

# Effects of carbon black on compression set with peroxide cross-linking elastomer

## 1. Introduction

One of the important parameters showing heat resistance of elastomer sealing materials is compression set (CS). CS is an indicator for the permanent distortion in case of loading at a certain temperature for a certain amount of time to the elastomer material in compression, and it is calculated as Figure1. For example, CS100% indicates that it is completely distortion and highly likely to end up in leakage. It is an effective measure to check durability of sealing materials.

Usually, carbon black (Carbon) is contained in elastomer materials as a reinforcing filler, and we can adjust their mechanical properties including tensile strength and stretch by changing the primary particle-size or the amount of Carbon added. However, it has become an issue in the product development scenes that there were often trade-offs between the mechanical properties and CS gained from blending Carbon.

It is well known that CS is correlated with effective cross-link density of elastomer in non-Carbon filled system. Therefore, it is possible that this trade-off is also related with effective cross-link density. However, we cannot properly evaluate properly the cross-link density in Carbon filled system with calculations of a general swelling test due to an effect of reinforcement of Carbon, and it was an issue that we could not analyze the correlation with CS.

Based on this, in this report, we analyzed the relationship between effective cross-link density of Carbon-filled systems and CS, using mainly dynamic viscoelasticity measurements. We also examined the causes of changes in CS of elastomer material with different types of Carbon fillers. We think that with this

analysis, we can contribute to controlling trade-offs between mechanical properties and CS, and to establish guidelines for selection of Carbon in accordance with demanded characteristics.

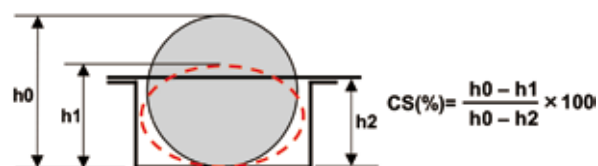


Figure1 Calculation of CS

## 2. Experiment

### 2-1) Preparation of samples

Composition of Carbon mixture in each sample is shown in Table1. We chose FKM (VDF-HFP-TFE copolymer) and EPDM (ethylene-propylene-diene copolymer) from among peroxide cross-linked systems, which are especially suitable to be used in high temperature environments, as the elastomer base materials. We prepared samples that were each blended with 3 different particle-sizes of Carbon (HAF: primary particle size is about 28 nm, MAF : primary particle size is about 38 nm, MT : primary particle size about 450 nm) for both polymers, and also made non-Carbon filled system as the control system. As for blended materials other than Carbon, we used 2, 5-Dimethyl-2, 5-di (tert-butyl peroxy) hexane as peroxide for both FKM and EPDM systems, and used triallyl isocyanurate as a cross-linking coagent. The same blending amount was set for each polymer system. In addition, with EPDM system, as other blended materials, the same blending amount of anti-aging substance, zinc oxide and processing aid were added to each sample.

Table1 Carbon blend compositions and physical properties

Sample	F-Control	F-A20	F-B20	F-C20	E-Control	E-A50	E-B50	E-C50	
<b>Polymer species</b>		<b>FKM</b>				<b>EPDM</b>			
Carbon black species	—	MT	MAF	HAF	—	MT	MAF	HAF	
Primary particle size (nm)	—	450	38	28	—	450	38	28	
N <sub>2</sub> absorption specific surface area (m <sup>2</sup> /g)	—	7	49	79	—	7	49	79	
Amount of carbon black (phr)	0	20	20	20	0	50	50	50	
Hardness (JIS A)	57	72	84	86	48	65	70	70	
Tensile strength (MPa)	5.2	14.9	21.6	22.5	1.7	9.7	16.6	16.8	
Elongation at break (%)	330	245	220	230	185	190	215	230	
100% Modulus (MPa)	1.2	2.6	5.9	5.4	1.2	2.6	5.3	3.4	
CS (%) at 200°C×72hr	N.D	14.8	17.6	21.2	9.1	13.4	21.4	31.6	

Polymers and each blended material were kneaded by 8-inch rolls. Afterwards, 2 mm-wide sheets and CS disc pieces ( $\Phi 29 \times 12.5t$ ) were created by compression pressure molding.

## 2-2) Evaluation methods

We have measured hardness, tensile strength, tensile breaking extension, 100% modulus and CS of each sample at 25°C according to JIS K6253, K6251 and K6262. We conducted swelling test by soaking EPDM sample for 72 hours, using toluene as solvent and calculated effective cross-linking density ( $\nu_s$ ) using a modified Flory-Rehner equation<sup>1)</sup>.

We carried out dynamic viscoelasticity measurements using DMS6100 (Seiko Instruments) under tension mode, rate of rising temperature at 2 °C/min, frequency at 10 Hz, applied distortion at 0.05 % and temperature range between -50°C and 150°C.

## 3. Results and discussion

### 3-1) Relationship between mechanical properties and CS

Table1 shows mechanical properties and CS of each sample. These are the results from blending 20phr of each Carbon in FKM system and 50phr in EPDM system.

With both FKM and EPDM systems, the smaller the particle-size of Carbon used, which is said to be better in reinforcement in general, the higher the increase in hardness and tensile strength. Although 100% modulus also showed similar tendencies, it decreased with HAF filled substance with the smallest particle size.

While with EPDM system, the smaller the particle size of Carbon used, the higher the increase in breaking elongation, FKM system showed a different tendency and F-Control, which is non-Carbon filled substance, showed the largest value.

With both FKM and EPDM systems, the smaller the particle size of Carbon used, the more CS increased and heat resistance was lowered. In addition, from the results of mechanical properties mentioned earlier, it was confirmed that there is a trade-off relationship between changes in CS dependent on the blended Carbon type, and hardness, tensile strength and 100% modulus. It should also be mentioned that it was not possible to measure CS of F-Control because the sample was broken by compression at measurement.

### 3-2) Correlation between effective cross-linking density and CS

Although it is well known that CS is correlated with effective cross-linking density measured by swelling test in non-Carbon filled system, the situation is different with Carbon-filled system. Figure2 shows the relationship between effective cross-linking density and CS measured by swelling test of EPDM system samples produced in this experiment.

It cannot be said that there is a correlation between effective cross-linking density and CS from these results. We consider this is due to the reinforcement effect of Carbon.

Cross-linking density is calculated in swelling tests according to the degree of swelling of the sample soaked in good solvent. Therefore, we consider that it would be difficult to calculate accurate effective cross-

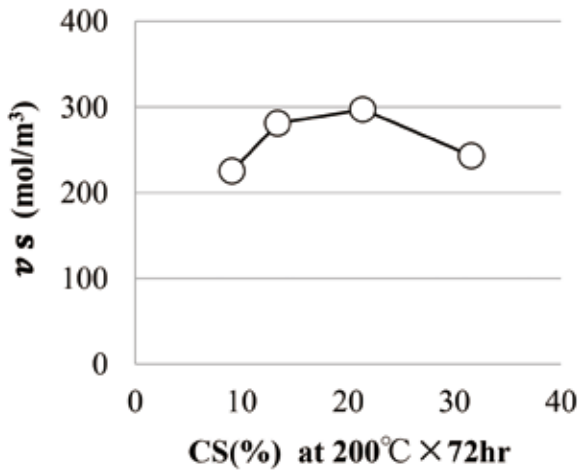


Figure2 Relationship between effective cross-linking density and CS from swelling test

linking density if natural swelling is disturbed by reinforcement property of Carbon.

### 3-3) Relationship between dynamic viscoelasticity properties and CS

Since the past, there is loss tangent, ( $\tan \delta$ ), as another indicator to show cross-linking density in non-Carbon filled system, which can be acquired by dynamic viscoelastic measurements. For example, Imoto and coworkers<sup>2)</sup> reported the higher the cross-linking density, the lower  $\tan \delta$  on the higher temperature side becomes. They said that the lower the cross-linking density is, the more terminal molecular chains which easily flow increase, and the larger  $\tan \delta$  becomes, which reflects energy loss due to forced vibration.

Iwabuki and coworkers<sup>3)</sup> report a good correlation between  $\tan \delta$  within the high temperature range and the cross-linked component amount (or uncross-linked component amount) obtained by pulsed NMR despite any type of filler. The  $\tan \delta$  within a high temperature range reflects relaxation due to the movement of terminal molecular chains even in Carbon-filled systems, and this can be an effective measure when analyzing the correlation between effective cross-linking density and CS.

Figure3 shows the relationship between  $\tan \delta$  and temperature in EPDM system samples. The smaller the particle size of Carbon used, the lower the peak value of

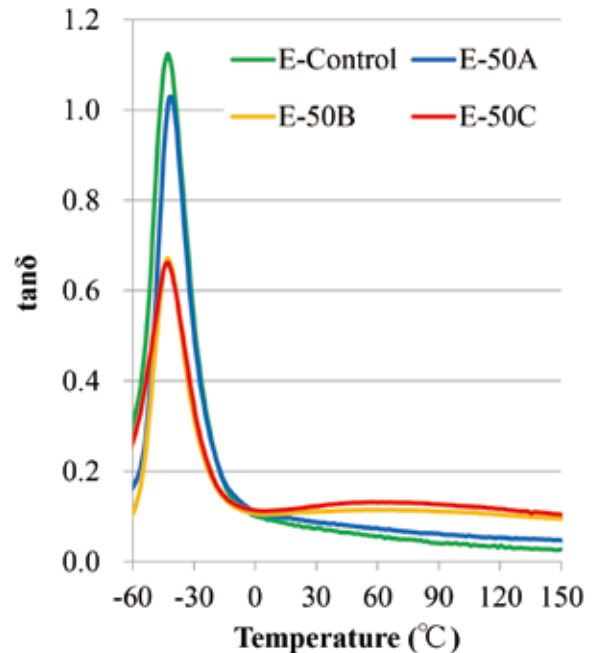


Figure3 Relationship between  $\tan \delta$  and temperature in EPDM systems

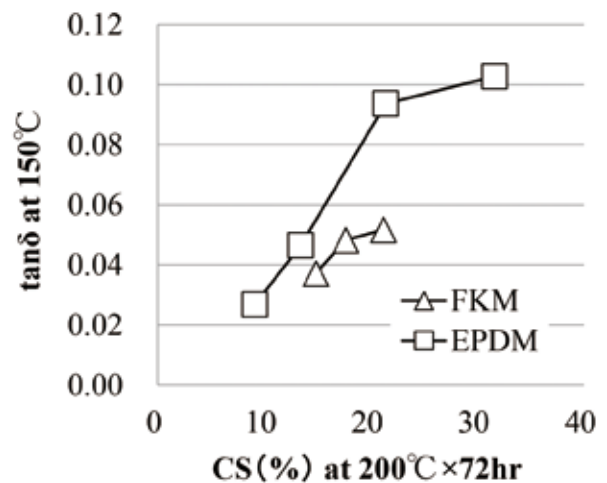


Figure4 Relationship between  $\tan \delta$  at 150°C and CS

$\tan \delta$  becomes, which we consider is exhibiting the reinforcement property of Carbon. On the contrary to the peak value, the smaller the particle size of Carbon added, the higher the value of  $\tan \delta$  on the high temperature side, which is regarded as reflecting relaxation due to the movement of terminal molecular chains.

Figure4 shows the relationship between  $\tan \delta$  and CS at 150°C in FKM and EPDM systems respectively. Unlike

the results of Figure2,  $\tan \delta$  increases according to the increase of CS both in FKM and EPDM systems, which tells us there is a correlation. If we assume  $\tan \delta$  at  $150^\circ\text{C}$  reflects the amount of relaxation due to the movement of terminal molecular chains, we consider that increase of  $\tan \delta$  means decrease of effective cross-linking density led to increase of CS. In addition, it suggests a possible effectiveness of  $\tan \delta$  within the high temperature range as an indicator of cross-linking density in Carbon-filled system.

### 3-4) Relationship between the total surface area of Carbon and $\tan \delta$

Figure5 shows a relation between the total surface area of Carbon filler in each sample and  $\tan \delta$  at  $150^\circ\text{C}$ . The total surface area of Carbon was calculated by multiplying the nitrogen absorption specific surface area ( $\text{m}^2/\text{g}$ ) for each Carbon shown in Table1, by the compound amount (g).

As a result, we found that  $\tan \delta$  increased according to the increase of the total surface area of Carbon filler for both FKM and EPDM systems and had a good correlation.

The basic structure of Carbon is a graphite structure, however on the surface, it possesses defective areas including oxygen, hydroxyl groups and structures in which graphite has undergone ring cleavage by hydrogenation, which are reported to become receptors

for free radicals<sup>4)</sup>. This means that increase of  $\tan \delta$  in accordance with increase of the total surface area of Carbon which was confirmed in Figure5 could have occurred because peroxide radicals, which was an initiator for cross-linking, was trapped due to the increase of defect areas on the surface of Carbon in elastomer and effective cross-linking density has decreased.

Together with the results of Figure4, this leads us to conclude that increase of the total surface area of Carbon in elastomer inhibits cross-linking reaction with peroxide, and increases CS by decreasing the effective cross-linking density.

Thus, when we design the recipe, since adding too much Carbon or small particle-sized Carbon increases CS, it is necessary to consider and determine appropriate Carbon type and blending amount while considering the balance with mechanical properties.

## 4. Conclusions

We found the following through analysis of the relationship between CS of peroxide cross-linked FKM and EPDM in Carbon-filled systems and effective cross-linking density using dynamic viscoelasticity.

- (1) The results of dynamic viscoelasticity measurements suggest the smaller the particle size of Carbon filler in both FKM and EPDM systems, the higher  $\tan \delta(150^\circ\text{C})$  increased and the larger the relaxation due to the movement of terminal molecular chains.
- (2)  $\tan \delta(150^\circ\text{C})$  has a good correlation with CS in both FKM and EPDM systems, and CS increased as  $\tan \delta$  increased, suggesting the possibility of an increase of CS in not only in non-Carbon filled but also in Carbon filled system with decrease of effective cross-linking density.
- (3) With increase of the total surface area of Carbon filler,  $\tan \delta(150^\circ\text{C})$  increased. This brings us to the conclusion that increase of the total surface area of Carbon in elastomer inhibits cross-linking reaction of peroxide and that decrease of effective cross-linking density would bring increase of CS.

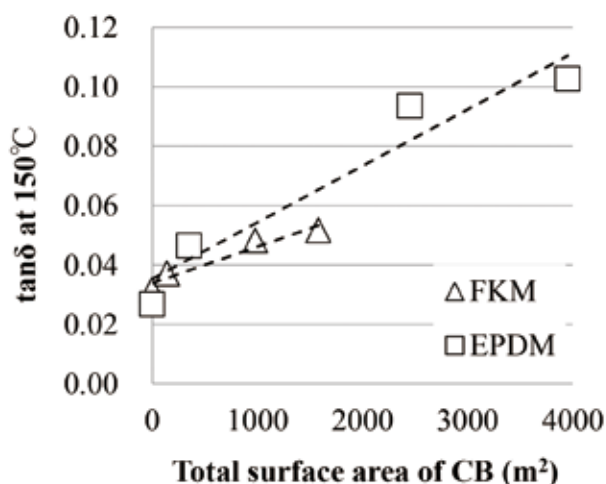


Figure5 Relationship between the total surface area of filled Carbon and  $\tan \delta$  at  $150^\circ\text{C}$

## 5. Acknowledgment

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This report analyzed a limited number of Carbon types. For planning better guidelines of Carbon selection, we think it is necessary to conduct a more multifaceted analysis that analyzes more varieties of Carbon and uses other analysis methods, which we plan to carry out in the future.

Finally, to proceed in this study, we were given a lot of support and advice from Junji Mizukado, Group Leader of the Chemical Materials Evaluation Group, Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology. We thank him very much.

## 6. References

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