



## Effect of Carbon Black Type on the Thermal Properties of Fluoroelastomer

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### ABSTRACT

*The main objective of the present work is to study the effect of carbon black (CB) microstructure on the thermal properties of Fluoroelastomer (Viton A). In order to study the microstructure effect of CB, three types of CB (N330, N660 and N990) were selected. Melt mixing method was employed for compound preparation. Vulcanization, mechanical properties before and after oxidative aging in oil and oven conditions, and thermal stability of the compounds were evaluated. Vulcanization characteristics of compounds revealed that CB with higher structure has higher minimum and maximum torque and lower vulcanization rate. Mechanical stability in oxidative aging and resistance to thermal degradation were all increased in CB containing composites. It can be attributed to CB characteristics and CB-polymer interaction which is different in various CB containing samples.*

**Key words:** Fluoroelastomer, Viton, Mechanical stability, Thermal stability

### INTRODUCTION

Fluoroelastomers (FKM or F-polymers) are used in many applications such as gaskets, seals, O-rings and fuel hoses in petroleum industry. This is due to their unique combination of useful mechanical properties coupled with the high resistance to fuel/oil and heat [1]. F-polymers are generally prepared by high-pressure, free radical emulsion polymerization [2]. One of these fluoroelastomers, Viton A, is a copolymer of vinylidene fluoride (VDF) and Hexafluoropropylene (HFP) developed by DuPont and was made available commercially in 1955. Many reports have been published on thermal degradation properties of FKM [3-6], where attempts have been made to establish degradation mechanisms. Many other reports have focused on chemical degradation of FKM rubbers in specific aggressive aqueous chemical environments [7-12].

In the rubber industry, fillers are used to reinforce the polymer matrix to achieve the required mechanical properties. Viton A is normally reinforced by carbon black (CB) as the active filler. In the lifetime of FKM products, they are exposed to sever conditions such as high temperature and chemical environments.

Hence, in the present work, different CBs having various surface energies, particle sizes and structures were taken and their effect on the thermal properties of fluoroelastomer (Viton A), vulcanization characteristics and required performances such as mechanical properties, stability in oxidative aging in oil and oven conditions and stability in thermal degradation were investigated. Vulcanization characteristics revealed that CB with lower particle size and higher structure has higher minimum and maximum torque and lower vulcanization rate in the compounds. Mechanical stability in oxidative aging and resistance to thermal degradation were all increased in CB containing composites. It is may be attributed to CB characteristics and CB-polymer interactions that are different at various CB containing samples.

### DESIGN, MATERIAL, PROCEDURE, TECHNIQUE OR METHODS

#### Materials and Methods

Fluoroelastomer (Viton A, DuPont, USA), Carbon black (CB N-330, N660, Ahvaz CB Co., Iran; N990, Cancarb, Canada), calcium hydroxide (Merck, Germany), magnesium oxide (Merck, Germany), Bisphenol AF (Sigma-Aldrich, Germany) and TPBPC (Merck, Germany) were mixed according to the recipe given in Table 1. Surface energy component of carbon blacks are shown in Table 2.

**Table -1 Formulation of Different Composites and their Designation**

Component	Green (phr)	CB990 (phr)	CB660 (phr)	CB330 (phr)
Viton	100	100	100	100
CB N990	0	30	0	0
CB N660	0	0	30	0
CB N330	0	0	0	30
MgO	3	3	3	3
Ca(OH)2	6	6	6	6
P Salt	0.5	0.5	0.5	0.5
BFAF	1.8	1.8	1.8	1.8

**Table -2 Surface Energy Component of Carbon Blacks**

	N330	N660	N990
Specific surface area N2 (BET) (m <sup>2</sup> /g)	76.5	39.4	7.9
Dispersive component of surface energy at 150 °C (mJ/m <sup>2</sup> )	196.9	124.7	78.7
Polar component of surface energy at 150 °C (mJ/m <sup>2</sup> )	85.9	71.1	58.8

Melt intercalation mixing method was employed for compound preparation using Brabender laboratory two-roll mixing mill with a friction ratio of 1:1.4 at room temperature. Vulcanization characteristics of compounds were determined by Monsanto Oscillating Disk Rheometer 100 at 177 °C. Rubber samples were vulcanized in an electrically heated hydraulic press at 177 °C for 10 minute. Uniaxial tension properties were studied by a Zwick/Roell 2030 tensile testing instrument according to ASTM D412, (5 specimens from each sample). IRHD hardness was measured with a Zwick hardness tester according to the standard ASTM D2240. Oven aging condition was applied in a hot-air oven at 120 °C for 24 hours at atmospheric pressure. Oil aging condition was applied in hot turbine oil at 120 °C for 24 hours at atmospheric pressure. Heat resistance was studied by a polymer laboratory series 1500 thermogravimetric analysis (TGA) in a temperature sweep from room temperature to +900 °C.

## RESULTS AND DISCUSSION

### Effect of CB Type on Vulcanization Characteristics

Vulcanization characteristics of the FKM and FKM/carbon black composites were summarized in Table 3. Minimum and maximum torques and the differences between them (MH–ML) for all CB containing samples are higher than unfilled FKM compound. This shows the reinforcing effect of this filler in the rubber compounds. Also, scorch and optimum cure times are longer when CB is present in the compound compared to the compounds without CB. During melt mixing process of uncured FKM with CB, FKM chains have contact with CB particles, and entangle or trap between carbon black aggregates. The rubber chains become highly immobilized and localized in the form of occluded or rubber shell [13].

The physical crosslinking between CB and FKM hinders the mobility of rubber chains and restrains the deformation of rubber. Lower deformation capability of FKM chains at certain torques, increase minimum requirement torques of rheometric vulcanization characterization. Hence, it is understandable that fillers with higher surface area have higher reinforcing effect on rubber. Therefore, the surface area of carbon black is a major reinforcing property of CB. Most properties, such as Mooney viscosity and 300% modulus of the filled rubber depend on the specific surface area of carbon black and ML is the one of them [6]. As the surface area of carbon black increases, the number of rubber chains entangling with carbon black aggregates as well as that of the cross-links climbs up[14]. ML increases correspondingly with increasing surface area of carbon black, as the number of rubber chains immobilized on the carbon black surfaces grows up. It can be seen in Table 2 that both the BET specific surface area and external surface area of N330 are higher than N660 and these properties of N660 are higher than those of N990. ΔM, the difference between MH and ML, is considered as the parameter to demonstrate the degree of chemical cross-linking. Chemical bonding of rubbers with the functional groups on carbon blacks is occurring during vulcanization [14, 15]. The chemical bonding of rubbers with carbon blacks increases the degree of chemical crosslinking that is higher at N660 compound. Cure Rate Index (VC1) is based on the difference between optimum vulcanization and incipient scorch time,  $VC1 = 100 / (\text{cure time} - \text{scorch time})$ . Higher structure CB (N330) filled FKM has lower vulcanization rate and the Green FKM has the highest vulcanization rate. CB decreases the vulcanization rate of FKM that may be attributed to diffusion limitation and lower chain mobility of FKM introduced by CB- FKM interactions. Diffusion limitations introduced by filler structure reduce the accessibility of vulcanizing agents to already limited polymer chains.

### Mechanical Properties and Stability in Oxidative Aging

Many FKM products are exposed to oxidative aging at oil or ozone conditions. Failure can happen due to oxidative aging which results in loss of mechanical properties. Therefore, strong mechanical properties and aging stability are necessary in FKM compound design.

Table -3Vulcanization Characteristics of fkm and fkm/Carbon Black Composites at 177 °C

	Green	CB990	CB660	CB330
Minimum Torque, ML (N.m)	1.97	2.40	2.87	3.25
Maximum Torque, MH (N.m)	5.96	8.37	9.29	9.56
$\Delta M = MH - ML$ (N.m)	3.99	5.97	6.42	6.31
Scorch Time, $T_1$ (Min)	2.89	2.55	2.42	2.30
Optimum Cure, $T_{90}$ (Min)	4.4	4.6	5.7	7.8
Cure Rate Index, $V_{CI}$	66.2	48.8	30.5	18.3

Table -4 Mechanical Properties at Various Aging Condition

	Green	CB990	CB660	CB330
Hardness before Aging	64	80	90	94
Hardness after Hot Air Aging	64	80	90	94
Hardness after Hot Oil Aging	61	80	90	94
Maximum Stress before Aging (MPa)	3.26	13.24	15.66	14.97
Maximum Stress after Hot Air Aging (MPa)	4.99	12.84	16.11	13.35
Maximum Stress after Hot Oil Aging (MPa)	5.22	13.77	16.57	14.79
Maximum Stress Change after Hot Air Aging (%)	53.18	-2.96	2.93	-10.80
Maximum Stress Change after Hot Oil Aging (%)	60.14	4.07	5.82	-1.23

Mechanical properties of vulcanized compounds before and after aging in oxidative aging at oil and oven conditions are shown in Table 4. Hardness increases correspondingly with increasing the surface area of carbon black, as the number of rubber chains immobilized on the carbon black surfaces grows up. Thus, the largest area of rigid rubber shell is obtained on the N330 surface since it has the largest external surface area, which is accessible for rubber molecules. This suggests that the external surface area of carbon black is indeed a major factor determining the hardness of FKM/carbon black composites. In fact, this generally agrees with the reports in the literature [15]. Oxidative aging has decreased the hardness of unfilled FKM (Green) at oil aging condition. Composites containing CB show no change in hardness as a result of aging compared to the one without CB. Hardness stability of CB containing composites can be correlated to the heat stability resulted from presence of CB particles.

CB has increased the maximum stress of FKM. N66 containing FKM has the highest maximum stress before and after aging among all. Effects of oxidative aging on stability of maximum stresses are shown in Figure 3. It can be noticed that aging has increased the modulus of Green compound. However, aging effects in composites containing CBs are less than their corresponding composites with no CB. Less change in mechanical properties of composites containing CBs can be correlated to heat stability resulted from presence of CB particles.

#### Effect of CB Type on Thermal Properties of Compounds

Results of thermogravimetric analysis (TGA) of all used CBs and vulcanized composites are plotted in Figure 1. Carbon black N330 loses weight at a lower temperature than N660 and N660 loses weight at a lower temperature than N990. However, the lower structure CB has higher thermal stability, but not any differences between thermal stability of CB containing rubbers. It can be seen that Green fluoroelastomer loses weight at a lower temperature than other composites. Diffusion limitations introduced by inclusion of CB structure, reduced the exchange rate of oxygen and produced degradation gases which in turn limit further rubber degradation.

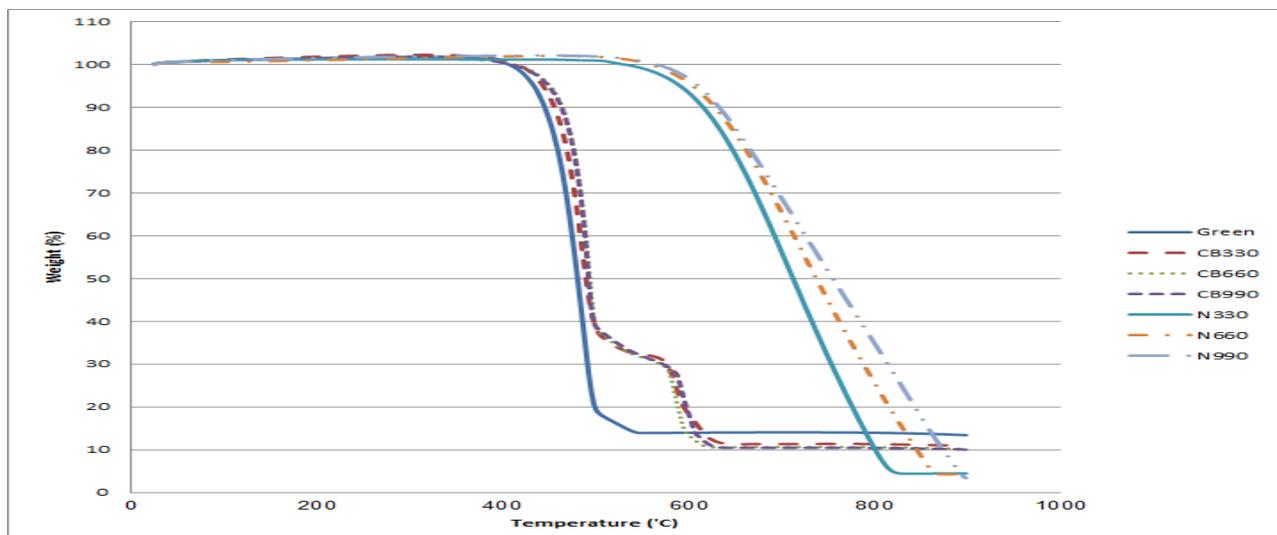


Fig. 1 Thermal gravimetric analysis of vulcanized rubber compounds

## CONCLUSION

To study the microstructure effect of CB, three types of CB (N330, N660 and N990) were selected and mixed with melt mixing method. Vulcanization characteristics results revealed that CB with higher structure has higher minimum and maximum torque and lower vulcanization rate in the compounds. Aging effects in composites containing CBs are less than their corresponding composites without CB. It can be attributed to CB characteristics and CB-polymer interaction that is different at various CB containing samples. Less change in mechanical properties of composites containing CBs can be correlated to heat stability resulted from presence of CB particles. Thermo-gravimetric analysis results showed the lower structure CB has higher thermal stability, but not any differences between thermal stability of CB containing rubbers.

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