AGC

Modification of Fluoroelastomers Based on TFE-P Copolymer

to Improve Cure Speed, Physical Properties and Mold Release

Your Dreams, Our Challenge

INTRODUCTION

Fluoroelastomers are used for applications where severe heat and chemical resistance are required. FEPM is based on an alternating copolymer of tetrafluoroethylene (TFE) and propylene (P). It is well known to have excellent chemical resistance against organic and inorganic acids and bases, especially amines formulated in various automotive lubricants. Fluoroelastomers consisting of vinylidene fluoride and hexafluoropropylene (FKM) are not as resistant to organic and inorganic bases, especially aqueous solutions of bases at high temperatures. However, FEPMs demonstrate difficulties in processability. For example, they exhibit insufficient performance with curability and mold release, especially in compression set processing. Several cure systems have been proposed to improve the curability and processability.[1, 2, 3, 4]

Most cure systems are made by introducing a cure-site monomer by polymerization. Common cure-site monomers are vinylidene fluoride, vinyl fluoride, vinyl chloride, trifluoroethylene, trifluoropropylene and pentafluoropropylene. Traditional cure promoters include quaternary phosphonium or ammonium salts. These cure systems improve curability and mold release, but base resistance, especially amine resistance, becomes worse due to the cure-site monomer.

This paper presents research we conducted to develop modified TFE-P that improves curability and mold release and provides good amine resistance and compression set. We demonstrate that a cure-site monomer can easily be copolymerized into the TFE-P backbone to solve the above-mentioned performance problems, while maintaining original TFE-P characteristics of resistance to heat, steam, and organic and inorganic acids and bases. In addition, it is possible to color the material.

EXPERIMENT

The tetrafluoroethylene-propylene copolymer used in this work is a commercially available conventional TFE-P, AFLAS® 100S. The vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer used in this work are commercially available peroxide-cure terpolymer FKMs.

Polymerization of modified TFE-P

Modified TFE-P was prepared by emulsion polymerization. A certain pressure and composition of gas-monomer mixture from TFE and P, based on the polymerization reactivity of each monomer, was first introduced into the autoclave, where deionized water and other ingredients had been charged. Then the polymerization was started. A gas-monomer mixture with the targeted polymer composition was fed during the polymerization to keep the pressure constant. The cure-site monomer was also continuously fed into the autoclave by a certain ratio to the feed of TFE/P. The emulsion obtained was treated to isolate the polymer by a salt coagulation method. The polymer isolated was washed and dried. The composition of the polymer was analyzed using FTIR and the fluorine content was measured.

Compound/vulcanization

All the ingredients were uniformly mixed with the polymer on a 2-roll mill to prepare the compound. The curability was measured using a rubber process analyzer RPA2000 with 3 degrees of arc at a frequency of 100 cpm at 177 °C for 12 minutes. The compound was cured under the conditions of a press cure at 170 °C for 10 minutes followed by a post cure at 200 °C for 4 hours, except in the case of the FKM, which was cured at 160 °C for 10 minutes followed by a post cure at 180 °C for 4 hours.

Physical properties of the vulcanization were measured in accordance with ASTM D412 and D2240. Chemical resistance was measured by recording the alteration of physical properties before and after immersion in several chemicals. Test fluids for chemical resistance were commercially available, and the contents were not exactly disclosed.

Adhesion

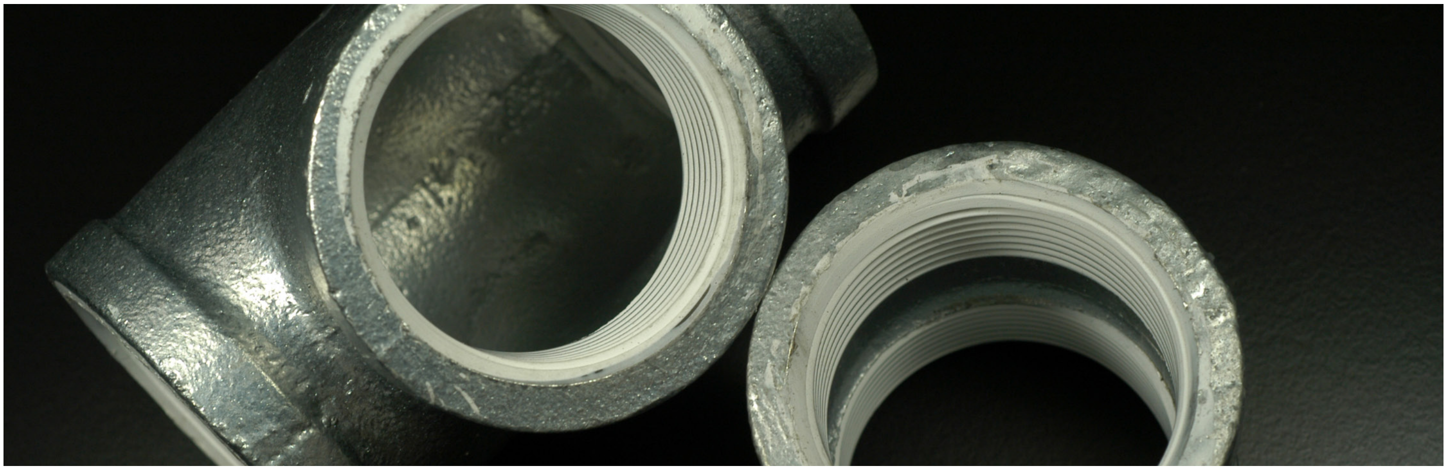
A silane coupling agent and additives were dissolved in an organic solvent to prepare an adhesion primer. For the adhesion test, SPCC, SUS-304, SUS-316 and aluminum were used as metal plates, and all were treated with zinc phosphate. The plates were washed and degreased with an organic solvent before use. The plates were coated with the primer and dried at 160 °C for 10 minutes, and then coated with the primer again and dried at 210 °C for 30 minutes. A curable compound was placed on the plates and pressed in the mold at 160 °C for 10 minutes followed by a post cure at 200 °C for 4 hours.

The condition for the steam exposure test was 135 °C and 160 °C for 70 hours. Adhesion strength was measured by 180-degree T-peel test. The remaining rubber was peeled, observed and evaluated for the survival rubber rate of adhesion interface between the metal and the rubber, %. A reading of 0% means complete interfacial peeling between the metal and the rubber (poor adhesiveness). A reading of 100% means breaking of rubber with no interfacial peeling (excellent adhesiveness).

RESULTS AND DISCUSSION

Polymerization of modified TFE-P

Modified TFE-P was made by emulsion polymerization. We examined several monomers thought to behave as a cure site according to the Q-e theory and conducted copolymerization tests. A certain monomer (CSM) showed excellent polymerization behavior to be copolymerized quantitatively with TFE-P to give a polymer with the targeted performance properties. The composition of the polymer was TFE/P=56/44 (mol %) with less than 1 mol % of CSM.



Formulation and physical properties

Formulation and physical properties of modified TFE-P, conventional TFE-P and terpolymer FKM are shown in Table 1, and compression set data is in Table 2. The amount in the table is written in parts per hundred by weight of the polymer (phr). Modified TFE-P must be optimally formulated to take full advantage of its physical properties. Note that the optimal formulation depends on the intended use.

Modified TFE-P is peroxide-curable. The best performing peroxide is Perkadox® P-14Sfl or Luperox® 101. TAIC is the recommended coagent and is required for the cure. Press cure conditions (temperature and time) should be decided in consideration of various factors, such as the size of parts, required properties, scorch safety and mold release.

To achieve the best physical properties, modified TFE-P also requires a post cure. The recommended standard condition is 200 °C for ≥ 4 hours. The strength can be further enhanced by adjusting the condition to 230 °C for ≥ 4 hours. Depending on the size of the part, the cure time must be optimized. Modified TFE-P is improved, especially regarding compression set, in comparison with conventional TFE-P and terpolymer FKM.

Table 1 – Formulation and physical properties of modified TFE-P in comparison with conventional TFE-P and terpolymer FKM

		Modified TFE-P Formula A	Modified TFE-P Formula B	Conventional TFE-P AFLAS 100S	Terpolymer FKM
Formulation (phr)	Polymer	100	100	100	100
	MT 990 carbon	30	30	30	20
	TAIC*	3	3	5	4
	Perkadox P-14Sfl**	1	–	1	–
	Luperox 101^	–	1	–	1.5
	Calcium stearate	1	1	1	–
Cure condition	Press cure (°C/min)	170/10	170/10	170/20	160/10
	Post cure (°C/hr)	200/4	200/4	200/4	180/4
Physical properties	Tensile strength (MPa)	23	21	20	20
	M100 (MPa)	6	5	7	3
	Elongation, %	220	250	230	290
	Density	1.6	1.6	1.6	1.9
	Hardness (Shore A)	70	70	70	71
Compression set	Button, 200 °C for 70 hr, %	14	15	26	14
Mooney viscosity (121 °C)	ML (1+4)	98	97	93	19
	ML (1+10)	96	95	85	16

*TAIC is triallylisocyanurate.
**Perkadox is a registered trademark of Akzo Nobel Chemicals, B.V.
^Luperox is a registered trademark of Arkema, Inc.

Table 2 – Compression set data of modified TFE-P in comparison with conventional TFE-P

Property	Units	Modified TFE-P Formula A	Conventional TFE-P AFLAS 100S
Compression set (button,[†] 22 hr @ 200 °C)	%	9	20
Compression set (button, 70 hr @ 200 °C)	%	14	29
Compression set (button, 168 hr @ 200 °C)	%	19	–
Compression set (button, 1000 hr @ 200 °C)	%	37	–
Compression set (O-ring,[‡] 22 hr @ 200 °C)	%	18	33
Compression set (O-ring, 70 hr @ 200 °C)	%	29	46
Compression set (O-ring, 168 hr @ 200 °C)	%	39	–
Compression set (O-ring, 1000 hr @ 200 °C)	%	75	–

†ASTM D-395 Type-1 specimen, Method B, 25% compression
‡JIS B 2401 P-26 / AS568-214 / BS1806-214, 25% compression

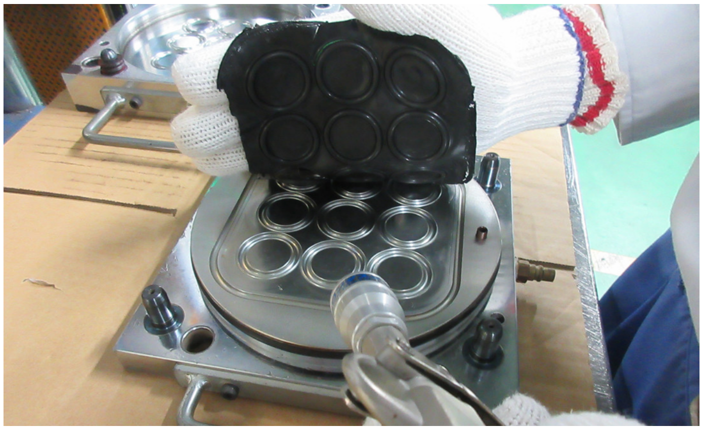
Table 3 – Curability of modified TFE-P in comparison with conventional TFE-P

Property	Units	Modified TFE-P Formula A	Conventional TFE-P AFLAS 100S
Min S’	dNm	11.8	11.2
Max S’	dNm	80.5	60.0
50% Cure	min	0.9	1.6
90% Cure	min	2.1	5.5

Table 3 shows curability of modified TFE-P in comparison with conventional TFE-P. Curing speed and Max S’ of modified TFE-P are much faster than conventional TFE-P. This demonstrates that good compression set is achievable.

One of the most important improvements achieved by modified TFE-P is in processability, especially in mold release. Figure 1 shows photographs of O-ring mold release by blowing air.

Figure 1 – Molding release of modified TFE-P



Resistance to Heat, Steam and Chemicals

Table 4 shows heat, steam and chemical resistance of modified TFE-P. In addition, modified TFE-P provides excellent steam, acid and base resistance where the volume change is fairly small.

Table 4 – Modified TFE-P resistance to heat, steam and chemicals

	Units	Modified TFE-P Formula A
Heat resistance @ 200 °C for 720 hr		
Change of tensile strength	%	11
Change of tensile elongation	%	1
Change in hardness	points	0
Heat resistance @ 230 °C for 720 hr		
Change of tensile strength	%	-12
Change of tensile elongation	%	11
Change in hardness	points	-3
Steam resistance @ 170 °C for 720 hr		
Change of tensile strength	%	-7
Change of tensile elongation	%	-7
Change in hardness	points	-1
Volume change	%	2
Hydrochloric acid 20% aq resistance @ 70 °C for 720 hr		
Volume change	%	3.1
Caustic soda (NaOH) 48% aq resistance @ 70 °C for 720 hr		
Volume change	%	0.4
Ethylene diamine resistance @ 25 °C for 720 hr		
Volume change	%	1.5
Aqueous ammonium 28% resistance @ 70 °C for 720 hr		
Volume change	%	2.7

Standard Oil – IRM 903

	Units	Modified TFE-P Formula A
Resistance @ 150 °C for 70 hr		
Volume change	%	11.8
Resistance @ 150 °C for 168 hr		
Change of tensile strength	%	-1
Change of tensile elongation	%	-8
Change in hardness	points	-7
Resistance @ 150 °C for 336 hr		
Change of tensile strength	%	3
Change of tensile elongation	%	-6
Change in hardness	points	-9
Resistance @ 150 °C for 1008 hr		
Change of tensile strength	%	22
Change of tensile elongation	%	-8
Change in hardness	points	-5

Service Fluid – SF105

	Units	Modified TFE-P Formula A
Resistance @ 150 °C for 70 hr		
Volume change	%	3.3
Resistance @ 150 °C for 168 hr		
Change of tensile strength	%	18
Change of tensile elongation	%	4
Change in hardness	points	-7
Resistance @ 150 °C for 336 hr		
Change of tensile strength	%	19
Change of tensile elongation	%	-7
Change in hardness	points	-6
Resistance @ 150 °C for 1008 hr		
Change of tensile strength	%	22
Change of tensile elongation	%	-8
Change in hardness	points	-5

Automatic Transmission Fluid – Dexron VI

	Units	Modified TFE-P Formula A
Resistance @ 150 °C for 70 hr		
Volume change	%	5.5
Resistance @ 150 °C for 168 hr		
Change of tensile strength	%	-6
Change of tensile elongation	%	-6
Change in hardness	points	-7
Resistance @ 150 °C for 336 hr		
Change of tensile strength	%	-1
Change of tensile elongation	%	-7
Change in hardness	points	-5
Resistance @ 150 °C for 1008 hr		
Change of tensile strength	%	-2
Change of tensile elongation	%	-2
Change in hardness	points	-4

Diesel Fuel – #2

	Units	Modified TFE-P Formula A
Resistance @ 150 °C for 70 hr		
Volume change	%	27.3
Resistance @ 150 °C for 168 hr		
Change of tensile strength	%	18
Change of tensile elongation	%	17
Change in hardness	points	-16
Resistance @ 150 °C for 336 hr		
Change of tensile strength	%	-21
Change of tensile elongation	%	-18
Change in hardness	points	-16
Resistance @ 150 °C for 1008 hr		
Change of tensile strength	%	-29
Change of tensile elongation	%	-22
Change in hardness	points	-20

Adhesion

Adhesion to metal is one of the most important technologies in sealing applications. Formulation, curing speed, molding conditions, composition of primer and the surface preparation of metal affect adhesion. Table 5 shows an adhesion formulation, and Table 6 shows the composition of the primer examined. Table 7 shows survival rubber rate of adhesion interface between the metal plate and the rubber, % and photographs of metal plates after the adhesion test. The primer prepared gave excellent adhesion. Adhesiveness of modified TFE-P Formula C was excellent compared to Formula A. Adhesiveness was maintained after steam exposure.

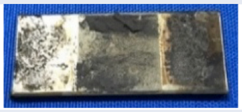
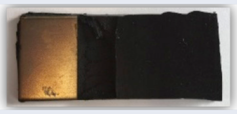
Table 5 – Adhesion formulation

		Modified TFE-P Formula A	Modified TFE-P Formula C
Formulation (phr)	Polymer	100	100
	MT 990 carbon	30	10
	TAIC	3	3
	Perkadox P-14Sfl	1	–
	Luperox 101	–	1
	Calcium stearate	1	1
	Celite	–	20
	MgO (high activity)	–	3

Table 6 – Composition of primer

Primer	Silane coupling agent
Remark	Commercially available, based on silane coupling agent

Table 7 – Rubber survival rate and photographs of metal plates after adhesion test

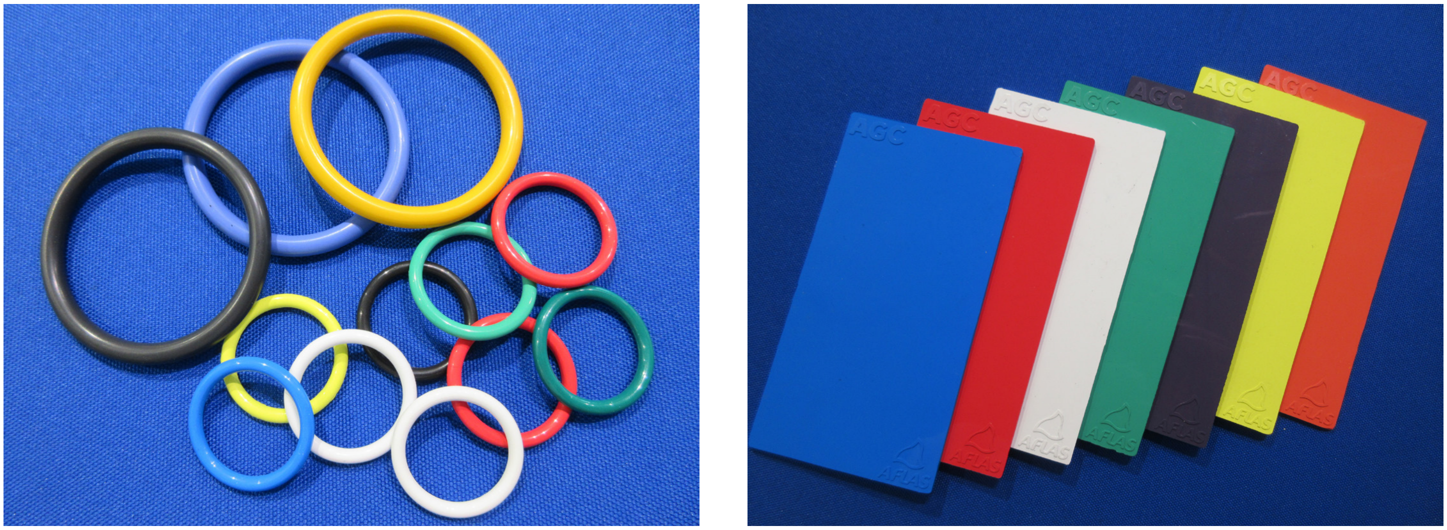
Metal species		Modified TFE-P Formula A	Modified TFE-P Formula C
SPCC	After post cure @ 200 °C for 4 hr		
	Survival rate of rubber, %	80	100
	After steam exposure @ 135 °C for 70 hr		
	Survival rate of rubber, %	30	100
	After steam exposure @ 160 °C for 70 hr		
	Survival rate of rubber, %	20	100
SUS304	After post cure @ 200 °C for 4 hr, survival rate of rubber, %	45	100
	After steam exposure @ 135 °C for 70 hr, survival rate of rubber, %	20	100
	After steam exposure @ 160 °C for 70 hr, survival rate of rubber, %	15	100
SUS316	After post cure @ 200 °C for 4 hr, survival rate of rubber, %	40	100
	After steam exposure @ 135 °C for 70 hr, survival rate of rubber, %	20	100
	After steam exposure @ 160 °C for 70 hr, survival rate of rubber, %	15	100
Aluminum	After post cure @ 200 °C for 4 hr, survival rate of rubber, %	30	100
	After steam exposure @ 135 °C for 70 hr, survival rate of rubber, %	25	100
	After steam exposure @ 160 °C for 70 hr, survival rate of rubber, %	20	100

Coloration

One of the most important improvements achieved by modified TFE-P is coloration. Figures 2 and 3 show photographs of raw rubber sheet and O-rings made of modified TFE-P. It is especially suitable for food processing machinery, for example, to prevent contamination, and it is easy to differentiate by color.

Figure 2 – Raw rubber of modified TFE-P

Figure 3 – O-rings and sheets of modified TFE-P



CONCLUSION

Modified TFE-P copolymerized with a specific cure-site monomer was developed to provide:

1. Outstanding compression set
2. Rapid cure
3. Improved mold release for better process and yield
4. Excellent heat, steam and chemical resistance equal to or better than the conventional TFE-P
5. Excellent adhesiveness to metal using silane coupling agents
6. Colorability

This modified TFE-P is now commercialized as AFLAS® 600X.

ACKNOWLEDGMENTS

The authors would like to acknowledge the work of AGC's Chiba Lab technicians for the data presented in this paper.

REFERENCES

[1] US Patent 4910260 to Asahi Glass Co., Ltd.

[2] US Patent 6300446 to Asahi Glass Co., Ltd.

[3] US Patent 6437028 to Asahi Glass Co., Ltd.

[4] US Patent 6703450 to DuPont Dow Elastomer, LLC.

AUTHORS

Keisuke Yagi, Fluoropolymer Material Chemist, Product and Development Engineer, AGC Chemicals Americas Inc. (Pennsylvania, United States)