this information into simulations, we think it will be possible to predict physical properties with high precision in the future.

4. Future Outlook

In this manner, techniques for elucidating the various characteristics of the filler dispersion structure and bound rubber are being established. It can be assumed that these various factors are operating and that they affect the viscoelastic behavior for the tire characteristics, but to elucidate the manner in which these factors act and actually contribute to tire properties, studies that consider each factor are necessary. In addition, attempts at analysis are being made using mechanical models that make use of the difference in glass transition temperature for bound rubber and rubber that is not bound.[22] Along with further developing techniques of this sort, we think it is important to establish detailed mechanical models by considering a variety of information such as the structures and properties of the polymers and compounding material.

If mechanical models that incorporate information conforming to a variety of real states can be proposed, we can predict structures (desirable parameters in mechanical models) that will provide desirable characteristics, and we can understand what factors we need to work with to achieve these. Therefore, we should be able to elucidate desirable forms for the structures of polymers that form the starting materials.

In particular, the possibility that the controlled polymer structure (primary structure, branch structure and modification morphology) has a large effect on the morphology of the bound rubber that typifies the dispersion structure of the filler has been suggested.

Moving forward, we think it will not only be important to precisely synthesize polymers having a variety of structures, but also develop materials comprehensively with a multifaceted approach in elucidating the relationships between compound rubber structural analysis and physical properties.

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