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A Study on the Factors for Improvement of Chemical and Physical Properties in Fluoric Rubber Coating for Use of the Extremely Acidic Environments

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It is known that the fluoric resin has the most outstanding properties in the extremely acidic environment of high temperature. However, this resin is the thermal hardening type that needs long time heat treatments above 250°C. It's impossible to use in situ in the extremely acidic environment such as a huge FGD ductworks or industrial chemical tanks. Furthermore, even the natural hardening type fluoric coatings which can be hardened less than 120°C can not be applied to the highly acidic environmental plants because of its chemical resistance. In this study, new fluoric coatings that has excellent thermal resistance, chemical resistance and corrosion resistance has been developed in order to solve above problems and to be applied to the large plant structures in the field. These newly developed coatings are organic and inorganic composite type that have fluoric rubber(100 wt%), fluoric resin(5~50 wt%), oxalates(5~30 wt%), inorganic fillers mixed with plate-type and bulk-type solids(20~150 wt%), hardeners(0.5~5 wt%), and hardening hasteners(0.1~3 wt%). The best chemical and physical properties of these coatings are acquired by variation of adhesive reinforcement agents, dispersants, leveling agents. Mixing ratios of plate-type and bulk-type inorganic fillers influence the thermal properties, abrasive resistance and chemical infiltration properties of coatings. The mixing control is also very important to have homogeneous surface and removing inner voids of coatings.

Keywords *: fluoric rubber, coatings, FGD duct*

1. Introduction

As industries have been developed, industrial facilities have been continuously constructed such as bridges, ships, refinery plants, storage tanks and power stations. Heavy duty coatings made of various ingredients have been also developed and widely used for preventing corrosion on these industrial facilities.

Among heavy duty coatings, there are epoxy, unsaturated polyester, silicon resin and fluororesin that are widely being used in relatively highly corrosive environments. However, in these coating materials, they have limit corrosion resistant characteristics in such extreme environments as high temperature, high chemical concentration and high erosive fluids. These coatings have been replaced by such corrosion resistant techniques as Teflon linings, super alloys and meting spraying coating, but these have also problems that are high construction costs and maintenance limits. For these reasons, high functional corrosion resistant coatings are actively being developed recently that are easy to apply with low costs like the general heavy duty coatings such as epoxy and unsaturated polyester etc.

In this study, a coating made of fluoroelastomers was developed that are used in various industries for their excellent heat resistance, chemical resistance and physical characteristics. This high functional fluoroelastomer coating will be applied to the industrial area in which traditional coatings and paints are inapplicable for its highly corrosive environments. These environments include FGD system in fossil fuel power plants in which high heat resistance and high acid resistance are needed.

1.1 The structure and characteristics of fluoroelastomers

Fig. 1 shows the general molecular structure of fluoroelastomers.[1)] Fluoroelastomers have excellent characteristics due to higher binding energy of C-F bond comparing to other organic resin. As fluorine contents(atomic %) in fluoroelastomers increases, the characteristics such as heat resistance, chemical resistance, ozone resistance, weather-

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	C-H	C-F	C-Cl
Bond Energy (Kcal)	99	116	81
Electronegativity	2.1	4.0	3.0
Covalent Radius (A)	0.37	0.72	0.99

$$-(CF_2\text{-}CH_2)_m\text{-}(\underset{\displaystyle\ \ }{\overset{\displaystyle CF_3}{|}}\!\!CF\text{-}CF_2)_n\text{-}(CF_2\text{-}CF_2)_o\text{-}$$

Fig. 1. Characteristics and molecular structure of fluoroelastomers

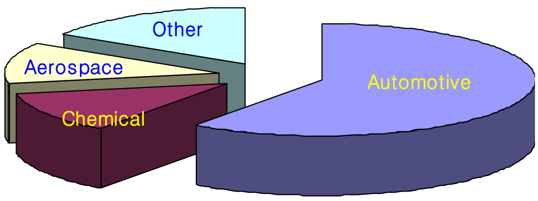


Fig. 2. Main application area of fluoroelastomers

ability.

Fluoroelastomers have been applied to special uses owing to these characteristics, in which rubber should have heat resistance and chemical resistance. Fluoroelastomers are widely used in automotive industry, chemical industry and aerospace industry as shown in Fig. 2. However, these are the form of solid for application that are gasket, O-ring, sheet and various components. The coating application as in this study is very rare case.

1.2 Application to FGD system

Table 1 explains the main reason that fluoroelastomers are selected for corrosion resistant materials of FGD system in fossil fuel power stations. Special coatings such as Novolac epoxy and unsaturated polyester have shown obvious limits in the use of corrosion resistant purpose in heavy oil fuel power stations. Fluoroelastomer is judged to be one of a few candidates for this severe corrosive environment.

Table 1. Comparison between FGD environments and characteristics of fluoroelastomers

No	FGD environments of heavy oil plants	Characteristics of Fluoroelastomers
1	High Temperature (80~200℃)	Heat resistance (> 200℃)
2	Extremely acidic solution(pH < -1)	Chemical resistance (> 80% H_2SO_4)
3	Vibration inside facilities	Rubber elasticity (High elongation)
4	Thermal shock with heat cycle	Rubber elasticity (High elongation)
5	Abrasion from combustion dust	Rubber elasticity (Softness)

1.3 Main composition and properties of fluoroelastomers

Although fluoroelastomers have excellent heat resistance, chemical resistance and physical properties, it is difficult to formulate them as a form of heavy duty coating materials in the industrial point of view. Fluoroelastomer coating have been limitedly applied to the automotive engine components and anti-adhesive rollers in duplicating machines etc.. Therefore the heavy duty coating of fluoroelastomers seems to be a nearly launching industrial area.

Main composition of fluoroelastomer coatings is summarized in Table 2 except solvents. Fluoric rubber, oxalates and hardener are ingredients that are related to the crosslinking reaction of general fluoroelastomers. Filler and additives are main functional components that make realize a long time corrosion resistance of fluoroelastomers as a heavy duty coating.[2)]

Fluoroelastomers are variously classified as their curing methods and weight percent of fluorine. This study approaches to the selection of fluoric rubber in the view of corrosion resistance. For the selection of it, corrosion resistance was evaluated with the method that the increased volume of test specimens immersed in H_2SO_4(95%, 23℃) for 14 days were measured after the specimens of specific size had been prepared varying with fluorine composition. In the results, the fluoroelastomer with 60% of fluorine showed 14% of volume increase. As the composition of fluorine increased, the volume increase rate of fluoroelastomer decreased so that only 2% of volume increase was reached in case of 70% of high fluorine added fluoroelastomer. From this result, it is noted that the fluorine rate in the fluoroelastomers can be selectively varied from lower level in less corrosiveness environment to higher level as required in the aggressive corrosion environment

Table 2. Main composition of fluoroelastomer coatings

Components	Composition (wt%)
Fluoric rubber	100
Fluoric resin	5~50
Oxalates	5~30
Inorganic filler - plate type	20~120
Inorganic filler - reinforced filler(nano size)	5~50
hardener	0.1~3
additives	1~3

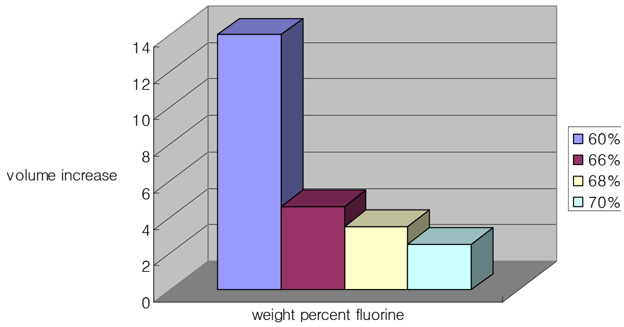


Fig. 3. Weight percent fluorine and acid resistance comparison

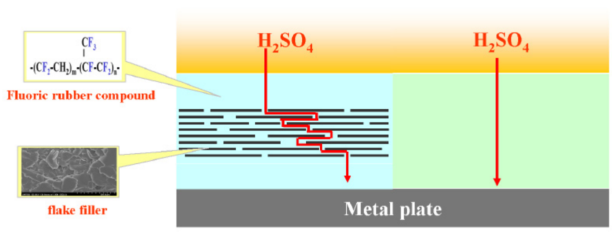


Fig. 4. Corrosion prevention mechanism of flake filler

of plants.

As mentioned above, less than 2% of volume increase was shown in the fluoroelastomer with 70% fluorine in 95% of H_2SO_4, relatively low temperature of 23℃, but this performance cannot meet the requirement for the heavy duty coating area in which both heat resistance and chemical resistance are needed. When the test temperature was raised to 100℃, more than 15% of volume was increased and surface failure of fluoroelastomer was occurred. In order to overcome this limitation, the corrosion prevention mechanism of flake was introduced to the selection of fillers in fluoroelastomers that were commonly applied to the traditional heavy duty coatings. Fig. 4 is the diagram shows the corrosion prevention mechanism of fillers. When coatings have general non-flake fillers or no fillers, sulfuric acid reach to metal surface and attack it through shortest distance of coating, but coating with flake filler has extended penetration distance of sulfuric acid through paths among flakes and it shows higher chemical resistance or long life expectancy.[3)]

In this study, a fluoroelastomer was developed with flake filler addition for long time corrosion resistance. Especially the influence of flake filler size to the corrosion resistance of fluoroelastomer was studied and the best filler size was selected for the coating materials with the highest performance.

There are various flake fillers such as mica, glass flake and mio etc. and one or a couple of them were applied.

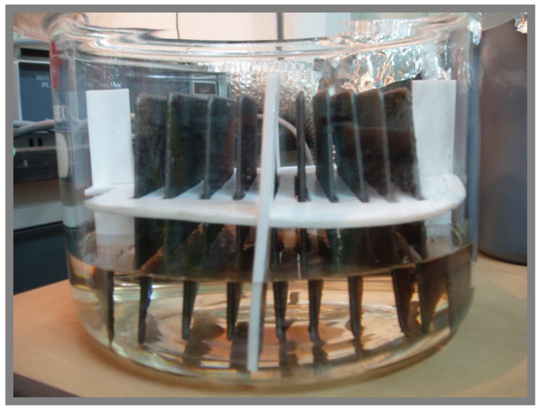


Fig. 5. Immersion test in sulfuric acid of fluoroelastomers(95% H_2SO_4, 90℃)

Once fluoroelastomers with various flake particle sizes were formulated, those were coated on metal specimens. These coated specimens were immersed in 90℃, 95% of H_2SO_4 solution for 14 days, and corrosion resistance test was performed for the size effect of flake filler on coatings, as shown in Fig. 5.

Fig. 6 shows the sulfuric acid immersion test results of specimens varying with the size of flake filler. The results were examined in the view of excellent corrosion resistance or corrosion failures according to the size of flake filler, and on the basis of them, Table 3 was derived.

When the size of flake filler was too small, enough corrosion resistance could not be appeared. As the size of it increased, it was found the corrosion resistance was manifested. However, when the size was too big, corrosion from the pinhole was occurred due to the gaps between flake fillers as shown in Fig. 6. Therefore too big size of flake filler is not desirable and it is concluded that less than 100 ㎛ of flake fillers are valid for the coatings.

One of other characteristics of fluoroelastomers is related to the high rubber elasticity with which they have high elongation and abrasion resistance maximized by the nano size of reinforced fillers.[4)] There are reinforced fillers such as fumed silica and carbon black that give fluoroelastomers to have abrasion resistance and elongation when these fillers are added in the range of not limiting the corrosion resistance, shown in Fig. 7. To determine the abrasion resistance, abrasion quantity was measured on the basis of Tabor abrasion ASTM D4060[CS-17, 1000cycle, 1000g load], and elongation was measured conforming to ASTM D638.[5),6)] The result shows that as reinforced addition of filler amount increases, elongation characteristics are improved. In the test result of abrasion resistance, when 5 wt% of reinforced filler was added, 48 mg of abrasion residue was produced but when 45 wt% was added, only 15 mg was produced.

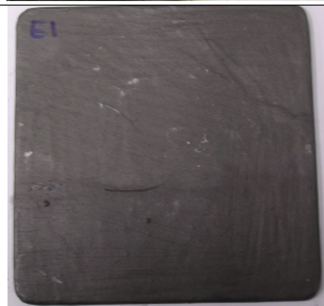
Before Test	After Test	Remarks
		Flake filler size : 4.5~15㎛ Result : Coating is infiltrated, corrosion is occurred on the matrix metal.
		Flake filler size : 80~110㎛ Result : Coating shows enough corrosion resistance.
		Flake filler size : 120㎛ Result : Coating shows pinholes and corrosion is occurred on the matrix metal.

Fig. 6. Immersion test result in sulfuric acid of coating with various flake filler size

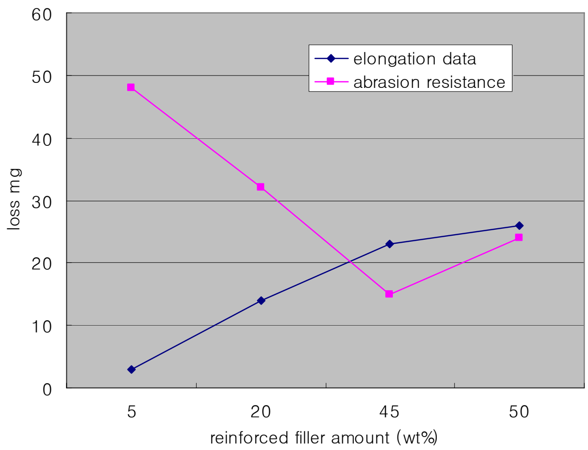


Fig. 7. Characteristics related to elasticity of coating with various amount of reinforced filler

From these results, it is concluded that characteristics of fluoroelastomers needed as heavy duty coatings can be improved from appropriate rate mixtures of flake fillers and reinforced fillers.

2. Conclusions

Epoxies and unsaturated polyesters have been widely used as traditional heavy duty coatings. However, these coatings have shown their limitations for application to the plants of extremely acidic environments. In order to solve this problem, a new kind of fluoroelastomer coating was developed and was tried to apply as a high resistant heavy duty coating. Results are as follows for the study of improvement in its characteristics.

1) Fluoric rubber has been widely used due to its high heat resistance, chemical resistance and physical properties. A new kind of fluoroelastomer coating was developed from these manifest characteristics. In comparison with corrosion resistance(in sulfuric acid) varying with fluorine composition, it was confirmed that fluoroelastomer with high fluorine has excellent acidic resistance need in extremely acidic environment.

2) Fluoroelastomer itself has excellent corrosion resistance but it cannot meet the characteristics needed for the use in extremely acidic environment such as FGD system. For the completion of its corrosion resistance, corrosion prevention mechanism of flake was introduced. The size of filler has a great effect on the corrosion resistance of fluoroelastomers, so that the best size of filler was evaluated for the best resistance in highly concentrated sulfuric acid. From this evaluation, a valid size of flake filler was selected for the use of target environment.

3) From the corrosion prevention mechanism of flake, the corrosion resistance of fluoroelastomer was greatly increased but other characteristics of coating needed for application such as high elongation, abrasion resistance and adhesiveness was decreased on the contrary. For solving these problems, reinforced filler was introduced, big im provements have been achieved.

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