

Aluminosilicate Filler for Fluoroelastomers

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Abstract—Four expanded aluminosilicate fillers and one diatomaceous earth filler from World Minerals Inc., member of IMERYS, were compounded into a fluoroelastomer, Dyneon FC 2181, at 15 to 45 phr. These natural fillers were found to be comparable to a carbon black and better than tested white fillers.

Index Terms — Aluminosilicate, Fluoroelastomers.

I. INTRODUCTION

Natural aluminosilicate cited in this article is often referred to as perlite in mineral industries and is an amorphous volcanic glass which can be expanded to 7 to 16 times of its original volume when heated appropriately. The expanded aluminosilicate can be further processed to achieve some unique properties which are desirable for different applications. World Minerals Inc., member of IMERYS, is a leading producer of natural aluminosilicate products. These products, along with a diatomaceous earth product line, find use in many applications such as filtration, lightweight plasters and mortars, horticulture, insulation, plastic reinforcement, etc. This article will study the effects on thermal and mechanical behavior of expanded aluminosilicates in fluoroelastomers.

Fluoroelastomers are high-end engineering elastomers used for seal and fuel line applications [1]. The polymeric articles are required to maintain good mechanical and thermal properties and chemical resistance at elevated temperatures. The fluoroelastomer, Dyneon FC 2181, is a copolymer containing vinylidene fluoride and hexafluoropropylene, and its own proprietary cure systems [1]-[5]. The fluoroelastomer must be cured through a combination of time, temperature and pressure to develop useful mechanical and thermal properties. Time and temperature are the most important variables and are determined by many factors, such as fluoroelastomer chemistry and morphology, cure system, acid and water acceptors, polymer processing aids, and fillers. Significant testing is generally needed to study and optimize the effects of these factors. In addition, the cure system of fluoroelastomers is generally proprietary, but manufacturers of fluoroelastomers often publish some basic data which help with the design of

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experiments.

II. EXPERIMENTAL METHODS

A. Materials

The materials and sources are listed in Table 1

Table 1. Materials and sources

Materials	ID or grade	Source
Fluoroelastomer	FC 2181	1
Aluminosilicate	AS-1	2
Aluminosilicate	AS-2	2
Aluminosilicate	AS-3	2
Aluminosilicate	AS-4	2
Diatomaceous Earth	DE	2
Carbon Black	MT Black N990	3
Calcium metasilicate	10 Wollastocoat®	4
Mica	Micarvor M20	5
Calcium Hydroxide	Ca(OH) ₂	6
Magnesium Oxide	MgO	7

Source: 1. Dyneon 3M, USA
2. World Minerals Inc. USA
3. Cancard, Canada
4. NYCO, USA
5. Imerys, UK
6. Rhenofit, CF, UK
7. Garolite, DE, UK

All samples from World Minerals Inc. are proprietary. Interested readers can contact World Minerals for additional information on these products.

B. Formulation and compounding

The following formulation was used for compounding:

Dyneon FC 2181	100 parts.
Calcium hydroxide (acid acceptor)	6 parts
Magnesium oxide (acid and water acceptor)	3 parts
Carnauba wax (processing aid)	1 part

All the fillers, except for the carbon black, were dried at 110 °C for 1 hour prior to compounding.

All compounding was accomplished on a two-roll mill at temperatures commencing between 45 °C and 85 °C. The first stage in compounding was to set the mill rotating at a moderate

speed to minimize the gap and to add all the cut pieces of the fluoroelastomer. The gap was then adjusted in the standard fashion to achieve a crepe on one of the rolls and a small 'bank' between. After three minutes or so, and an increase in temperature due to the shear forces generated, the filler was added as quickly as it could be absorbed, followed by 'knifing' to assist distribution. After an additional five minutes mixing, calcium hydroxide, magnesium oxide, and carnauba wax were added and incorporated with the roll gap being adjusted to allow cross cutting and blending. During this time the temperature increased, particularly with the higher filler content formulations. Once a homogeneous crepe had been achieved, after a total time of around 30 min, the crepe was cut from the mill, stored for 2 hours, and then followed by the second stage compounding by re-milling for 10 minutes. Most of the compounds were very 'sticky' on the rolls making removal difficult. The second stage of compounding was to maximize the dispersion of filler, but a separate test (data not shown) indicated that there was no difference between one-stage and two-stage compounding. The crepe from the

second stage was cut from the mill for subsequent processing.

A small sample of each crepe was tested in the Monsanto rheometer at 177 °C to establish cure condition for each compound. Press curing was at 177 °C under pressure for a time that was determined from Monsanto rheometer. Post cure was at 230 °C for 18 hours in air. Heat aging was at 230 °C for 72 hours.

III. RESULTS AND DISCUSSIONS

A. Rheological properties

The rheological properties are shown in Table 2. All fillers except mica accelerate the curing process. The time for 90% cure reduces from 11 minutes for the unfilled fluoroelastomer to about 4 minutes for the filled fluoroelastomer. Mica appears to give the least cure acceleration.

Table 2. Rheological properties at 177 °C. Monsanto Moving Die Rheometer (MDR 2000) 100 cpm, 0.5 arc.

Filler (phr)	ML Inch-lb	ts ₂ min	t ₅₀ min	t ₉₀ min	MH Inch-lb	Cure time min
None (Fluoroelastomer)	10	1.5	2.5	11	80	14
Carbon black (30)	13	1.25	2	4	106	5
Carbon black (45)	14	1.5	2.5	4	124	6
AS-1 (15)	11	1.25	2.25	4	93	5
AS-1 (30)	16	1.5	2.25	3	112	6
AS-1 (45)	16	1.5	2	4	122	5
AS-2 (30)	15	1.5	2	2.5	116	5
AS-3 (30)	14	1.75	2.5	3.5	112	6
AS-4 (30)	12	1.5	2	3.5	108	5
AS-4 (45)	16	1.5	2.25	3	118	5
DE (30)	16	1.5	2	2.5	126	6
DE (45)	14	1.5	2	4	124	6
Calcium metasilicate (30)	13	1.5	2	6	98	6
Calcium metasilicate (45)	15	1.25	1.75	4	102	6
Mica (30)	12	2.5	3.75	6	90	8
Mica (45)	14	3	5.5	9.5	92	12

Nomenclature in Table 2:

ML – Minimum torque

ts₂ – Time to 2 inch-lb rise from minimum torque

t₅₀ – Time to 50% cure

t₉₀ – Time to 90% cure

MH – Maximum torque

B. Properties of post cured sheets

All compounds were press-cured based on the cure time in

Table 2 and post-cured at 230 °C for 18 hours in air to develop maximum tensile strength and compression set resistance. Mechanical properties of all compounds after post cure are presented in Table 3.

Table 3. Mechanical properties of compounds (standard deviation in brackets)

Filler (phr)	Shore A	M25 MPa	M100 MPa	Tensile MPa	Elong. %	Tear N/mm	Comp. Set
None (Fluoroelastomer)	53	0.6 (0.02)	1.2 (0.04)	8.4 (0.9)	312 (30)	15.0 (0.7)	21.4
Carbon black (30)	71	1.5 (0.03)	5.0 (0.07)	13.9 (1.5)	218 (17)	35.9 (3.5)	24.1
AS-1 (15)	63	1.0 (0.03)	3.3 (0.15)	10.8 (1.4)	240 (38)	33.0 (1.1)	23.8
AS-1 (30)	75	2.2 (0.2)	10.3 (0.5)	13.8 (0.4)	154 (15)	41.5 (2.5)	25.9
AS-2 (30)	74	1.9 (0.05)	8.6 (0.4)	12.3 (0.4)	152 (11)	47.0 (6.1)	24.4
AS-3 (30)	73	2.0 (0.2)	9.4 (0.9)	14.5 (0.5)	179 (16)	41.4 (6.6)	23.2
AS-4 (30)	77	2.4 (0.2)	11.0 (0.4)	13.7 (1.1)	133 (14)	46.6 (3.1)	25.3
DE (30)	74	1.6 (0.06)	6.7 (0.4)	13.0 (0.3)	207 (17)	40.7 (4.1)	24.0
Calcium metasilicate (30)	64	1.1(0.05)	4.6 (0.4)	12.0 (0.4)	236 (12)	29.5 (3.4)	22.4
Mica (30)	69	2.3 (1.7)	6.2 (0.1)	12.1 (0.7)	274 (26)	39.5 (1.6)	24.5
Carbon black (45)	79	2.1(0.08)	6.8 (0.5)	13.9 (1.2)	185 (23)	39.1 (6.6)	26.6
AS-1 (45)	79	3.4 (0.3)	14.1(0.7)	15.7(0.6)	119 (11)	46.6 (4.5)	30.9
AS-4 (45)	81	4.8 (0.5)	17.5 (0.1)	16.9 (0.7)	96 (11)	46.9 (6.0)	29.4
DE (45)	74	2.2 (0.1)	7.9 (0.4)	10.3 (0.6)	158 (14)	43.2 (2.0)	30.4
Calcium metasilicate (45)	71	1.5 (0.05)	7.1 (0.5)	11.5 (0.4)	159 (11)	37.3 (6.7)	25.4
Mica (45)	74	2.2 (0.1)	7.9 (0.4)	10.3 (0.6)	158 (14)	43.2 (2.0)	30.4

Nomenclature in Table 3:

M25 – Modulus at 25% elongation

M100 – Modulus at 100% elongation

Tensile – Tensile stress at yield

Elong. – Elongation at break

Tear – the tensile force required to tear a pre-slit specimen.

Carbon black is a filler designed for fluoroelastomers and can be added at high loadings without losing elasticity. In Dyneon’s literature, this filler is most frequently used for reference in testing the thermal and mechanical properties of different fluoroelastomers and for comparing with other fillers.

All fillers except mica and calcium metasilicate reinforce the fluoroelastomer more than carbon black as indicated by the increased hardness and moduli (M25 and M100) which measure the deformation resistance of compounds. Some of the physical properties of these fillers are given in Appendix Table A1. The median size of the aluminosilicates are approximately 20 µm, except AS-3 which has a median size of about 12 µm. The particle sizes are much larger than the carbon black which is reported by the manufacture to be 280 nm (0.28 µm). The surface area of these fillers, as shown in Table A1, are about 5 m²/g except for carbon black which has a surface area of 9.3 m²/g.

Tensile strength, which is the maximum stress reached in stretching a test specimen, is similar for all compounds at 30 phr loading. The polymer chains are highly stretched at the maximum stress state. The stress developed depends on the chain length between crosslinks. The crosslink can be chemical and physical as well as temporary entanglements. When

polymer chains are highly stretched, the local motion such as rotating and slipping of filler particles becomes very restricted, which brings about an increased resistance to elongation [6]. As a result, while carbon black provides a large number of crosslinks to the polymer through its large number of particles and high surface area, the aluminosilicate and DE fillers, despite the low surface area, provide a similar effect through their unique features in shape, pore size, and short-distance interfacial interactions. This may explain why the tensile strength achieved for the formulations containing carbon black, aluminosilicate or DE are all about the same at 30 phr loading level. SEM (Scanning Electron Microscope) evaluation showed (photo not shown) that all the aluminosilicate fillers were platelet shaped. As compared to calcium metasilicate and mica, the higher tensile strength of aluminosilicate-filled compounds may result from the higher hardness and platelet feature of aluminosilicate. Further increase in the filler loading from 30 to 45 phr causes continued increase of tensile strength for aluminosilicate-filled compounds but no change for carbon black-filled compounds. This suggests that the aluminosilicate filler may offer performance advantages in some applications at high loading levels as compared to carbon black. The high modulus for aluminosilicate-filled compounds also suggests that the unique shape feature of these fillers provide more hindrance to the polymer segment motion at low elongation.

Elongation at break is the mechanical property at high specimen stretch. While modulus measures the deformation resistance at relatively low deformation, the elongation at break measures the deformation resistance at the maximum deformation and is a good indicator for the degree of crosslinking. At high crosslinking, a small elongation can cause a large increase in the tensile strength. As compared to

carbon black, calcium metasilicate, mica, and DE, the low elongation of the compounds that are filled with aluminosilicates clearly show stronger reinforcement. As mentioned earlier, the aluminosilicates evaluated are primarily platelet shaped but also contain some angular particles. AS-4 may contain more platelet particles as suggested by its high Hegman value. All these irregular shape features could contribute to the decreased elongation. It is well known that the mica is also platelet, but mica is generally softer than aluminosilicate and has layered structures. The holding force between the layers is weak. Accordingly, mica can be exfoliated if a sufficient shear force is applied. Therefore mica is expected to hinder the polymer chain motion in a weaker manner as compared to platelet aluminosilicate, particularly at high specimen stretch. This would explain why platelet aluminosilicate shows stronger reinforcement than mica.

Tear strength is the tensile force required to tear a pre-slit (notched) specimen and can be similarly discussed as for tensile strength. The tearing force is concentrated on the slitting point and any minor defects along the slitting line and anisotropic properties of specimen will affect the measurement. A higher error is expected as compared to the error in the measurement of tensile strength. As shown in Table 3, all fillers appear to have the same effect on the tear strength if the large standard deviation of testing is taken into account.

The compression set is a measurement of the ratio of viscous to elastic components for a given deformation and is the percentage of original compression that is not recovered after the force is removed from specimen. For seal applications, low compression set is desired. As shown in Table 3, the compression sets of all compounds are approximately 25% for all fillers, with the aluminosilicates and other fillers slightly worse than carbon black, particularly at 45 phr loading. The compression set resistance of carbon black filled fluoroelastomer, on the other hand, is also lower than the unfilled fluoroelastomer. The samples experienced a heat treatment of 200 °C for 70 hours before measuring compression set. This implies that the polymer chains have sufficient time to interact with fillers. The possible mechanisms are:

1. There is no chemical reaction between the filler and the polymer during compression. But the irregular shape (like angle, plate, pore, and fiber) of fillers, the improvement of filler dispersion (for nanosized carbon black), and the increased intermolecular forces could create additional hindrance to polymer chain motion and therefore hinder the restoration.
2. There is a chemical reaction which increases the chemical crosslinking points between filler and polymer during compression. The increased crosslinks restrict restoration of polymer chains to their original state.

For carbon black, it is generally believed that there is no chemical reaction and hence the decreased compression set resistance is likely only due to the intermolecular force and some degree of steric hindrance.

Compression set resistance measures only the restoration capability after compression. A good filler must also demonstrate other good mechanical properties. As shown in Table 3, the unfilled fluoroelastomer has the highest compression set resistance but its low tensile strength, low hardness and low modulus make it less useful for seal applications.

Since carbon black is considered a good filler for fluoroelastomers, DE would also be a good filler and a potential replacement for carbon black (except color).

C. Effect of heat aging

Heat aging is evaluated to see if the compounds show any degradation or significant change in mechanical properties during extended exposure to high temperature. The compounds were aged in air for 70 hours at 230 °C and the properties are given in Table 4.

Table 4. Effect of heat ageing (change in percent)

Filler (phr)	Wt. Loss %	Hardness (Units)	M100 %	Tensile %	Elong. %
None (Fluoroelastomer)	1.3	+ 3.0	+ 3	+ 2	- 6
Carbon black (30)	1.0	+ 3.3	+ 6	- 10	- 12
Carbon black (45)	0.9	+ 2.5	+ 18	- 6	- 16
AS-1 (15)	0.5	- 0.7	+ 9	+ 5	- 5
AS-1 (30)	1.0	+ 1.1	- 2	- 4	- 5
AS-1 (45)	1.1	+ 0.8	- 2	- 4	+ 17
AS-2 (30)	1.0	+ 1.4	+ 16	+ 6	- 4
AS-3 (30)	1.1	+ 1.6	+ 21	- 6	- 30
AS-4 (30)	1.1	+ 0.3	+ 5	+ 2	- 4
AS- 4(45)	1.1	+ 0.9	- 16	- 14	- 1
DE (30)	1.4	+ 1.0	+ 14	< 1	- 6
DE (45)	1.6	+ 0.6	+ 7	+ 7	+ 3
Ca. metasilicate (30)	1.2	+ 2.5	- 4	- 2	- 10
Ca. metasilicate (45)	1.1	- 0.6	+ 29	+ 10	- 8
Mica (30)	1.0	+ 1.4	+ 18	< 1	- 29
Mica (45)	1.7	+ 0.8	+ 38	+ 30	- 4

The compounds can be best compared with carbon black at 30 and 45 phr loadings. The weight loss is small for all compounds, indicating minimal degradation. The compounds filled with carbon black show higher hardness change although the increase is small as compared to other compounds. All other properties (M100, tensile strength, and elongation) show an irregular trend so additional testing is necessary to obtain more data for analysis. Nevertheless the heat aging test shows that there is no obvious degradation of the compounds and no significant deterioration in reinforcement properties, particularly for the aluminosilicate filled compounds.

IV. CONCLUSIONS

World Minerals' aluminosilicate products can be processed via proprietary technology to provide highly effective fillers for fluoroelastomer formulations. These natural fillers, along with select diatomaceous earth products, can provide fluoroelastomers compositions with various thermal and mechanical properties that are desirable for different applications.

APPENDIX

Table A1. Physical properties of fillers

Sample ID	AS-1	AS-2	AS-3	AS-4	DE	Carbon black	Calcium metasilicate	Mica
Median size, μm	21.2	20.8	12.1	17.3	8.4	0.28	3.1	19.2
Surface area, BET								
m ² /g	4.5	3.3	5.1	4.8	3.1	9.3	3.3	6.3
Porosimetry								
Total intrusion								
Volume, mL/g	4.6	4.7	3.6	5.6	3.5	0.9	0.7	1.7
Pore Diameter, μm	5.1	5.5	13.6	11.7	3.1	-	1.0	2.3
Porosity, %	87	89	69	76	84	58	1	76
Color								
L	90.7	92.0	90.8	91.9	96.5	21.2	96.7	90.4
a	0.9	0.5	0.8	0.5	0.1	0.1	0.1	0.0
b	3.8	2.6	3.5	2.8	2.1	-0.1	1.6	4.9
Blue light	77.4	81.3	77.9	80.8	90.3	4.6	91.2	75.5
Green light	82.8	84.9	82.8	84.7	93.2	4.5	93.5	81.8
Wet Density								
Lb/ft ³	15.6	15.6	17.8	13.8	23.6	39.7	61.0	34.7
Oil Adsorption								
%	207	177	201	227	149	58	42	88
Water Absorption								
%	264	242	209	288	167	91	42	129
Hegman (oil)	1.0	0.5	2.7	4.5	5.5	-	7.0	6.5

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