Development of a novel cross-linking agent with excellent resistance to high-temperature vapour

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Seals, such as elastomer O-rings, are used to prevent the leakage of vapour from the ductwork or devices through which it flows. The temperature of the vapour that is often present in industrial processes continues to increase. Therefore, there is a requirement for sealing materials that are proven to work under conditions that involve high-temperature vapour. This article describes the development of a cross-linking agent for perfluoroelastomer that has two features – resistance to high-temperature vapour and cross-linking efficiency.

Vapour is used in a wide range of industrial processes. Seals, such as elastomer O-rings, are used to prevent vapour from leaking from the ductwork or devices – used, for example, in semiconductor production equipment and chemical plants – through which it flows.

The temperature of the vapour that is often present in industrial processes continues to increase. Therefore, there is a requirement for sealing materials that are proven to work under conditions that involve high-temperature vapour.

In such cases, sealing materials made from perfluoroelastomer (FFKM), copolymer of tetrafluoroetylene (TFE) and perfluoroalkylvinylether (PAVE) are used, but increasingly these are not sufficiently resistant to high-temperature vapour. This means that their performance needs to be further improved.

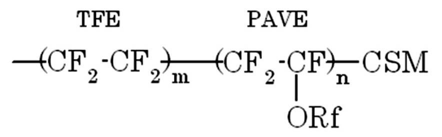
Nichias Corp has been engaged in the research and development of cross-linking agents for FFKM. For example, this work has covered the use of the triazine ring as a cross-linking catalyst.[1] The company's researchers have developed a novel cross-linking agent which is resistant to vapour at temperatures ≥ 300°C. This material has been commercialised as "BLAZER O-ring-S2", TOMBO No 2675-S2.

Cross-linking structure and design principle

FFKM does not have double bonds or C–H bonds in its main chain, as shown in **Figure 1**. For this reason it is difficult to form a bridge between the main chains of FFKM using normal cross-linking methods, involving sulfur or peroxide. Therefore, a cure site monomer (CSM) – a monomer that contains a reactive site (for example, nitrile group, iodide and bromide) – is introduced to the FFKM.

Properties, such as heat resistance and resistance to high-temperature vapour, are determined by the cross-linking structure created by the reaction between the CSM and a co-agent. Typical varieties of CSM; cross-linking structures; upper temperature limit; and upper limit for the vapour temperature are shown in **Table 1**.

As is shown in the table the triazine ring cross-linking structure delivers good heat resistance, but its upper limit for the vapour temperature is not greater than 100°C. On the other hand, the fluorinated diene cross-linking structure has both high heat and vapour resistance, but its upper temperature limit does not reach 300°C.



$$-(CF_2\text{-}CF_2)_m-(CF_2\text{-}\underset{ORf}{CF})_n-CSM$$

Figure 1. Structure of FFKM – perfluoroalkyl group (Rf) and cure site monomer (CSM).

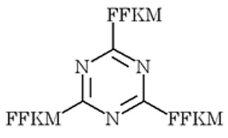
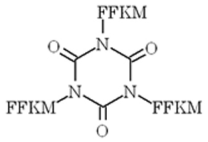
CSM	Cross-linking method	Cross-linking structure	Upper temperature limit	Upper limit for the vapour temperature
CN	Cross-linking catalyst (phosphorus or stannum compounds)	 Triazine ring	320°C	100°C
I, Br	Peroxide	 Triallyl isocyanurate	200°C	200°C
		FFKM-CH=CH-$(CF_2)_n$-CH=CH-FFKM Fluorinated diene	280°C	280°C

Table 1. Varieties of cure site monomer (CSM).

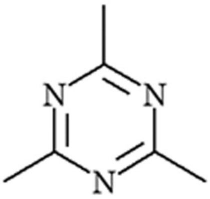
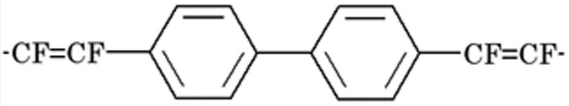
Cross-linking structure	Activation energy [kcal/mol]
 Triazine ring	17
$-CH=CH-(CF_2)_6-CH=CH-$ Fluorinated diene	35
$-CF=CF-(CF_2)_6-CF=CF-$ Structure A	32
	45

Table 2. Simulation results of vapour resistance.

A new cross-linking structure is needed in order to develop FFKM sealing materials that are resistant to vapour at temperatures ≥ 300°C.

Such a cross-linking structure must:

- provide excellent resistance to high-temperature vapour; and
- be created efficiently using a cross-linking agent and FFKM.

In addition, it is important to consider side reactions between cross-linkers, and also the dispersibility in FFKM, to enable efficient cross-linking reactions to occur.

Cross-linking structure design

Using computer simulation, Nichias performed screening of potential cross-linking structures that possess a good resistance to high-temperature vapour.

The required activation energy for a reaction between the designed model compounds and water vapour was obtained through molecular orbital calculations. The higher the activation energy the model compound has, the more resistant it is to high-temperature vapour.

In considering a structure with a high cross-linking reactivity to FFKM, vapour resistance and heat resistance, we simulated "Structure A", which is fluorinated diene with excellent heat and vapour resistance – with fluorine substituted for its vinyl groups – and "Structure B", which is equivalent to Structure A, but with benzene rings introduced (**Table 2**).

In addition, as benchmarks, we also simulated the triazine ring that is sensitive to vapour, and fluorinated diene, with resistance to vapour at a temperature of approximately 300°C. The calculated activation energies are also shown in Table 2.

As expected Structure A is inferior in terms of its resistance to high-temperature vapour, compared with fluorinated diene, because it has lower activation energy. In contrast, the activation energy of Structure B is higher than that of fluorinated diene and, therefore, as anticipated, it has good resistance to high-temperature vapour.

Based on these results we synthesised a cross-linking agent that basically takes the form of Structure B, and conducted a series of demonstration experiments.

Test method

Sample preparation: compound and specimens

Compounds were prepared by mixing raw materials in an open roll mill for a period of 20 minutes. We used FFKM, including iodine as the CSM, peroxide as the reaction initiator, and the newly designed and synthesised cross-linking agent or fluorinated diene (as a benchmark cross-linking agent) as the raw materials.

The compounds were loaded into a mould, and pressed at a temperature of 190°C to make O-ring specimens (AS568-214).

Characterisation

It is necessary to reconcile resistance to high-temperature vapour of cross-linking structure with cross-linking density in order to use FFKM as a sealing material intended for applications involving high-temperature vapour.

If the compound has good resistance to high-temperature vapour, but a low cross-linking density, its mechanical strength and sealing properties are low and, therefore, it will not be an appropriate sealing material. Therefore, it is important to evaluate the relationship between resistance to high-temperature vapour and the cross-linking density of the compound cross-linking structure.

Evaluation of resistance to high-temperature vapour

We used the swelling change rate to evaluate the resistance of the O-ring to high-temperature vapour. The swelling change rate was calculated by the expression given below in **Formula 1**.

Water and the specimen were put into a pressure-tight case (made by Taiatsu Techno Corp) (**Figure 2**) and were held at a temperature of 300°C for 40 hours in an oven. The weight swelling rate after exposure to saturated vapour pressure was then calculated.

Swelling change rate [%] =

(the specimen weight swelling rate after saturated vapour exposure [%] – the specimen weight swelling rate before exposure [%]) / the specimen weight swelling rate before exposure [%] × 100 (1)

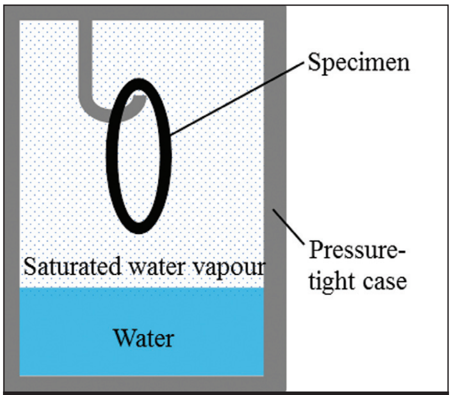


Figure 2. Resistance to high-temperature vapour test.

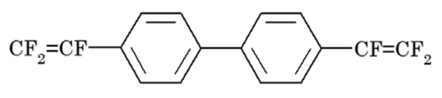


Figure 3. Structure of FB-S.

…where the specimen weight swelling rate after saturated vapour exposure is equal to the weight swelling rate of the specimen soaked in Fluorinert after vapour exposure; and the specimen weight swelling rate before exposure is equal to the weight swelling rate of the specimen soaked in Fluorinert before vapour exposure.

Cross-linking density

The cross-linking density was evaluated using the weight swelling rate. The specimen was cut into 10-mm lengths and soaked in Fluorinert FC-3283 (made by 3M Japan) at 60°C until swelling equilibrium was reached. Then, the specimen weight was measured and the weight swelling ratio was calculated using the expression given below in **Formula 2**. The low weight swelling ratio suggested a high cross-linking density.

Weight swelling ratio [%] =

(the specimen weight after testing [g] – the specimen weight before testing [g]) / the specimen weight before testing [%] × 100 (2)

Evaluation result

The simulation results suggested that the novel Structure B might be able to endure high-temperature vapour at 300°C. Therefore, we synthesised 4 ,4’-bis(trifluorovinyl)biphenyl (FB-S) (**Figure 3**) as a cross-linking agent that can form cross-linking Structure B, and studied the resistance to high-temperature vapour and cross-linking efficiency of the FB-S cross-linking structures.

Resistance to high-temperature vapour

The evaluation results for the resistance of cross-linked FFKM with FB-S to high-temperature vapour, and with fluorinated diene (1 ,6-divinylperfluorohexane) as a benchmark, are shown in **Figure 4**.

The swelling change rate of cross-linked FFKM with FB-S is low and it was found that this cross-linked structure is superior to the fluorinated diene cross-linking structure in its resistance to high-temperature vapour as simulated by computer modelling.

Cross-linking efficiency

The evaluation result covering the cross-linking density of cross-linked FFKMs with FB-S and fluorinated diene are shown in **Figure 5**.

Cross-linking with FB-S results in a higher weight swelling ratio and lower cross-linking density than cross-linking with fluorinated diene. The cross-linking density was not improved even when higher concentrations of cross-linking agent were added, and the test condition was modified.

Thus, FFKM cross-linked with FB-S has excellent resistance to high-temperature vapour, but has low mechanical strength and poor sealing properties, which means that it is unsuitable for use in sealing materials.

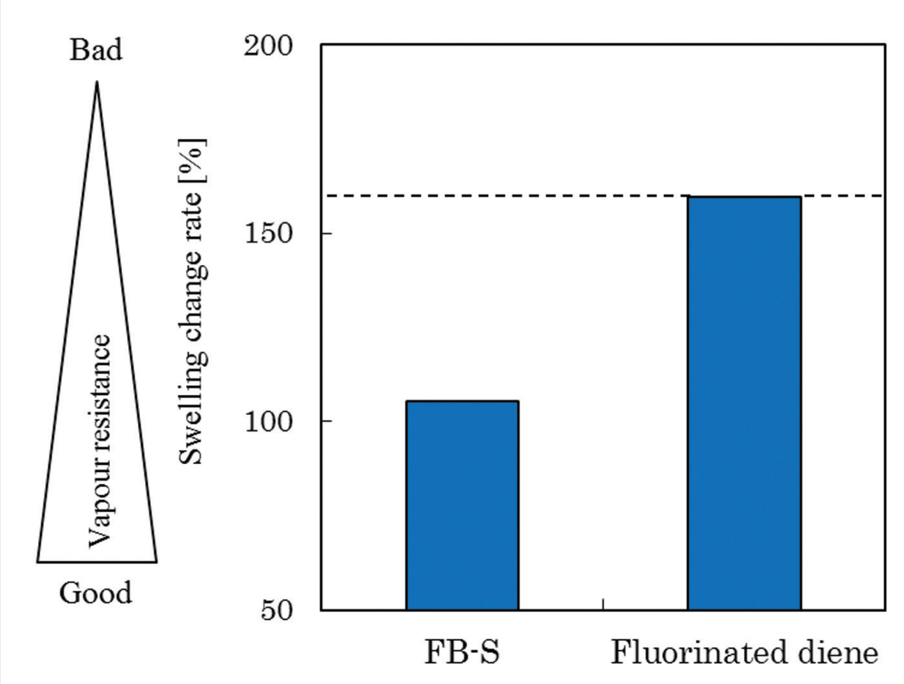


Figure 4. The evaluation results of high-temperature vapour resistance of FB-S (300°C × 40 hr).

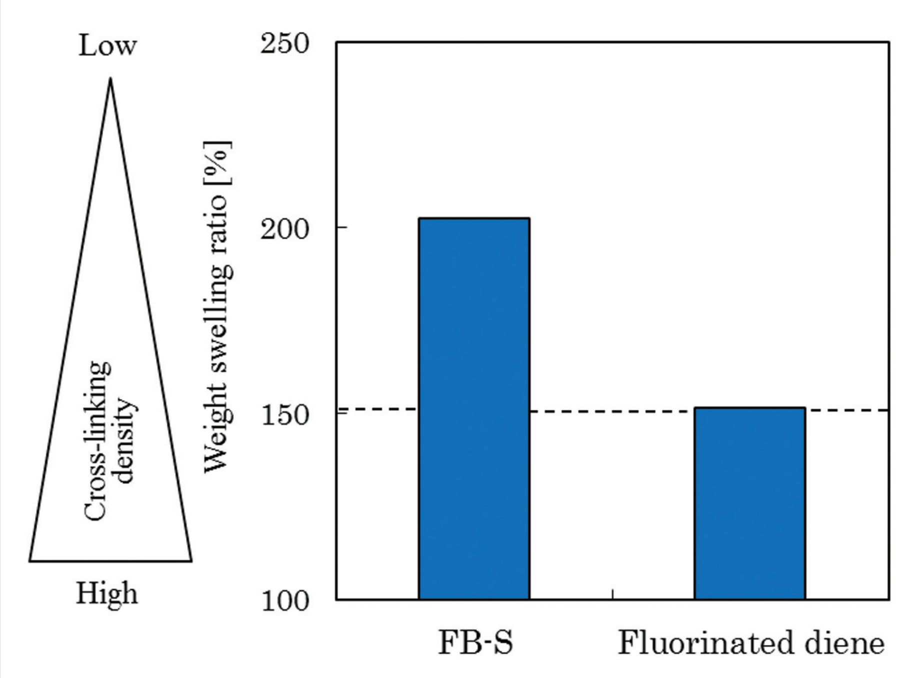


Figure 5. Measurement of cross-linking density of FB-S.

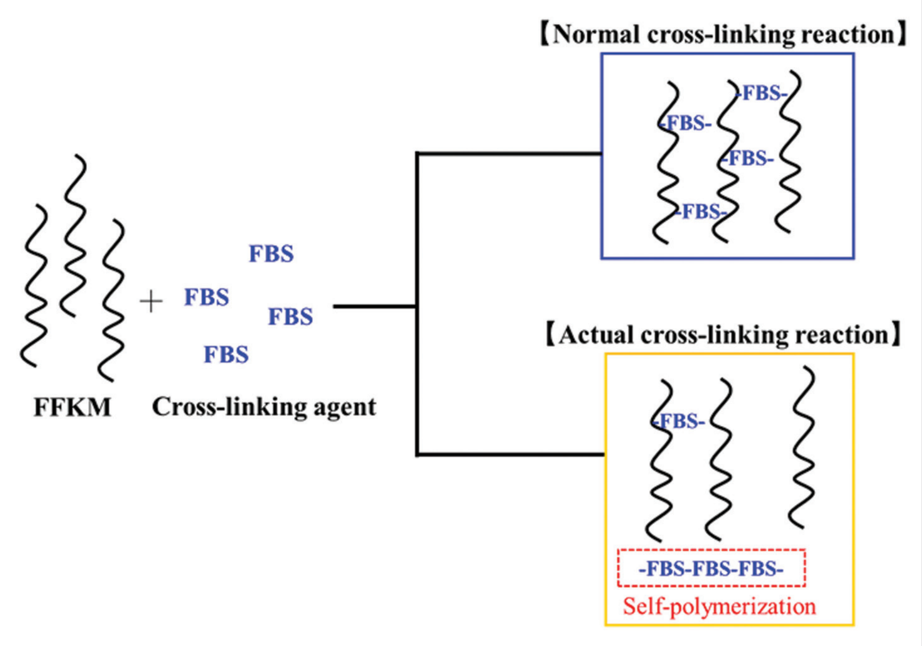


Figure 6. Estimated figure of cross-link scheme of FB-S.

Cause of decreasing cross-linking efficiency

We researched the cause of the decreasing FB-S cross-linking efficiency. It is known that the cyclic compound of (trifluorovinyl) benzenes (reacting site of FB-S) is obtained by heat.[2]

It is thought that self-polymerisation preferentially occurs and FB-S cross-linking efficiency decreases because the structure of FB-S has two trifluorovinylbenzenes connected to each other (**Figure 6**). For this reason, self-polymerisation of FB-S was investigated.

Fluorinated diene or FB-S, and peroxide, as the initiator, were dissolved in dimethyl sulfoxide and heated to 190°C for 5 minutes. After heating, the reaction rate was calculated by determining the quantity of unreacted fluorinated diene or FB-S with NMR. The results are shown in **Figure 7**.

Whilst the solution of fluorinated diene was substantially transparent, the solution of FB-S became cloudy because of the generation of dimethyl sulfoxide – an insoluble polymer. In addition, it was found that 50% of FB-S was consumed by self-polymerisation, from the results of quantitative NMR.

From the above, it was thought that the self-polymerisation of FB-S occurred in addition to the cross-linking reaction with FFKM, and the cross-linking density of FB-S, therefore, became low. To improve the cross-linking density it is necessary to better manage the self-polymerisation as a side reaction and dispersibility of the cross-linking agent.

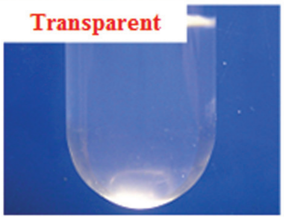
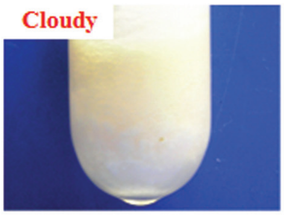
Cross-linking agent	0 minute	5 minnutes	Reaction rate
Fluorinated diene	Transparent 	Transparent 	10%
FB-S	Transparent 	Cloudy 	50%

Figure 7. Self-polymerisable FB-S.

Improving cross-linking efficiency

There are two methods that can be used to improve cross-linking density.

One entails inhibiting the self-polymerisation, whilst the other involves a way of dispersing the cross-linking agent more uniformly by increasing the affinity of the cross-linking agent for FFKM.

To inhibit self-polymerisation, we designed a cross-linking agent structure with steric hindrance, and synthesised the cross-linking agent, 4, 4'-bis (pentafluoroisopropenyl)biphenyl (TM-S), which introduced the trifluoromethyl group (CF_3 group), with large steric hindrance, to the α-position in trifluoro vinyl benzene – this being the reaction site of FB-S. (**Figure 8**)

To disperse the cross-linking agent more uniformly, we designed a cross-linking agent structure that has a small difference in fluorine content from FFKM, and synthesised the agent, 1, 6-bis [4-(trifluorovinyl)phenyl]dodecafluorohexane (RF-S) (**Figure 9**) – introducing the perfluoroalkyl group between benzene rings of FB-S.

The evaluation results of the cross-linking density of FFKMs cross-linked with TM-S and RF-S are shown in **Figure 10**.

The cross-linking density of RF-S was equal to fluorinated diene as the benchmark, however, TM-S cross-linking density decreased. When compared with verification results of the same test method (Figure 7), inhibition of self-polymerisation was confirmed, as we intended. However, it is suspected that the decrease in cross-linking efficiency was caused by a reduction in cross-linking reactivity with FFKM because of steric hindrance.

The evaluation results covering the resistance to high-temperature vapour of RF-S improved cross-linking density are shown in **Figure 11**. The resistance to high-temperature vapour of RF-S cross-linked FFKM is better than that of the fluorinated diene cross-linking structure. Therefore, it was suggested that RF-S cross-

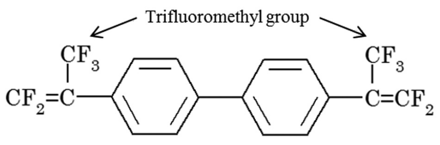


Figure 8. The structure of TM-S.

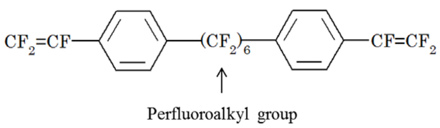


Figure 9. The structure of RF-S.

linked FFKM is capable of withstanding vapour at 300°C.

Solubility between the solvent (Fluorinert FC-3283) dissolving (having an affinity for) the FFKM and cross-linking agent was confirmed visually. The evaluation results of this affinity are shown in **Figure 12**.

It is noticeable that FB-S, with low cross-linking density because of self-polymerisation, was practically insoluble in the solvent, whilst RF-S was freely soluble. Taking the factors mentioned above into consideration, we think that reaction sites of FFKM and RF-S make it easy for them to access each other because of uniform dispersibility of RF-S, therefore the cross-linking efficiency of RF-S is improved.

From the above results, it can be seen that we developed the cross-linking agent RF-S with improved cross-linking efficiency. This cross-linking agent enables the company to develop sealing materials, made from FFKM, that are resistant to high-temperature vapour ≥ 300°C.

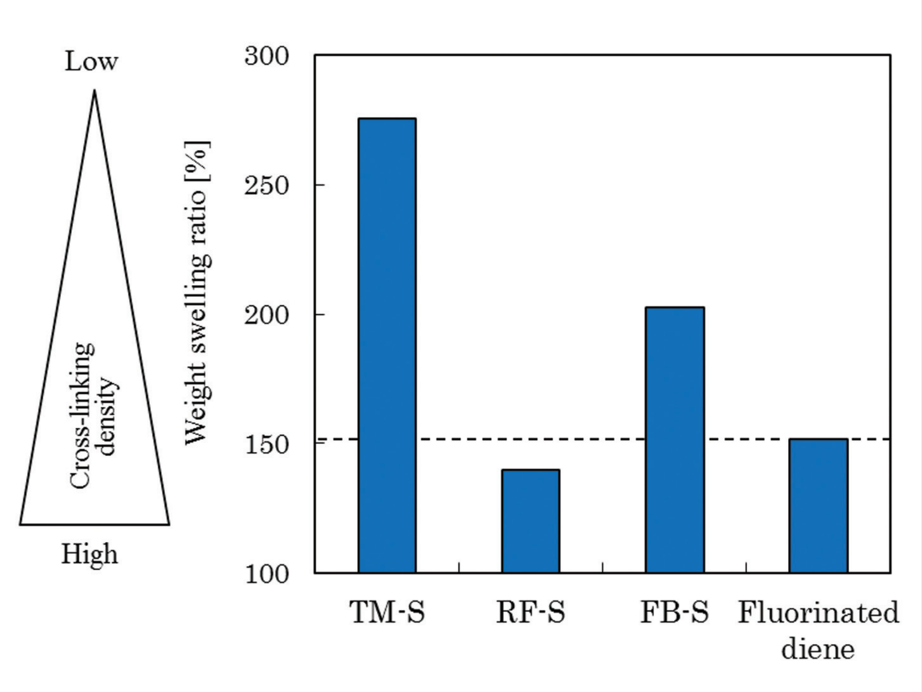


Figure 10. Examination results of cross-linking density of TM-S and RF-S.

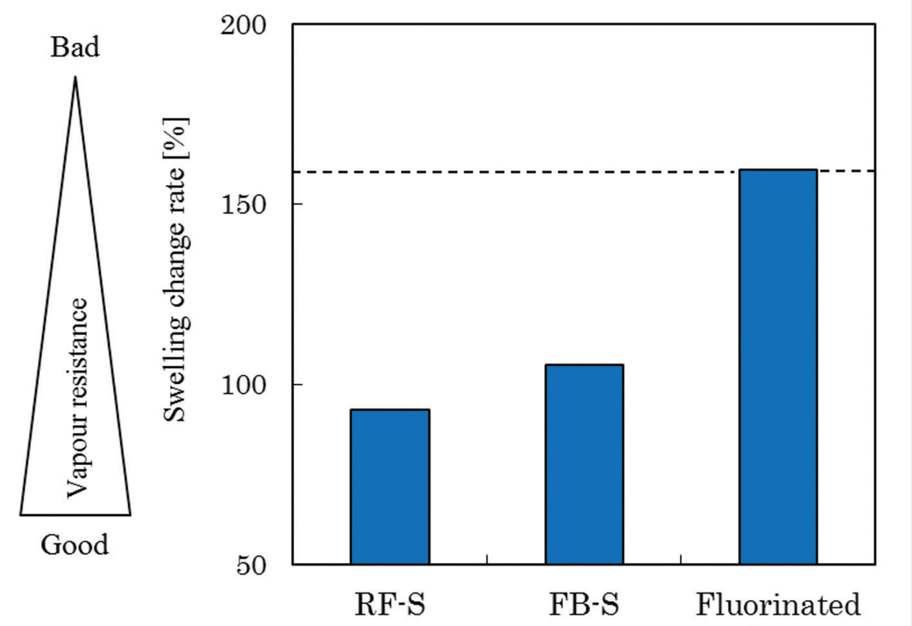


Figure 11. The evaluation results of resistance to high-temperature vapour (300°C × 40 hr).

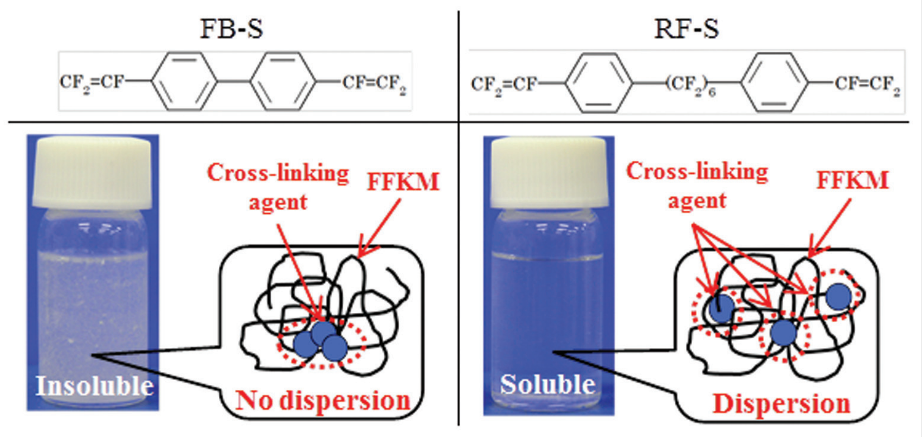


Figure 12. The evaluation (visual) results of the affinity of RF-S.

Conclusion

In this article, we have described a cross-linking agent (patented) that has two features: resistance to high-temperature vapour and cross-linking efficiency. This has been achieved by introducing aromatic rings and perfluoroalkyl groups to the structure of this cross-linking agent.

It is often difficult for processing manufacturers to design polymer structures. However, our struggle with the design and synthesis of a cross-linking agent has enabled Nichias to develop distinguished products.

It is forecast that the requirements of sealing materials used in semiconductor production equipment and chemical plants are becoming more and more functional and diversified. Therefore, we continue to promote research and development to contribute to the needs of the fundamental technology of “designing cross-linking agents”.

References

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2. A.D. Asandei, R.A. Weiss, I.W. Moran, Y. Chen and Gobinda Saha, *Polymer Preprints* 2004, 45(1), pp. 1010.

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