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Fluoroelastomer with different properties and its application to automotive interiors

TECHNICAL REPORT

This paper introduces fluoroelastomers which are increasingly expected to be applied to automotive interiors as a material that responds to changes in the needs of the automotive market.

Background of development

In recent years, the automotive industry has been in a "one transition period in 100 years," and megatrends such as CASE and MaaS are drastically changing the existing concept of cars. For example, looking at sharing, a part of CASE, services, and opportunities to use and share the same vehicle with many unspecified users are increasing throughout the city. In such a usage situation, there is a greater need than ever before for interior components to be resistant to odors and stains, and even if odors and stains appear, they must be easy to remove.

In addition, the global COVID-19 pandemic, which still showed no sign of abating at the end of 2020 when this paper was being written, has completely changed the way people live. Not only wearing a mask but also sanitizing our hands and the things we often touch have become a part of daily life. There have been reports that frequent contact with disinfectants such as ethanol and sodium hypochlorite solutions cause discoloration of daily commodities whose components have not been selected for their chemical resistance and bleed-out of additives. We also saw manufacturers issuing warnings to people to refrain from sterilizing objects with alcohol. In automotive interiors, where genuine leather and plastics are often used, there will be an increasing need for materials and coatings that are not only antibacterial and antiviral but also resistant to chemicals in anticipation of daily sterilization.

The value of the passenger car itself as a tool of personal mobility has been reassessed by these changes in hygiene needs and, in a larger sense, by the COVID-19 pandemic. In fact, city lockdowns and stagnant economic activity worldwide have severely impacted automotive sales in many countries. However, the stunning recovery in car sales after the lockdown in some countries is seen mainly due to new purchasing behavior that avoided public transportation and switched to commuting and traveling by one’s own car. As such new groups of shoppers perceive cars not only as a means of transportation but also as an extension of their personal space, cars are required to be a place where people can feel comfortable and at ease, like at home or in their rooms, and at the same time, to incorporate individual preferences in terms of color tones and patterns. Moreover, many demands new materials that achieve unexampled design in automotive interiors.

Fluoroelastomers are drawing attention as a new material in consumer fields such as wearable devices, which have a lead due to hygiene, antifouling, and design needs, and the demand is expanding. It has become more common to see people wearing high-function and high-end watches with brightly colored watch straps made of rubber on the street. The application of fluoroelastomers has long been limited to industrial fields such as the internal combustion engines of automotives utilizing their high heat and chemical resistance. Recently, the establishment of toning technology for fluoroelastomers has eliminated such restrictions. As seen in watch straps made of rubber for wearable devices, for example, the applications are expanding that emphasize not only their industrial functionality but also their design aspects, such as their unique texture and vivid colors. This paper introduces fluoroelastomers which are increasingly expected to be applied to automotive interiors as a material that responds to the above changes in the needs of the automotive market.

2. Manufacturing process of fluoroelastomer products

2-1. Manufacturing process of fluoroelastomers

It can be applied by conventional methods such as needle dispense, jet dispense or spin coating, etc. Fluorite, a raw material of fluoroelastomers, is a natural mineral mainly composed of calcium fluoride (CaF_2), an inorganic compound. As a constituent element of the crust, the ratio of fluorine is higher than other elements. The polymers can be produced by synthesizing fluorinated monomers from fluorite via fluorocarbon gas and polymerizing the fluorinated monomers. Then, a wide variety of molded products with rubber performance are obtained by curing full-compound manufactured by kneading polymers with various compounding agents such as cross-linking agents in a molding process.

2-2. Molding process of fluoroelastomers

Curing (cross-linking) is required to demonstrate useful properties as a rubber. Curing progresses by applying heat and pressure to uncured rubber (full-compound), in which various chemicals such as curing agents are compounded in polymers. Two typical curing systems for fluoroelastomers are as follows:

・ Bisphenol curable

It has excellent heat resistance, and compression set resistance (sealability).

・ Peroxide curable

It has excellent mechanical properties, flex resistance, acid resistance, and steam resistance.
Compression, extrusion, and injection molding are used as molding methods.

・ Compression molding

This method molds and cures rubber products by placing uncured rubber into a mold cavity of a compacting machine and pressurizing the mold between heated hot plates of a curing press. It is easy to operate and widely used.

・ Extrusion molding

In this method, uncured rubber preheated in a cylinder using an extruder is plasticized by a screw, extruded, and then continuously molded into tubes and other shapes through a die. Steam curing is often used to progress the curing reaction after extrusion.

・ Injection molding

In this molding method, uncured rubber preheated in an extruder is injected into a mold set at a curing temperature at high speed to mold and cure rubber products quickly.

3. Physical properties and applications of fluoroelastomers

3-1. Physical properties of fluoroelastomers

Fluoroelastomer is mainly composed of carbon and fluorine atoms. The bond between carbon and fluorine atoms has significantly higher bonding energy than the bond between carbon atoms and hydrogen atoms that form generic resins and rubbers and has smaller polarizability. As such, they have various properties as follows.

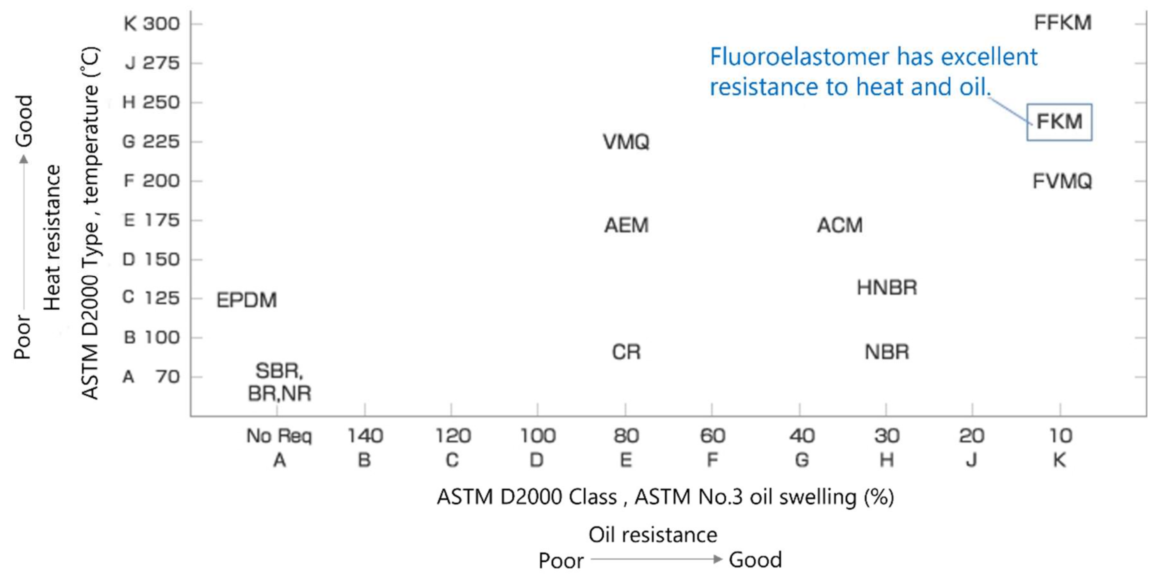
Heat resistance, chemical resistance, flame resistance, ozone resistance, weather resistance, low-dielectric constant, electrical insulation, water repellency, water resistance, oil repellency, and oil resistance

Figure 1. Comparison of rubber properties

Properties \ Type	FKM	VMQ	ACM	NBR	EPDM	Features of fluoroelastomers (FKM) (reasons for developing the property)
Specific gravity	1.8	1.0	1.0	1.0	0.9	The fluorine atom is heavier than hydrogen.
Heat resistance	◎	◎	○	△	○	No double bond in the main chain, high C-F binding energy.
Low-temperature resistance	△	◎	○	◎	◎	The main chain is not likely to act.
Electrical properties	○	○	△	△	◎	The C-F bond has a dipole moment (-CF2-CH2- is asymmetric and has a high dielectric constant with polarity).
Solvent resistance	◎	◎	○	△	○	It swells in similar substances (swells larger in certain solvents, such as fluorinated solvents).
Flame resistance	◎	○	▲	▲	▲	High C-F binding energy.
Steam resistance	◎	○	×	△	○	Basically, the higher the heat resistance, the better, although it depends on the composition.
Acid resistance	◎	○	△	○	◎	High C-F binding energy.
Alkaline resistance	△	◎	△	○	◎	Under severe conditions, a dehydrofluorination reaction occurs in the VdF portion.
Oil resistance	◎	△	○	○	×	Low affinity with HC-based solvents.
Permeability resistance	◎	▲	○	○	△	Low affinity with HC-based solvents, poor molecular motion.

Excellent ◎ > ○ > △ > ▲ > × Poor

Figure 2. Comparison of heat and oil resistance of rubbers



3-2. Example applications of fluoroelastomers

Fluoroelastomers are used in oil seals, valve stem seals, bearing seals, fuel hoses, turbocharger hoses, O-rings, gaskets, and pressure regulator membrane diaphragms for their high functionality. Although most of them are used for automotive parts, they are also widely used as industrial products in a wide range of industries, including construction machinery, steelmaking, food, semiconductors, energy, and office automation.

4. Fluoroelastomer properties meeting emerging needs

Although fluoroelastomers have been used mainly as industrial products, the following properties can be identified for automotive interior materials.

4-1. Durability and chemical resistance

As mentioned above, fluoroelastomers have excellent resistance to heat, water, oil, chemicals, ultraviolet rays, and steam. This means that their appearance and texture are not likely to change even when used in various environments for long periods. They are also less likely to change their physical properties due to chemicals such as disinfectants and to experience a sudden break, discoloration, or stickiness caused by hydrolysis, which is concern with rubber materials. Therefore, the excellent texture can be maintained for continued comfortable use.

4-2. Low aromaticity

On the assumption of daily use, the difference in the aromaticity between fluoroelastomer and silicone rubber was tested to examine the resistance to odor spreading. The odor index was measured after the fluoroelastomer pieces, and silicone rubber pieces were immersed in mustard and curry for one hour, then removed and washed with dishwashing detergent. The results of each are shown in the table below.

The odor concentration of fluoroelastomer was more than ten times greater.
Compared with silicone rubber, while the fluoroelastomer had almost no odor, the odor spread to the silicone rubber*1. The fluoroelastomer can solve the problem of odor spread, which is typical of rubber.
*1 : Odor Assessment Brochure, Office of Odor, Noise and Vibration, Environment Management Bureau, Ministry of the Environment Government of Japan

Figure 3. Aromaticity test results

Aromaticity test result

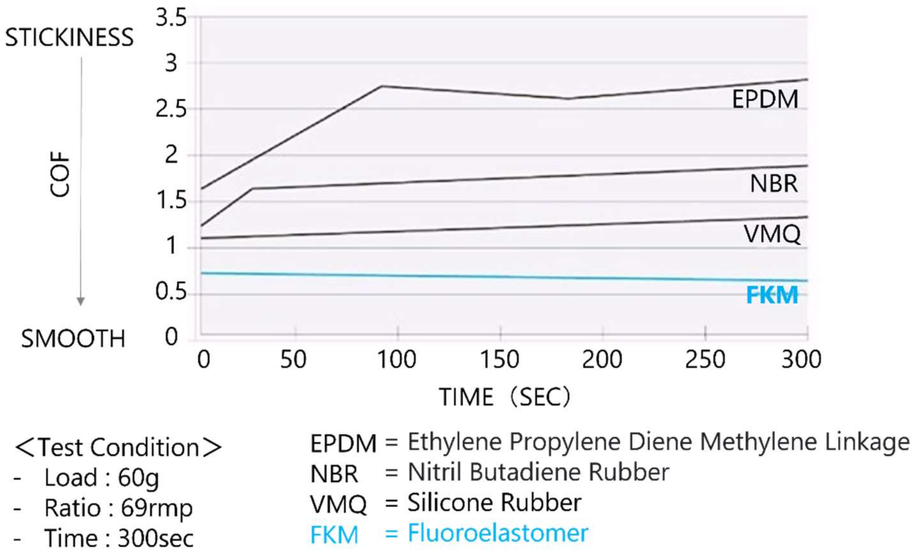
	Curry	Mustard
Fluoroelastomer	12.6	16.7
Silicine rubber	25.7	22.5

The results are shown in the odor index. The odor index is a quantification of the degree of odor using the human sense of smell and is defined as follows:
Odor index = 10 × log (odor concentration). No odor is felt if the odor index is 21 or smaller.
Odor concentration: Indicates how many times the original odor should be diluted to eliminate odor.
For example, if the original odor is diluted 100 times and no odor is felt, the odor concentration is 100.

4-3. Texture

Different textures can be developed without any additives by changing the surface texturing, such as a mirror surface or matte finish. It feels pleasant to the touch and can create a sense of luxury with a texture, unlike rubber. Moreover, the supple touch feeling continues without being affected by external impact. Figure 4 shows the changes in the friction coefficients of the rubber sheet surfaces of EPDM (ethylene propylene diene monomer), NBR (nitrile butadiene rubber), VMQ (silicon rubber), and FKM (fluoroelastomer). As a result of the sliding test under the test conditions of 60 g of loads and 69 rpm of rotation speed for 300 seconds, the friction coefficient of the FKM rubber sheet surface was lower than that of the other rubber sheet surfaces, and the change in the friction coefficients in the sliding test was also small.

Figure 4. Difference in the friction coefficient of rubbers



Spongy moldings can also be produced by compounding a foaming agent. They are lighter than ordinary moldings and have cushioning properties.

They can be bonded to other materials such as SUS and aluminum, and the function and texture of fluoroelastomers can be added to the desired parts.

4-4. Texture antibacterial and antifungal compositions

With the growing hygiene needs due to the global COVID-19 outbreak and the increasing use of automotive by car sharing with many unspecified users, the market needs for antibacterial and antiviral properties in automotive interiors are expected to increase. Although fluoroelastomers with excellent chemical resistance are considered durable for cleaning with various disinfectants, antibacterial and antifungal properties were also examined. The results are shown below.

The test was conducted by compounding antibacterial and antifungal agents, which are powdery, easy to compound into rubber, and have met the stringent safety standards, into fluoroelastomers.The antibacterial activity test was performed according to JIS Z2801:2000. The antibacterial activity values were calculated for Escherichia coli and staphylococcus aureus, respectively.
In the antifungal activity test, 71 arbitrarily selected fungi were cultivated under certain conditions for a certain period, and their growth was evaluated visually.

It was proven that antibacterial and antifungal activity could be added to fluoroelastomers without compromising their workability and general physical properties of the rubber by compounding antibacterial and antifungal agents.

Figure 5. Results of Antibacterial activity test and Antifungal activity test

Antibacterial activity test results (JIS Z2801:2000) *1

	Escherichia coli	Staphylococcus aureus
Fluoroelastomer	0	0
Fluoroelastomer + A *2	4.7	3.6

*1. Indicates antibacterial activity values. A value of 2.0 or higher is considered antibacterial (kill ratio of 99% or higher).
*2. A, an antibacterial and antifungal agent, was compounded with fluoroelastomers for testing.

Antifungal activity test results *1

	Days of cultivation			
	7	14	21	28
Fluoroelastomer	1	2	2	4
Fluoroelastomer + A *2	0	0	0	0

*1. Fungi were cultivated at a temperature of 28–30˚C and humidity of 85% or higher (relative humidity), and their growth was evaluated visually.
0: No growth, 1: growth of 10% or lower, 2: growth of 10– 30%,
3: growth of 30–60% or lower, 4: complete growth of 60% or higher
*2. A, an antibacterial and antifungal agent, was compounded with fluoroelastomers for testing.

4-4. Toning compositions

We have established the toning technology of fluoroelastomers for which toning is difficult. This technology allows the development of various colors, from clear and vivid colors to chic colors. Various colors are visually appealing, and the development of diverse goods becomes possible.

Figure 6. Rich color variation

5. Development of new applications

As mentioned above, most demand for fluoroelastomers has been for use in "invisible" fields such as around the internal combustion engines of automotives under high temperatures and oil atmospheres. However, in recent years, in new fields such as wearable devices, in addition to the chemical stability that has been a significant factor in the selection of fluoroelastomers, the unique texture resulting from their high specific gravity has shattered the stereotype of "rubber = cheap goods.” They are well-received as a new material that creates a sense of luxury. The growing hygiene need following the COVID-19 outbreak has accelerated the movement to extend their application to fashion, interior, kitchen, healthcare, and other areas.

Moreover, the above trend is not limited to household goods, and we are aware of the growing need for automotive interiors because of the recent increase in inquiries from the automotive industry. Therefore, we produced a prototype of a steering wheel cover to provide a concrete image of the application to automotive interiors and to understand the properties of fluoroelastomer more intuitively by directly holding it.

Figure 7. Prototype of a colored fluoroelastomer steering wheel cover (the orange and red parts are made of fluoroelastomers)

In the automotive interior, the steering wheel cover is the main part that the driver's hands touch, and it has a significant impact in terms of the proportion of the driver's range of vision, making it the interior component for which the market has the greatest expectations for the application of fluoroelastomers. However, for industrial mass production, it is necessary to solve issues such as establishing a stable and inexpensive processing method to follow and fix the steering wheel. In this respect, studies on the application to shift levers, switches, and buttons are considered more practical for mass production.

In terms of target markets for the application, we are looking not only at the new car market but also at the aftermarket-parts market, where there is a need for a wider variety of designs and color tones, and at custom parts for services such as sharing, where hygiene needs are expected to be even greater than for personal cars.

We are committed to technological development, quality improvement, and stable supply to provide solutions utilizing fluoroelastomers, which are available in a rich range of color variants, to meet the ever-increasing hygiene and design needs in the automotive interior field.

Note: This product was developed as an industrial product, not for medical or food use. In addition, when fluoroelastomers are used for applications that come in contact with the human body, such as wristwatch-type wearables, their biocompatibility needs to be verified.