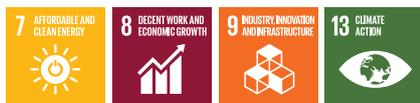


# Development of EPDM with Excellent Cold Resistance

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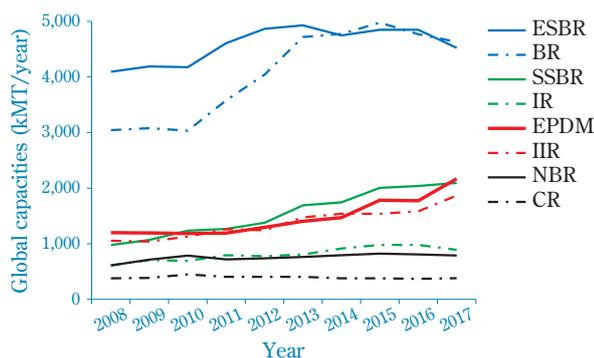


In recent years, demand has been increasing for rubber products having rubber elasticity in a low temperature range, that is, excellent cold resistance. In order to improve the cold resistance of rubber products, it is extremely important to improve the cold resistance of the main component, synthetic rubber. We have developed novel ESPRENE® EPDMs that have excellent cold resistance which is greater than conventional EPDMs by controlling composition distribution and copolymerizability with our proprietary technology. In this paper, we introduce the development of EPDMs with excellent cold resistance.

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## Introduction

The production capacity for ethylene propylene diene copolymer rubber (EPDM) is on a scale next to styrene butadiene rubber (SBR) and butadiene rubber (BR) among the synthetic rubbers (Fig. 1).<sup>1)</sup> Unlike natural rubber (NR) and diene rubbers such as SBR and BR, the main chain for EPDM does not have double bonds,



ESBR: Emulsion styrene-butadiene rubber  
BR: Polybutadiene rubber  
SSBR: Solution styrene-butadiene rubber  
IR: Polyisoprene rubber  
EPDM: Ethylene-propylene-diene terpolymer  
IIR: Butyl rubber  
NBR: Acrylonitrile-butadiene rubber  
CR: Polychloroprene rubber

**Fig. 1** Trend of synthetic rubber production capacities in the world  
Created using data from cited reference 1).

so it is superior in terms of weather resistance, ozone resistance and heat resistance. In addition, since it does not have polar groups, the intermolecular force is low, so it also has the characteristic of being highly fillable with fillers. Because it has these characteristics, EPDM has applications in rubber automotive components such as various types of weatherstripping, radiators/heater hoses, brake hoses and various types of vibration isolating rubber as well as other applications and is used in a wide variety of applications such as waterproof sheets, building packing, electrical cables, improved materials for weather resistance and ozone resistance over diene rubbers such as NR, raw material for thermoplastic elastomers and viscosity index improvers for mineral oil.<sup>2)</sup>

While the characteristics for mechanical strength, viscoelastic properties, heat resistance, cold resistance, etc. required for each of these applications are different, component manufacturers and automobile manufacturers are improving safety in rubber products and comfort in automobiles; therefore, they are always trying to create products with superior physical characteristics and quality and have many needs for improvements in the synthetic rubber for raw materials. Among the characteristics that are required, one important characteristic is cold resistance. Having rubber elasticity even at low temperatures, that is, superior cold resistance, is connected to reliability in rubber products at low temperatures. Therefore, research and development are being carried out for cold resistance in EPDM, and for exam-

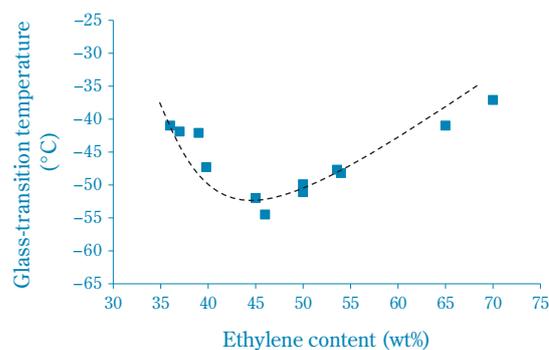
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ple, there been reports of improving low temperature range characteristics using the aspects of polymer structure and compounding for EPDM.<sup>3)</sup> Recently, the requirements for rubber products with superior cold resistance at low temperatures have been increasing. For example, with the dissemination of fuel cell vehicles (FCV), hydrogen stations are being installed in various regions, and when an FCV is filled with hydrogen, temperature increases because of adiabatic compression of the gas; therefore, hydrogen is cooled to  $-40^{\circ}\text{C}$ . Therefore, seals that have sealing performance at the low temperature of  $-40^{\circ}\text{C}$  are required for dispensers.<sup>4)-6)</sup> Furthermore, in cold regions such as those in North America, Europe and Russia, the pursuit for safety and comfort greater than that of conventional rubber products can be thought of as another factor. Thus, in recent years, there has been a focus on this cold resistance for which there are increasing demands, and since we have been successful in developing ESPRENE<sup>®</sup> EPDM, which has cold resistance improved over conventional EPDM through Sumitomo Chemical Co., Ltd. proprietary technology, we will give an introduction to it.

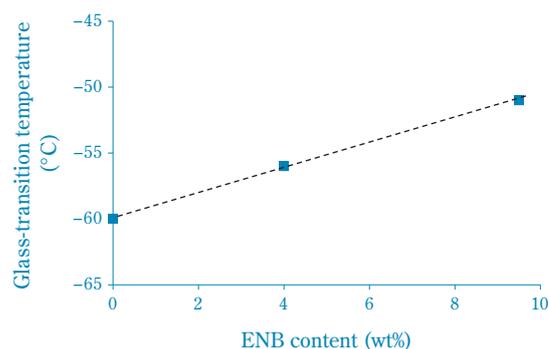
## EPDM Polymer Structure and Cold Resistance

### 1. EPDM Monomer Composition Ratios and Glass Transition Temperatures

The cold resistance of EPDM is one important characteristic, and research and development are becoming more active than it has been conventionally. Linning et al. are studying the relationship between propylene content and crystallinity in ethylene propylene copolymer rubber (EPM) by x-ray diffraction and have reported that if the propylene content is 40 wt% (31 mol%) or less, the ethylene portion crystallizes.<sup>7)</sup> Furthermore Maurer et al. have shown a relationship between EPM ethylene/propylene copolymer ratio and glass transition temperature ( $T_g$ ).<sup>8)</sup> The ethylene content of commonly marketed EP(D)M is approximately 40 - 80 wt%, but it has been reported that at an ethylene content of around 55 wt% (65 mol%),  $T_g$  becomes an extremely small value. Moreover, it has been found that  $T_g$  rises in EPM in which the ethylene content is lowered more than the ethylene content leading to the extremely small value for  $T_g$ . This can be thought of as being caused by an increase in the number of methyl groups ( $-\text{CH}_3$ ), which are bulkier than hydrogen, with the increase in the propylene content, making the rotational movement of the polymer chain being slower.<sup>9)</sup>



**Fig. 2** Ethylene content and  $T_g$  of several EPDMs



**Fig. 3** ENB content and  $T_g$  of several EPDMs

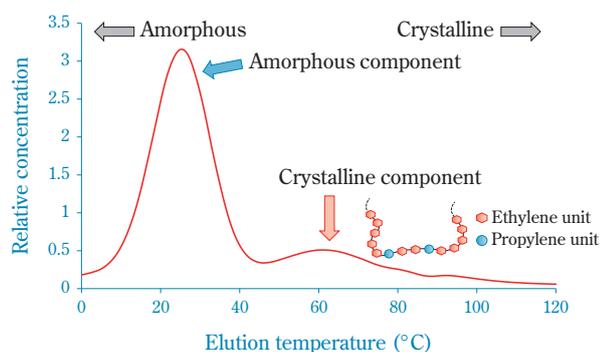
In EPDM, to which a diene component, which is a third component, is introduced, the same relationship as with EPM also arises, and the relationship between ethylene content and  $T_g$  is shown in **Fig. 2**. Ethylene chains depend on the polymerization catalyst and polymerization conditions for the EPDM, and while the ethylene content making  $T_g$  the smallest is not fixed, it has been reported that the ethylene portion can be crystallized when sequences of seven or greater ethylene units are formed,<sup>7)</sup> and it is said that chains with 16 or more form crystals that can be detected by x-ray diffraction.<sup>10)</sup> Therefore, it has become clear that the copolymer ratio for ethylene and propylene and the proportion of ethylene chains have a large effect on the cold resistance of EPDM. Furthermore, the diene content also affects  $T_g$ , and when 5-ethylidene-2-norbornene (ENB) was used as the diene component,  $T_g$  tended to increase with the increase in ENB content (**Fig. 3**). It is thought that since ENB is a monomer that is bulkier than ethylene and propylene,  $T_g$  increases.

### 2. EPDM Composition Distribution and Ethylene Chains

The ethylene/propylene composition ratio, composition distribution, molecular weight, molecular weight

distribution, type of diene component, diene content, branching, etc. can be cited for the EPDM polymer structure, but the ethylene/propylene composition ratio is thought to have the greatest effect on cold resistance. By making the composition of EPDM have a low ethylene content, the cold resistance increases remarkably, but in recent years, with EPDM that is simply low in ethylene content, the standards required for cold resistance cannot always be met. As a cause for this, it is thought that it is dependent on the ethylene content distribution even though the average ethylene content for conventional low ethylene content EPDM is low; therefore, there is EPDM with an ethylene content higher than the average ethylene content included. Furthermore, even with the same ethylene content, it is speculated that ethylene crystallization will occur easily if the proportion of ethylene chains in the polymer chains is high.

To analyze the composition content distribution, EPM with an ethylene content of 49 wt% was used and thermal gradient interaction chromatography (TG-IC) was measured (Fig. 4). The TG-IC measurement conditions are as follows. Measurement solvent: ortho-dichlorobenzene, measurement temperature:  $-15 - 160^{\circ}\text{C}$ . TG-IC is an analytical method that separates components with different crystallinity using the strength and weakness of polymer crystalline component adsorption on graphite,<sup>11)</sup> and is characterized by being able to separate them even if with a low crystallinity synthetic rubber like EPDM and obtain information on composition distribution. With TG-IC, the higher the elution temperature for a component the greater the crystallinity of the component is. As a result of the TG-IC measurements, it was found that the main components were noncrystalline components that eluted at  $20 - 30^{\circ}\text{C}$ , but crystalline components that eluted in the neighborhood of  $60^{\circ}\text{C}$  were also present. If it were only EPM with 49 wt%



**Fig. 4** Analysis of composition distribution of EPM

ethylene content, the ethylene content would be sufficiently low, so it can be assumed that this crystalline component would not be present; therefore, this suggests that EPM with an ethylene content higher than 49 wt% is present. The presence of this crystalline component can be thought of as having an adverse effect on the cold resistance of rubber products. Therefore, to produce EPDM with cold resistance superior to conventional low ethylene content EPDM, it can be assumed that reducing the proportion of this crystalline component and increasing the proportion of noncrystalline components is important.

Next, we measured  $^{13}\text{C}$  NMR for EPM with an ethylene content of 49 wt% the ethylene chains. The measurement conditions for  $^{13}\text{C}$  NMR measurements were as follows. Measurement solvent: 1,2-dichlorobenzene / 1,2-dichlorobenzene- $d_4$  (80/20 volume ratio), measurement temperature:  $130^{\circ}\text{C}$ , chemical shift value standard: tetramethylsilane. It has been reported that the ethylene chain proportion (EEE) and the product of the monomer reactivity ratio ( $r_1r_2$ ) can be analyzed by  $^{13}\text{C}$  NMR,<sup>12)</sup> and in this article  $r_1$  and  $r_2$  are the ethylene and propylene reactivity ratios, respectively. EEE is the proportion of the ethylene-ethylene-ethylene triad distribution in all triads (letting an ethylene unit and a propylene unit be the two constituent units with a constituent chain being formed from three constituent units). When  $r_1r_2$  is 0, it indicates that one of the monomers is not continuously polymerized and alternating co-polymerization is formed, and when  $r_1r_2$  is 1, it indicates that the probability of continuous polymerization of the same monomer and the probability of not being continuous is the same. When  $r_1r_2$  is greater than 1, the probability of polymerization occurring continuously among the same monomer is large, and the blocking properties of the polymer obtained increase. Furthermore, this indicates that the higher the proportion of EEE, the easier it is for the ethylene portion to crystallize.

The EPM  $r_1r_2$  was 0.71 and alternating copolymerizability was not so high; therefore, we were able to confirm that occurrences of ethylene chains were possible. Furthermore, the EEE proportion was 22 mol%, this can be thought of as meaning that some of these ethylene chains were crystallized components. From the above, it can be assumed that a reduction in the proportion of crystallized ethylene will form an EPDM structure with superior cold resistance because of an increase in the alternating copolymerization during polymerization and a reduction in the proportion of ethylene chains.

**Table 1** Characteristics of EPDMs used in this work

Name	Unit	Novel EPDM-1	Novel EPDM-2	EPDM-A	EPDM-B	EPDM-C	EPDM-D
Catalyst		Modified vanadium	Modified vanadium	Vanadium	Vanadium	Metallocene	Metallocene
Mooney viscosity (ML 1+4 125 °C)		53	83	59	81	58	65
Ethylene content	wt%	46	49	50	51	35	40
ENB content	wt%	8.5	3.5	10.0	3.5	14.0	9.0

**Table 2** Raw materials and compound position

Ingredient	Function	phr	wt%
EPDM	Polymer	100	49.6
FEF CB (N550)	Filler	60	29.8
Paraffinic oil	Plasticizer	30	14.9
Zinc oxide	Activator	5	2.5
Stearic acid	Activator	1	0.5
Sulfur	Curative	1.5	0.7
ZDBC (BZ)	Accelerator	2	1.0
TMTD (TT)	Accelerator	0.5	0.2
DPIT (TRA)	Accelerator	0.5	0.2
MBT (M)	Accelerator	1	0.5
Total		201.5	100

## Test Methods

### 1. Raw Materials

The EPDMs used for these tests is shown in **Table 1**. Novel EPDM-1 and Novel EPDM-2 are newly developed EPDMs with superior cold resistance; EPDM-A and EPDM-B were polymerized using vanadium based Ziegler-Natta catalysts, and EPDM-C and EPDM-D are commercial EPDM polymerized using a metallocene catalyst. The ethylene content is low for all of them, and it can be assumed that EPDMs with superior cold resistance were chosen. The ethylene content and ENB content are values measured by Sumitomo Chemical (ethylene + propylene + ENB = 100 wt%). In addition, **Table 2** shows the mixtures used during kneading in these tests.

### 2. Kneading and Vulcanization Conditions

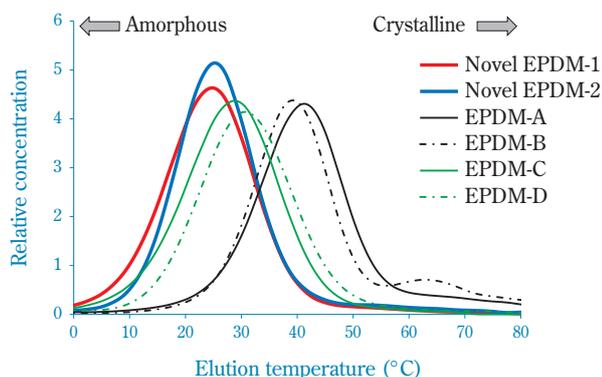
Raw materials other than the vulcanizing agent and vulcanization accelerator were kneaded using a 1.7 L Banbury mixer. The filling rate was 65%, the rotational speed of the rotor was 60 rpm, and the kneading time was 5 minutes. The vulcanizing agent and vulcanization accelerator were kneaded for 3 minutes at 40°C using an 8 inch roll. The kneaded compound was press

formed for 15 minutes at 170°C using a press molding machine to obtain a vulcanized rubber sheet (pressed sheet).

## EPDM Molecule Design for Superior Cold Resistance

As described above, the molecule design for EPDM with superior cold resistance not only has a low ethylene content, but also suppresses occurrences of high ethylene content components, in other words, can be thought of as improving the cold resistance by narrowing the composition distribution. Furthermore, it can be assumed that reducing the ethylene crystallinity by reducing ethylene chains in the polymer by increasing the alternating copolymerization of ethylene and propylene during polymerization is important. As a result of our studies, we found that by innovation in the catalyst and polymerization conditions, we obtained Novel EPDM-1 and Novel EPDM-2, which are EPDMs with superior cold resistant molecule designs of this type. We will give an explanation of the molecule design of these EPDMs by comparing them with EPDM-A through EPDM-D, which are typical ones polymerized with Ziegler-Natta catalysts and metallocene catalysts.

The composition distributions of the six types of EPDM analyzed by TG-IC are shown in **Fig. 5**. The main peaks for EPDM-A and EPDM-B were present furthest to the high temperature side (approximately 40°C); in a temperature range of 60°C or greater eluted components were confirmed, and we found that crystalline components were present. The peaks for EPDM-C and EPDM-D were shifted toward the low temperature side, and we found that almost no crystalline components were present. On the other hand, the peaks for Novel EPDM-1 and Novel EPDM-2 were furthest to the low temperature side, and furthermore, since almost no eluted components were present as with EPDM-A and EPDM-B, the proportion of crystalline components is



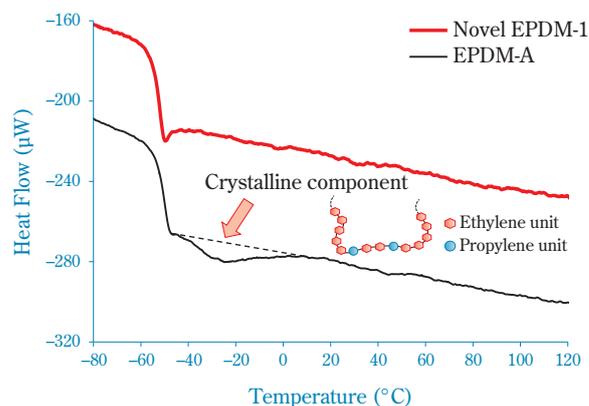
**Fig. 5** Analysis of composition distribution of EPDMs

extremely small. We were able to confirm that the composition distributions for this Novel EPDM-1 and Novel EPDM-2 are extremely narrow and that the composition distributions had almost no crystalline components present as was expected.

Next,  $T_g$  and the  $T_g$  width for the six types of EPDM were analyzed using a differential scanning calorimeter (DSC) (Table 3). The measurement conditions for the DSC were a temperature increase rate of 5°C/min for the first run. Compared with EPDM-A, EPDM-C and EPDM-D, which had approximately the same ENB content, it was found that Novel EPDM-1 had the lowest  $T_g$  and the narrowest  $T_g$  width. The result of  $T_g$  width being narrow indicates a structure with a narrow composition distribution identical to the results obtained from TG-IC. Furthermore, Novel EPDM-2 exhibited the lowest  $T_g$  even when compared with EPDM-1 and EPDM-B, which have almost the same ENB content.

Novel EPDM-2 has lower ENB content than EPDM-1, so it has a low  $T_g$ . While almost no crystalline components are present in EPDM-C and EPDM-D, the ethylene content is extremely low and many methyl groups are present; therefore, the rotational motion of the polymer chain is slow, and it can be presumed that  $T_g$  will be high.

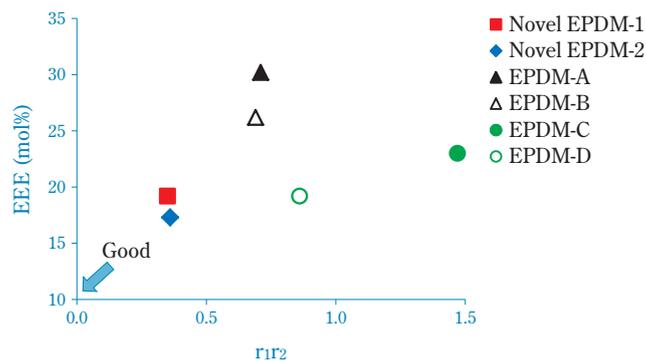
The DSC chart for Novel EPDM-1 and EPDM-A is shown in Fig. 6. It was found that EPDM-A had an endothermic peak in the neighborhood of 25°C, and this



**Fig. 6** DSC charts of Novel EPDM-1 and EPDM-A

component can be thought of as being the same as the crystalline component that eluted in the neighborhood of 60°C in TG-IC. Since this crystalline component crystallizes at approximately 0°C or lower, it is thought to have a bad effect on cold resistance. This endothermic peak is not present for EPDM-1, and this is data that supports the TG-IC result of almost no crystalline components being present. It was confirmed that it is possible to greatly reduce the crystalline component at low temperatures by making the composition distribution narrow in this manner.

The  $r_1r_2$  and the ethylene chains for the six types of EPDM analyzed by  $^{13}\text{C}$  NMR are shown in Fig. 7 and Table 4.



**Fig. 7** Product of monomer reactivity ratio and ratio of ethylene chain of each EPDM

**Table 3** The width of  $T_g$  and  $T_g$  of each EPDM

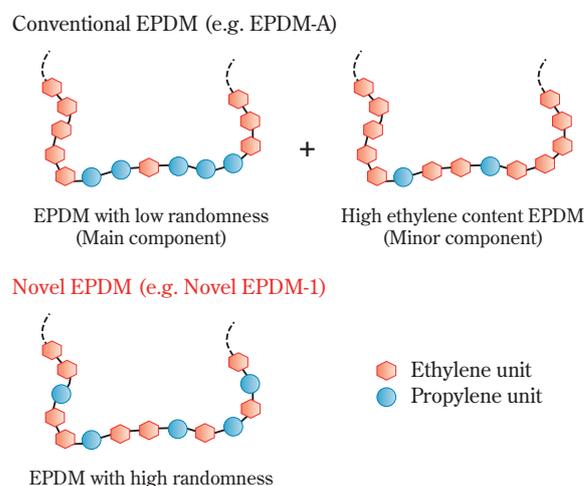
Name	Unit	Novel EPDM-1	Novel EPDM-2	EPDM-A	EPDM-B	EPDM-C	EPDM-D
$T_g$	°C	-53	-58	-50	-56	-40	-46
Width of $T_g$	°C	4.0	3.5	5.1	5.8	4.8	4.9

**Table 4** Product of monomer reactivity ratio and ratio of ethylene chain of each EPDM

Name	Unit	Novel EPDM-1	Novel EPDM-2	EPDM-A	EPDM-B	EPDM-C	EPDM-D
$r_1r_2$		0.35	0.36	0.71	0.69	1.47	0.86
EEE	mol%	19.2	17.3	30.2	26.2	23.0	19.2

While EPDM-A and EPDM-B have  $r_1r_2$  smaller than 1 and the blocking properties during polymerization are not high, the ethylene content is comparatively high; therefore, the proportion of ethylene chains is high. A result of the proportion of ethylene chains being high agrees with the analytical results up to this point of crystalline components being present. Even though  $r_1r_2$  is somewhat higher for EPDM-D than for EPDM-A and EPDM-B, the proportion of ethylene chains is low. This can be assumed to be caused by the ethylene content being low at 40 wt%. EPDM-C had the largest  $r_1r_2$  at 1.47; therefore, it is presumed that polymerization among monomers of the same type could easily occur continuously during polymerization. However, since the ethylene content of EPDM-C is extremely low at 35 wt%, it is thought that the proportion of ethylene chains is not very high. On the other hand,  $r_1r_2$  for Novel EPDM-1 and Novel EPDM-2 are 0.35 and 0.36 respectively, and it was confirmed that the alternating copolymerizability was the highest. Furthermore, it was found that the proportions of ethylene chains were the lowest, and that the polymer structure was such that ethylene crystallization did not occur easily. The ethylene contents for Novel EPDM-1 and Novel EPDM-2 were 46 wt% and 49 wt% respectively, and even though the ethylene content was high compared with EPDM-C and EPDM-D, this suggests that alternating copolymerizability is high also because the proportion of ethylene chains is low.

We can conclude that because of the composition distribution being narrow for Novel EPDM-1 and Novel EPDM-2, there is a large reduction in the high ethylene content components which form crystalline components and a large increase in the proportion of the noncrystalline components. Furthermore, the alternating copolymerizability is increased, and the crystallization of ethylene chains is also suppressed by the reduction in the proportion of ethylene chains. Images of the polymer chains for EPDM-A as well as Novel EPDM-1 and Novel EPDM-2 are shown in Fig. 8. It is expected that the cold resistance of vulcanized rubber will be greatly enhanced by this kind of molecular design.

**Fig. 8** Image of polymer chain of conventional EPDM and novel EPDM

## Cold Resistance of Vulcanized Rubber

### 1. Method for Evaluating Cold Resistance

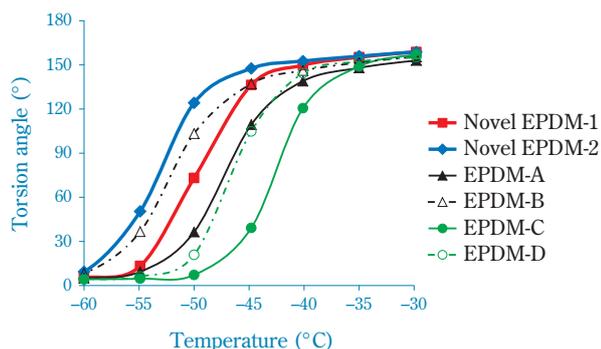
In the mixtures given in Table 2 for the previously described types of EPDM, kneading was performed with the same kneading conditions and press molding carried out to obtain the vulcanized rubber sheets. We measured the cold resistance of each of these vulcanized rubber products using these vulcanized rubber sheets. As methods for evaluating the cold resistance of the vulcanized rubber, there are the Gehman torsion test, low temperature retraction test (TR test), compression set (C. set), etc., and they are provided for in JISK 6261 and JISK 6262. In the development of actual rubber products, evaluation tests envisioning methods of use and the environment in each application are used.

### 2. Cold Resistance According to Gehman Torsion Test

The Gehman torsion test is an evaluation method for finding torsion rigidity by applying torsion to a test piece (vulcanized rubber sheet) through a torsion wire over a temperature range from freezing temperatures to room temperature and measuring the torsion angle of the test piece. The results of the Gehman torsion tests on the vulcanized rubber sheets of the six types

**Table 5**  $T_g$  and ratio of modulus in Gehman torsion test of vulcanized rubber

Name	Unit	Novel EPDM-1	Novel EPDM-2	EPDM-A	EPDM-B	EPDM-C	EPDM-D
<b>Vulcanized Properties</b> (Press cured 170°C×15min)							
Gehman torsion test							
$T_g$	°C	-51	-56	-50	-54	-43	-47
T2	°C	-44	-50	-36	-44	-37	-41
T5	°C	-47	-53	-46	-50	-40	-45
T10	°C	-50	-55	-48	-52	-42	-46
T100	°C	-55	-60	-55	-59	-48	-52

**Fig. 9** Relation between temperature and helix angle in Gehman torsion test of vulcanized rubber

of EPDM are shown in Fig. 9 and Table 5. T2, T5, T10 and T100 indicate temperatures of 2, 5, 10 and 100 times a modulus of 23°C, and the lower ones indicate superior cold resistance.

The ranking for T100 is substantially the same as the ranking for  $T_g$  given in Table 3 for the six types of EPDM and shows that the influence of  $T_g$  is great. Comparing Novel EPDM-2 and EPDM-B in Fig. 9, the start of the curves for torsion angle are substantially the same, but after that the rise in the torsion angle for Novel EPDM-2 is sharper. It can be assumed that since Novel EPDM-2 has a smaller amount of crystalline components than EPDM-B, the torsion angle accompanying increases in temperature is greater. This relationship is the same for EPDM-1 and EPDM-A. On the other hand, since  $T_g$  is high for EPDM-C and EPDM-D, the temperature for the start of torsion angle increase is high, and we determined that there is a problem with flexibility at low temperatures. Thus, in Gehman torsion tests, it was found that the effects of  $T_g$  and crystallinity were great, and Novel EPDM-2 was most superior when compared with the conventional EPDMs.

### 3. Cold Resistance by TR Testing

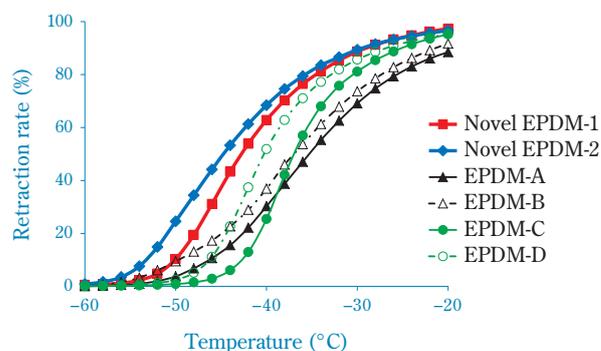
The TR test is carried out for finding out the temper-

ature when a test piece (vulcanized rubber sheet) frozen at a low temperature after elongation recovers elasticity with increases in temperature and can achieve a fixed degree of contraction.

The results of the TR test on the vulcanized rubber sheets of the six types of EPDM are shown in Fig. 10 and Table 6. The contraction percentage for TR10, TR30, TR50 and TR70 show temperatures of 10%, 30%, 50% and 70%, and the lower they are, the more superior the cold resistance is.

Comparing Novel EPDM-1 with EPDM-A, EPDM-C and EPDM-D, it was understood that all were excellent according to the indices TR10 - TR70. The presence of crystalline components in EPDM-A can be thought of as a cause of the degradation of cold resistance. EPDM-C is thought to be the worst for TR10 because  $T_g$  is high for it. Crystalline components are substantially nonexistent for Novel EPDM-1 and  $T_g$  is low; therefore, it shows extremely superior cold resistance in TR test. Moreover, since TR10 ranking is substantially the same as the  $T_g$  ranking shown for the six types of EPDM in Table 3, it shows that TR10, which is an index of when contraction starts, is greatly affected by  $T_g$ .

Furthermore, comparing Novel EPDM-2 with Novel

**Fig. 10** Relation between temperature and retraction rate in low temperature retraction test of vulcanized rubber

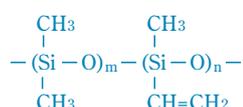
**Table 6** TR10, TR30, TR50 and TR70 in low temperature retraction test of vulcanized rubber

Name	Unit	Novel EPDM-1	Novel EPDM-2	EPDM-A	EPDM-B	EPDM-C	EPDM-D
<b>Unvulcanized Properties</b>							
Mooney viscosity (ML 1+4 100°C)		48	75	51	77	58	68
<b>Vulcanized Properties</b> (Press cured 170°C×15min)							
TR test (50% elongation)							
TR10	°C	-50	-53	-46	-50	-43	-46
TR30	°C	-46	-49	-40	-42	-40	-43
TR50	°C	-43	-45	-35	-37	-37	-40
TR70	°C	-38	-40	-30	-31	-34	-36

EPDM-1, even more superior cold resistance is shown in all of the indices TR10 - TR70. This can be assumed to be not only because these have a narrow composition distribution and high alternating copolymerizability, but also because  $T_g$  is low because ENB content is low at 3.5%. As with the Gehman torsion tests, it also turned out that novel EPDM-2 had the most superior cold resistance in the TR test. On the other hand, the results for Novel EPDM-1 were second in excellence next to Novel EPDM-2 for TR10 - TR70, but since the Mooney viscosity is the lowest among the six types of EPDM, the Mooney viscosity of the compound is low, and it is assumed that it will be superior in processability and formability. In other words, Novel EPDM-1 can be said to have a polymer structure preferable for applications and mixing in which processability and formability are important and where low viscosity is required.

### Aiming for Substitutes for Other Types of Rubber

As has been discussed to this point, Novel EPDM-1 and Novel EPDM-2 exhibit superiority to conventional EPDM in the various indices for cold resistance. On the other hand, among rubber products, there are substitutions of other synthetic rubbers for synthetic rubbers that are highly functional but have high cost. For example, silicone rubber can be cited as a synthetic rubber having superior cold resistance. Among the silicone rubber types, vinyl methyl silicone rubber (VMQ) is general-purpose and widely used (Fig. 11). To verify that

**Fig. 11** Vinyl methyl silicone rubber

Novel EPDM-1 and Novel EPDM-2 can be substituted for VMQ, we carried out a comparative evaluation of cold resistance.

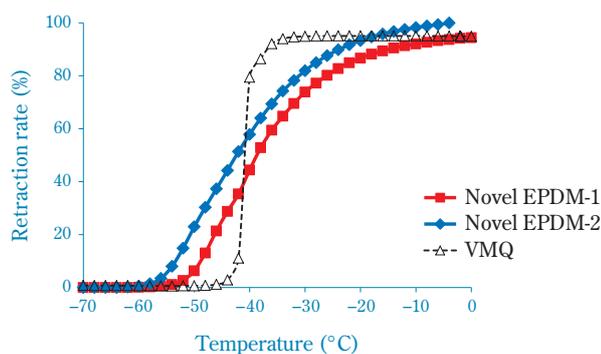
For the VMQ, we used SH851U manufactured by Dow Corning Toray Co., Ltd. SH851U and RC-4 (50P) (2,5bis(tert-butylperoxy)-2,5-dimethyl hexane, 50% master batch), which is a cross-linking agent, were kneaded at 0.6 phr for three minutes at 40°C using an 8 inch roll. The kneaded compound was press molded for 10 minutes at 170°C using a press molding machine. Next, secondary cross-linking of the pressed sheet obtained was carried out for four hours at 200°C in a gear oven and a cross-linked rubber sheet (pressed sheet) obtained.

Moreover, since the cross-linking agent use in the VMQ cross-linking was an organic peroxide (PO), kneading using a mixture that used the PO shown in Table 7 was also carried out for Novel EPDM-1 and Novel EPDM-2 to match the types of cross-linking agent. Other than changing the press molding conditions to 170°C at 20 minutes, cross-linked rubber sheets (pressed sheets) were fabricated under the same conditions as used previously.

The results of evaluating Novel EPDM-1 and Novel EPDM-2 with VMQ in the TR test are shown in Fig. 12 and Table 8. The rate of contraction of VMQ was

**Table 7** Raw materials and compound position

Ingredient	Function	phr	wt%
EPDM	Polymer	100	49.6
FEF CB (N550)	Filler	60	29.8
Paraffinic oil	Plasticizer	30	14.9
Zinc oxide	Activator	5	2.5
Stearic acid	Activator	1	0.5
Dicumyl peroxide	Crosslinking agent	2.7	1.3
Ethylene glycol dimethacrylate	Co-agent	2	1.0
Total		200.7	100



**Fig. 12** Relation between temperature and retraction rate in low temperature retraction test of vulcanized rubber

**Table 8** TR10, TR30, TR50 and TR70 in low temperature retraction test of vulcanized rubber

Name	Unit	Novel EPDM-1	Novel EPDM-2	VMQ
<b>Vulcanized Properties</b> (Press cured 170°C×15min)				
TR test (50% elongation)				
TR10	°C	-49	-53	-40
TR30	°C	-43	-48	-40
TR50	°C	-38	-42	-39
TR70	°C	-33	-36	-39

greater at temperatures of  $-40^{\circ}\text{C}$  or greater, and TR70 was superior. On the other hand, in the low temperature region under  $-40^{\circ}\text{C}$ , the rate of contraction of Novel EPDM-1 and Novel EPDM-2 was greater than that for VMQ, and they were superior in terms of TR10 - TR50. Furthermore, C. set at  $-50^{\circ}\text{C}$  was 100% for VMQ, while it was 84% and 80% for Novel EPDM-1 and Novel EPDM-2, respectively, and excellent C. set at  $-50^{\circ}\text{C}$  was confirmed.

Thus, Novel EPDM-1 and Novel EPDM-2 were superior in cold resistance to VMQ in the low temperature range of less than  $-40^{\circ}\text{C}$ , and it was suggested that they could be substituted for VMQ according to the application and required physical properties.

## Conclusion

As has been described in this article, we have introduced some of the development of EPDM with superior

cold resistance. Novel EPDM-1 and Novel EPDM-2 have a narrow composition distribution compared with conventional EPDM and a molecular design with high copolymerizability; therefore, crystallized components are greatly reduced, and the proportion of ethylene chains is reduced. Using this molecular structure, we were successful in improving various kinds of cold resistance, and we expect this to contribute to increased functionality in various types of rubber products. Every year the level of performance required of rubber products is increasing, and higher-level technology is being required. Moving forward, we would like to continue this technical development and focus on the development of EPDM that responds to changes in rubber product structure and the required performance.

## References

- 1) "Worldwide Rubber Statistics", International Institute of Synthetic Rubber Producers, Inc. (2017), p. 11.
- 2) Gomu Kougyou Binran [Handbook of Rubber Industry] 4th ed., THE SOCIETY OF RUBBER SCIENCE AND TECHNOLOGY, JAPAN Ed., THE SOCIETY OF RUBBER SCIENCE AND TECHNOLOGY, JAPAN; 1994; p.309.
- 3) Y. Oda, SUMITOMO KAGAKU, **1978-I**, 45 (1978).
- 4) J. Yamabe *et al.*, Nippon Gomu Kyokaiishi, **83**, 159 (2010).
- 5) S. Nishimura, Nippon Gomu Kyokaiishi, **86**, 360 (2013).
- 6) A. Koga, Nippon Gomu Kyokaiishi, **89**, 307 (2016).
- 7) F. J. Linnig and E. J. Parks, *J. Applied Polymer Sci.*, **8**, 2645 (1964).
- 8) J. J. Maurer, *Rubb. Chem. Tech.*, **38**, 979 (1965).
- 9) Shinban Gomu Gijutsu no Kiso [A New Version of Basic Rubber Technology], Rev. Ed., THE SOCIETY OF RUBBER SCIENCE AND TECHNOLOGY, JAPAN Ed., THE SOCIETY OF RUBBER SCIENCE AND TECHNOLOGY, JAPAN; 2002; p.100.
- 10) J. F. Jackson *et al.*, *J. Polym. Sci. Part A*, **1**, 2119 (1963).
- 11) R. Cong *et al.*, *Macromolecules*, **44**, 3062 (2011).
- 12) M. Kakugo *et al.*, *Macromolecules*, **15**, 1150 (1982).

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