Development of EPDM Grades with Good Processability Characteristics –Specialized Polymer Design for Anti-Vibration Rubber–

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The production process for cured rubber requires several steps, including mixing by an internal mixer, mixing by an open roll, molding with an extruder and vulcanizing using hot-air tunnel, and this is one of the reasons for higher production costs than other resin parts. In recent years we have aimed at the development of ethylene-propylene-nonconjugated diene rubber (EPDM) grades with good processability characteristics that minimize production costs. We have already included in our line-up the new grade "Esprene® 7456" as a Good Processability grade designed for continuous vulcanized sponges.

In this report, we present our new Good Processability EPDM grade cured by a peroxide curing system which is designed for anti-vibration rubber parts. This new grade has excellent roll mixing processability even with a low loading formulation, and provides high performance for anti-vibration rubber parts especially for next-generation muffler hangers.

This paper is translated from R&D Report, "SUMITOMO KAGAKU", vol. 2007-I.

Introduction

The worldwide demand for ethylene-propylene-non-conjugated diene rubber (EPDM) was 1002 thousand tonnes[1]. Because EPDM is a rubber which does not contain any unsaturated structure in its main chain, it has excellent weatherresistance, ozone resistance and heat resistance, and the absence of polar groups also means that its inter-molecular interactions are weak and so it has excellent filler loading characteristics. Because of this, it is widely used in automotive parts such as weatherstrips, heat-insulating cover materials, noise damping materials, anti-vibration rubber parts, radiator and heater hoses and brake hoses, and also in a wide range of other industrial applications such as an additive for diene rubbers such as natural rubber (NR) to improve weather resistance, to improve impact resistance and low temperature resistance for thermoplastic resins such as polypropylene (PP), TPE raw materials, and also to improve the viscosity index of mineral oils[2]. Of these applications, the demand for EPDM in the automobile industry, particularly in the Asian region, is projected to grow by an average of 3.7% (approximately 40,000 tonnes) annually up until the year 2010[1].

In general, the processed used in order to manufacture rubber products include a process using an internal mixer to mix in additives such as reinforcing agents, plasticizing agents, extenders and processing aids (Mixing (1) in **Fig. 1**), and a process using an open roll to mix in curing agents, curing accelerator

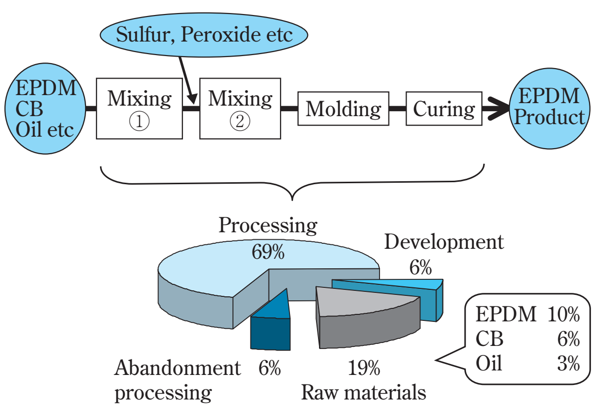


Fig. 1 Simplified cost model of EPDM product [Quoted from reference 3)]

and, if required, foaming agents (Mixing (2) in Fig. 1) to produce a compound which is capable of being cured; this is then shaped using an extruder or mold while heat is applied in order to promote cross-linking reactions to produce rubber products with their well-known resilience.

The majority of cured rubber products made using EPDM are manufactured by means of this same process. In the case of thermoplastic resin molded products, all that is usually required is to simply mold the resin material as it was originally purchased, and so the processing cost tends to form a large proportion of the final product cost for rubber products (Fig. 1). Accordingly, reducing the cost of EPDM products is dependent on making the processing steps more efficient.

Until now, we have concentrated on improving the efficiency of the Mixing (1) step by controlling the molecular weight distribution to achieve a balance between mixing performance and shape retention in our sponge grade products which have already been released into the market as a Good Processability EPDM (Esprene® GP).

We have now been giving attention to the Mixing (2) step using our company's unique technology to improve processability, and we have succeeded in obtaining a balance between anti-vibration rubber characteristics and roll mixing processability which has been hitherto unknown. This paper describes our use of this technique to develop a Good Processability grade of EPDM for anti-vibration rubber.

Anti-vibration rubber for automobiles

Anti-vibration rubber for automobiles is used for parts such as torsional dampers and engine mounts in the engine compartment, center bearing supports in the drive train, and upper link bushings and muffler hangers in the drive control system (**Fig. 2**). The development grade has been used in its largest quantities as muffler hangers which are easily affected by exhaust temperatures. These rubber parts are used to connect the muffler to the vehicle body, and they have the function of preventing the vibration which is generated by the muffler from being transmitted to the vehicle body. According to recent trends, increases in the temperature of exhaust gases as a result of a higher degree of exhaust gas purification and more efficient uses of fuel energy has tended to increase the temperature of the exhaust system, so that muffler hangers are also required to withstand higher temperatures.

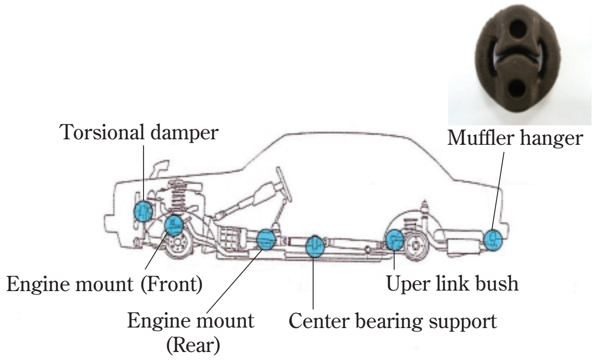


Fig. 2 Anti-vibration rubber parts of Automotive

Conventional cross-linking has mostly been carried out using sulfur. However in the case of sulfur cross-linking, a stiffening phenomenon (hardening deterioration) can easily occur as a result of cheavage and re-linking of the sulfur-sulfur bonds due to heat. This deterioration does not only affect the mechanical properties of the rubber, but also has an adverse effect on its anti-vibration performance, so that the amount of vibration increases over time. From now on, we believe that there will be a gradual trend toward the use of peroxide-based curing systems which are more stable against heat in order to provide improved heat resistance and improved product performance.

Dynamic-to-static modulus ratio

The most important properties which indicate the anti-vibration performance of anti-vibration rubber is the dynamic-to-static modulus ratio.

The dynamic-to-static modulus ratio is the ratio between the dynamic elastic modulus and the static elastic modulus, and is an indicator of the level of body interior noise. For example, a vehicle with a 1500cc 16-valve engine generates a vibration force of 100 Hz when driving at medium speed. The dynamic-to-static modulus ratio is the ratio between the dynamic elastic modulus E' (MPa) which corresponds to this 100 Hz and the static elastic modulus Es (MPa) which corresponds to the initial stress of supporting the engine. The lower the resulting value, the smaller the amount of body interior noise, meaning that more comfortable driving will be possible (**Fig. 3**).

When sulfur-cured rubber and peroxide-cured rub-

$$\text{Dynamic-to-static modulus ratio} = \frac{\text{Dynamic elastic modulus}}{\text{Static elastic modulus}} = \frac{\text{Storage elastic modulus (100Hz) E'}}{\text{Storage elastic modulus (1Hz) Es}}$$

Fig. 3 Dynamic-to-static modulus ratio[4]

ber which otherwise have the same formulations are compared, the latter has a dynamic-to-static modulus ratio which is approximately 15% worse than the former (**Table 1**). This can be attributed to the fact that peroxide-cured rubber has a lower cross-linking density (rubber elasticity) than sulfur-cured rubber.

One of the measures that can be taken regarding the structure of EPDM in order to address the problem of a worsening of the dynamic-to-static modulus ratio that accompanies peroxide curing is reducing the number of polymer chain ends which cause energy losses at high frequencies by increasing the molecular weight and/or creating a narrower molecular weight distribution. In addition, other measures that can be taken from the formulation point of view are to reduce the viscosity factor by reducing the amount of reinforcing agents such as carbon black, or to increase the amount of cross linking agent to increase the elasticity. However, each of the methods just mentioned have a tendency to result in losses in the roll processability for the rubber compounds, and also increasing the amount of cross linking agent greatly increases the formulation costs (**Table 2**). Accordingly, the goal has been to develop an EPDM with an excellent balance between roll processability and dynamic-to-static modulus ratio without increasing the formulation costs.

Table 1 Dynamic-to-static modulus ratio of different curing system[4]

	Sulfur curing system	Peroxide curing system
Dynamic-to-static modulus ratio	1.65	1.90

Table 2 Correspondence of poor Dynamic-to-static modulus ratio for Peroxide curing system[4]

	<EPDM structure>	<Formulation>
Counter measures for improvement	• High MW • Narrow MWD	• Low loading • Increase curing agent
defect	• Poor mixing processability	• Poor mixing processability • Cost up

Molecular design of Good Processability EPDM for anti-vibration rubber

One of the methods that has been proposed in order to improve the balance between the processability and the dynamic-to-static modulus ratio of EPDM, assuming that a sulfur-curing system is being used, is to combine low-molecular weight EPM which does not have any crosslinking sites (dienes) with EPDM which does contain dienes[5]. In such cases, the low-molecular weight EPM does not react with the sulfur, and so it does not take part in the three-dimensional network of the rubber and this keeps the effect on the dynamic-to-static modulus ratio to a minimum. However in the case of peroxide-curing systems, the low-molecular weight EPM is also included as part of the three-dimensional network, so that it becomes difficult to avoid a worsening of the dynamic-to-static modulus ratio.

Here we will describe the molecular design for the Good Processability EPDM for anti-vibration rubber which we have developed to be suitable for peroxide-curing systems, while comparing it to the structure of conventional EPDM (**Fig. 4**). The structures indicated by the blue lines in the graphs are those of our EPDM for anti-vibration rubber which has been polymerized using a conventional method, and the structures indicated by the red lines are the newly-developed Good Processability EPDM for anti-vibration rubber. One of the distinctive features of the Good Processability EPDM is that the molecular weight distribution forms a wide bimodal curve, compared to the unimodal curve for the conventional EPDM. With this molecular design, good roll mixing processability is maintained at the low-molecular weight side, while the dynamic-to-static modulus ratio has been improved at the high-molecular weight side. However, if the molecular weight distribution is simply widened, then the effect of the low-molecular weight portion will cause a worsening of the dynamic-to-static modulus ratio, and so this point was remedied by maintaining characteristics for two composition distributions. One was the molecular weight distribution with regard to the ethylene content, and the other was the same for the diene content. It is known that in general, the higher the ethylene content or the higher the diene content in peroxide-cured EPDM, the higher is the crosslinking efficiency, resulting in the formation of a better three-dimensional network linking structure[6), 7)]. The ethylene content in conventional EPDM is fairly constant with respect to the molecular weight, whereas our newly-developed product has been designed so that the portions with lower molecular weight tend to have a higher ethylene content, so that the low-molecular weight portions can also form into network linking structures with greater efficiency, which suppresses increases in the viscosity factor. In addition, if we look at the high-molecular weight portion of the Good Processability EPDM, it can be seen that the drop in diene content is only slight in the range where the molecular weight is at its highest. This provides a further reduction in the dynamic-to-static modulus ratio. We succeeded in creating this complex molecular design in a single polymerization step by use of a new catalyst which we have developed[8].

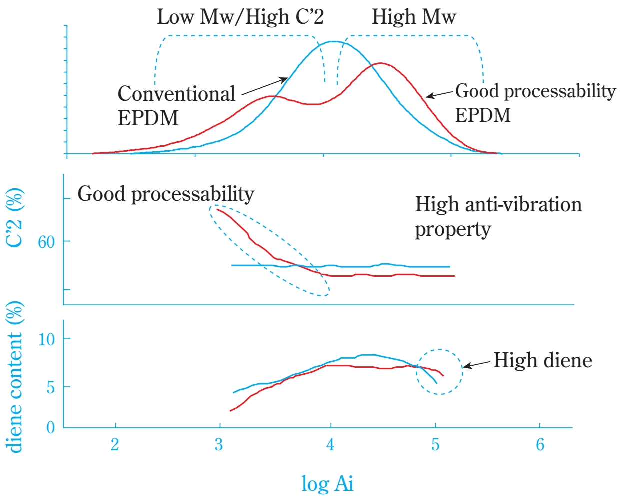


Fig. 4 EPDM polymer design for high Roll mixing processability and for low dynamic-to-static modulus ratio[4]

Furthermore, the roll mixing processability for the Good Processability EPDM is controlled by means of λ_b (extension to break) and θ_d (deformation index) (**Fig. 5**)[9].

θ_d (Eq. 1) gives the ratio between the breaking energy density U_{be} for an ideal elastic body (Eq. 2) and the breaking energy density U_b for a visco-elastic body (Eq. 3), and this is used as a roll processability index. If $\theta_d = 1$ then the body is fully elastic, and if $\theta_d < 1$ then the body is visco-elastic. For a fully plastic body, the value of θ_d can be expressed by (Eq. 4). According to this index, the standard for a product with excellent roll processability is for λ_b to be 7 or more and θ_d to be 0.1 or more. Conventional EPDM has a large value for λ_b but a small value for θ_d, meaning that it has a high viscosity factor and its roll processability is not so good. On the other hand, the Good Processability EPDM shows a good balance between the values for λ_b and θ_d, which means that it has excellent roll processability. The excellent roll processability of the Good Processability EPDM is due to the high value for the maximum true stress σ_m. This occurs because the Good Processability EPDM is designed so that the ethylene content increases for lower molecular-weight portions as mentioned earlier, in contrast to the conventional EPDM where the ethylene content is basically constant for all molecular weights. This means that the low-molecular weight portions of the Good Processability EPDM can also form into network linking structures with greater efficiency, which suppresses increases in the viscosity factor and allows a suitable value for σ_m to be maintained.

$$\theta_d = U_{be} / U_b \qquad \text{(Eq. 1)}$$

$$U_{be} = (\sigma_m/2)(\lambda_b^2 + 2\lambda_b^{-1} - 3)/(\lambda_b^2 - \lambda_b^{-1}) \qquad \text{(Eq. 2)}$$

(σ_m : Maximum true stress,
λ_b : Extension to break at maximum true stress)

$$U_b = (l_o/V)\int_1^{\lambda_b} F d\lambda = \int_1^{\lambda_b} (F/A_o)\, d\lambda \qquad \text{(Eq. 3)}$$

(l_o : Initial length, V : Volume,
A_o : Initial cross-sectional area, F : Stress)

$$\theta_d = (\lambda_b^3 - 3\lambda_b + 2)/2(\lambda_b^3 - 1)\ln\lambda_b \qquad \text{(Eq. 4)}$$

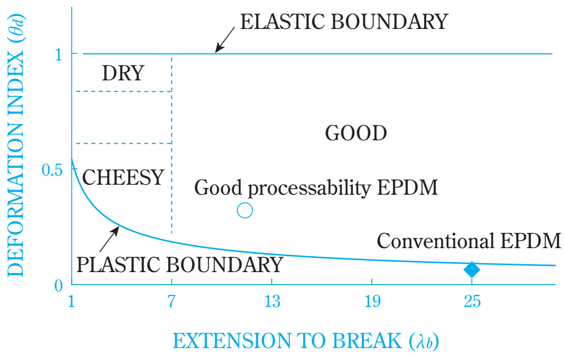


Fig. 5 Zone classification for roll mixing

Comparison of structural values for Good Processability EPDM for anti-vibration rubber and conventional EPDM

The high level of molecular design mentioned earlier makes it possible to lower the average molecular weight compared to conventional anti-vibration rubber grades, and it is possible to reduce the amount of extender oil added. A result of this is that it gives a greater allowance in formulation design to the processor (low loading formulation/high loading formulation, low hardness/high hardness). In addition, low-priced process oils can be added by the processor, which is a contributing factor in reducing formulation costs (**Table 3**).

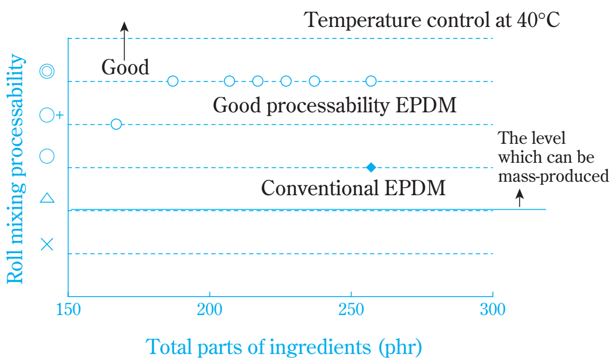
Table 3 Structure values of Good processability EPDM

EPDM	Conventional EPDM	Good processability EPDM
Mw	1,100,000	980,000
diene content (%)	6.5	6.5
diene	ENB	ENB
extend oil (phr)	70	30

Test results

1. Relationship between formulation amount and roll processability

The Good Processability EPDM was evaluated with seven different formulations containing varying amounts of carbon black and oil (**Fig. 6**)[8].



(remark ◎ : excellent, ○+ : very good, ○ : good, △ : not bad, × : poor)

Fig. 6 Relation of Total parts ingredients and Roll mixing processability[4]

The roll mixing processability of conventional EPDM presents difficulties because holes appear in the compound, and the compounds peels off and falls from the roller at intermittent intervals. On the other hand, the roll mixing processability for Good Processability EPDM maintains a high level of quality with no bagging (lifting up or hanging down from the roller), holes appearing or ragged edging of the compound even with low loading (low formulation quantities), making it clearly superior in this aspect of performance compared to conventional EPDM (**Fig. 7**).

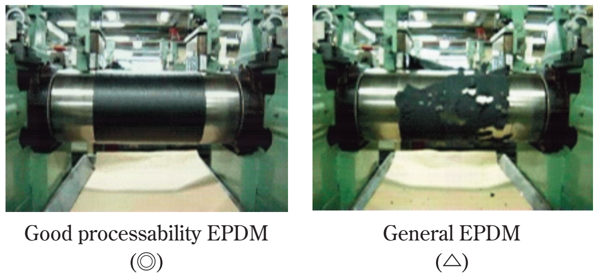


Fig. 7 Roll mixing processability of Good processing EPDM and EPDM[10]

2. Relationship between formulation amount and tensile strength

Conventional EPDM which has been peroxide-cured tends to have a low tensile strength because of low loading, whereas the Good Processability EPDM maintains a high level of tensile strength even at low loading. Because the roll processability for conventional EPDM deteriorates at low loadings, the reinforcing agent does not get dispersed sufficiently during the roll process, and this is the likely reason for the drop in tensile strength. On the other hand, the Good Processability EPDM has excellent roll processability even at low loading, and so the reinforcing agent can be dispersed evenly throughout, which enables the tensile strength to be maintained at a high level. In addition, the tensile strength of Good Processability EPDM which has been peroxide-cured is even superior to the tensile strength of conventional EPDM which has been sulfur-cured (**Fig. 8**).

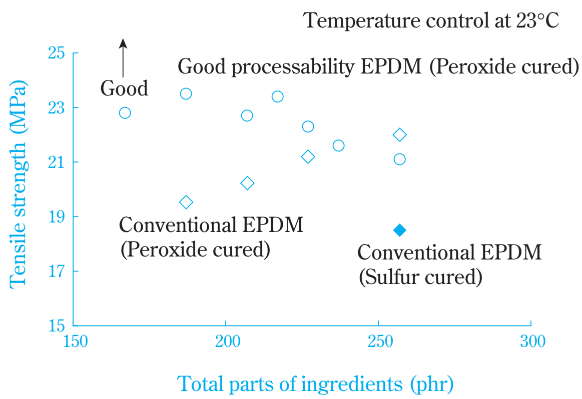


Fig. 8 Relation of Total parts ingredients and Tensile strength

3. Relationship between formulation amount and dynamic-to-static modulus ratio (original)

At the same formulation amounts, the dynamic-to-static modulus ratio for the peroxide-cured Good Processability EPDM is about the same as for the conventional EPDM, but at low loading rates, the Good Processability EPDM exhibits a low dynamic-to-static modulus ratio which surpasses the ratio for conventional EPDM[8] (**Fig. 9**).

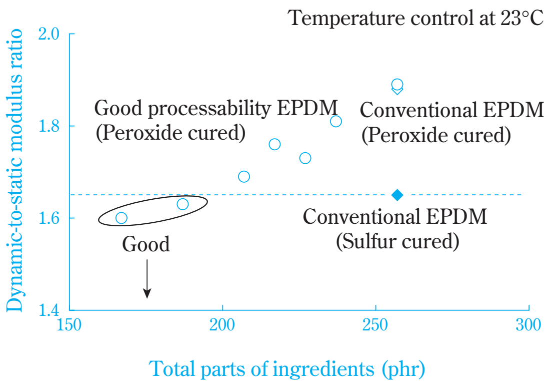


Fig. 9 Relation of Total parts ingredients and Dynamic-to-static modulus ratio[4]

4. Relationship between roll processability and dynamic-to-static modulus ratio (original)

Because the cross-linking density of conventional EPDM drops when the curing method is changed from a sulfur-cured system to a peroxide-cured system, the dynamic-to-static modulus ratio also deteriorates. For identical formulation amounts, the Good Processability EPDM exhibits about the same dynamic-to-static modulus ratio as conventional EPDM, but it has excellent roll processability. Because of the excellent roll processability of Good Processability EPDM, it is feasible to reduce the loading of the formulation with the purpose of obtaining an improvement in the dynamic-to-static modulus ratio. In other words, in addition to the fact that the Good Processability EPDM has excellent roll mixing processability, it also exhibits a low dynamic-to-static modulus ratio which is superior to that of conventional sulfur-cured EPDM, even though the Good Processability EPDM is peroxide-cured (**Fig. 10**).

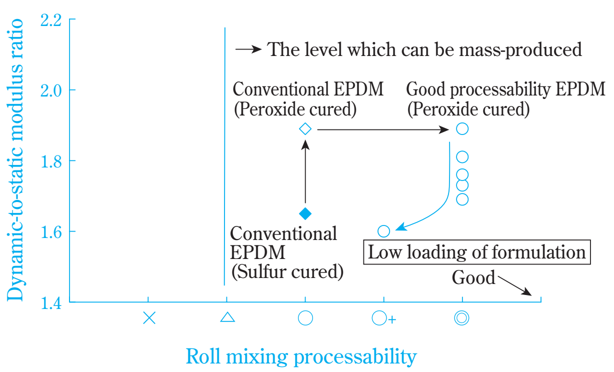


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Fig. 10 Relation of Roll mixing processability and Dynamic-to-static modulus ratio[4), 10)]

5. Heat aging resistance of the dynamic-to-static modulus ratio

The dynamic-to-static modulus ratio for conventional EPDM which has been sulfur-cured becomes higher (i.e. worsens) after heat treatment (**Fig. 11**). On the other hand, EPDM which has been peroxide-cured maintains the same dynamic-to-static modulus ratio before and after heat treatment, regardless of the EPDM structure. For sulfur-cured EPDM, the cross-linking form is changed from polysulfide bonds into monosulfide bonds as a result of heating (**Fig. 12**). When this disassociation of the polysulfide bonds occurs, the formation-S radicals (thiyl radicals) attack the double bonds in the EPDM and an automatic oxida-

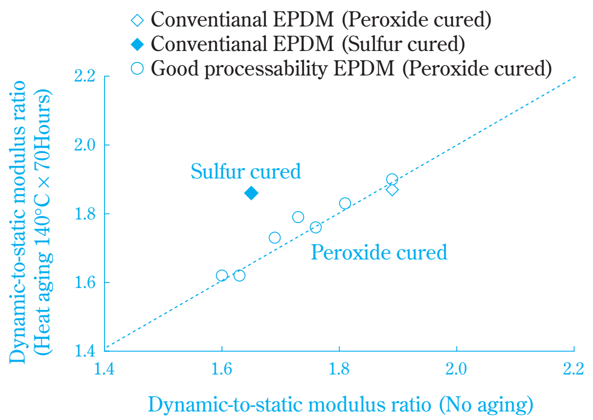

Fig. 11 Heat resistance of Dynamic-to-static modulus ratio[4]

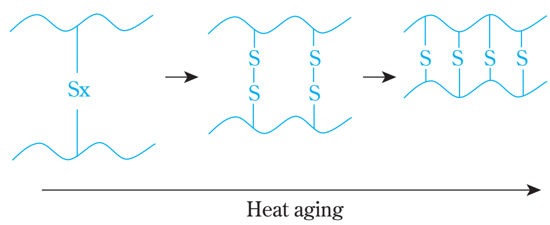

Fig. 12 Change of the cross-linking form which depends on heat aging (sulfur cured)

tion reaction occurs. The heat-induced aging of sulfur-cured products reduces the rubber elasticity and results in an almost-rigid body. This means that the dynamic-to-static modulus ratio of sulfur-cured EPDM becomes worse as a result of heat-induced aging, and therefor heat causes a deterioration not only in the mechanical properties of the rubber but also in its anti-vibration characteristics. In addition, EPDM which has been peroxide-cured has stable mechanical properties and anti-vibration characteristics with regard to the effects of heating, making them an ideal anti-vibration rubber material for use in muffler hangers where heat-resistance specifications are important.

6. Relationship between roll mixing processability and dynamic-to-static modulus ratio after aging

The physical properties after heat aging are important for products with heat-resistant specifications, and so if we compare the different grades again with this in mind, it can be seen that the Good Processability EPDM shows an excellent balance between processability and physical characteristics (**Fig. 13**).

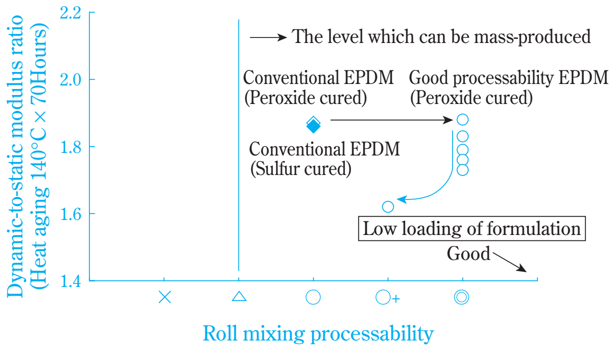

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Fig. 13 Relation of Roll mixing processability and Dynamic-to-static modulus ratio (140°C × 70Hours Heat ageing)

7. Good Processability EPDM line-up

The surrounding temperatures where muffler hangers are used can vary considerably, and so we investigated the performance of Good Processability EPDM in both high-temperature and low-temperature regions.

In particular, the temperature dependence of the dynamic-to-static modulus ratio was investigated while giving specific attention was given to the propylene content (C3' content) of the Good Processability EPDM. DSC measurements for the Good Processability EPDM with differing C3' content confirmed the existence of heat absorption peaks resulting from microcrystalline portions around temperatures of approximately 40°C for all EPDM samples. The heating amount (ΔH) for EPDM with a C3' content of 20% was approximately 21 J/g, whereas as the C3' content was increased to 23% and 30% respectively, the heating amount decreased, so in other words it was apparent that the microcrystalline portions decreased as the C3' content was increased (**Fig. 14**).

EPDM C3' content	(%)	20	23	30
ΔH	(J/g)	20.9	8.1	2.2

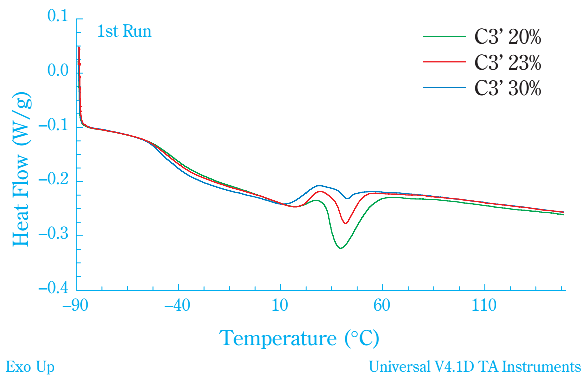

Fig. 14 Relation of C3' content of Good processability EPDM and DSC ΔH

Next, the temperature dependence of the dynamic elastic modulus for Good Processability EPDM with differing C3' content is shown (**Fig. 15**). The temperature dependence of the dynamic elastic modulus varies depending on the C3' content of the EPDM such that the temperature dependence of the dynamic elastic modulus becomes larger for lower levels of C3' con-

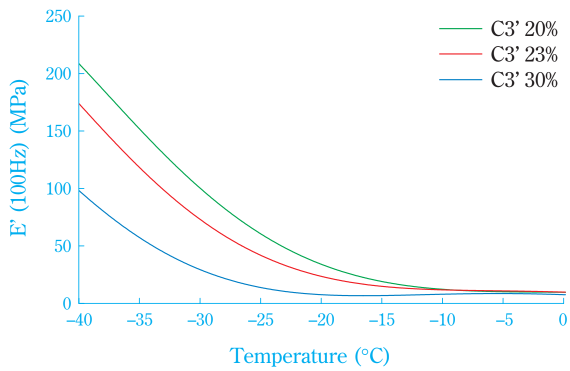

Fig. 15 Relation of Temperature and Dynamic elastic modulus

tent. When the temperature dependence of the dynamic elastic modulus is high, the dynamic elastic modulus becomes higher at low temperatures, and the amount of vibration transmitted via the muffler hangers to the vehicle body increases. Accordingly, it is important to minimize the temperature dependence of the dynamic elastic modulus in low-temperature regions, and so it is recommended that the C3' content of the Good Processability EPDM be set to a high amount.

The roll mixing processability is controlled by λ_b (extension to break) and θ_d (deformation index) as mentioned earlier, and the excellent roll mixing processability shown by the Good Processability EPDM is a result of the high maximum true stress σ_m. The molecular structure is designed so that there is a higher ethylene content in the lower molecular weight portions, so that the low-molecular weight portions of the Good Processability EPDM can form into network linking structures with greater efficiency, which suppresses increases in the viscosity factor and allows a suitable value for σ_m to be maintained.

DSC measurements for the Good Processability EPDM showed the existence of heat absorption peaks resulting from microcrystalline portions around temperatures of approximately 40°C for all EPDM samples regardless of their differing C3' content, which shows that these microcrystalline portions are a contributing factor to the elasticity and to the maintenance of a suitable value for σ_m.

8. Balance between roll mixing processability and anti-vibration characteristics

The Good Processability EPDM has quite superior roll mixing processability compared to conventional EPDM. By making use of the excellent roll mixing processability of the Good Processability EPDM to carry out peroxide-curing at low loading, the tensile strength and the dynamic-to-static modulus ratio also produce values which are excellent, giving the Good Processability EPDM an excellent balance between roll mixing processability and anti-vibration characteristics compared to conventional sulfur-cured EPDM (**Table 4**).

Table 4 Characteristics of various EPDM

EPDM Cured system	Conventional EPDM Sulfur	Conventional EPDM Peroxide	GP-EPDM Peroxide	GP-EPDM Peroxide Low loading
Mixing processability	○	○	◎	◎
Tensile strength	△	○	○	◎
1) Dynamic-to-static modulus ratio	○+	○	○	◎
2) Dynamic-to-static modulus ratio	×	○	○	◎

1) No aging
2) Heat aging

(remark ◎ : excellent, ○+ : very good, ○ : good, △ : not bad, × : poor)

Conclusion

The situation regarding EPDM is continually changing in line with the structure of the automobile industry and the needs of society, and it is impossible to escape the need of increasing globalization and environmental measures. Our Good Processability EPDM for anti-vibration rubber was developed from the point of view of seeds, but it can also definitely be seen as a product which meets certain needs (environmental measures). We have worked on developing the Good Processability EPDM series beginning with the high-diene type which needs less mixing time than before and which has already been released into the market for sponge applications, and we are gradually extending our scope. We would like to present our results for this high-diene Good Processability EPDM in a separate paper. And from this point on we hope to continue putting our efforts into the development of EPDM grades which can accommodate changes in automobile functions and performance demands.

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