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THE EFFECT OF CLAY INCORPORATION ON THE MECHANICAL PROPERTIES OF FLUOROELASTOMER

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ABSTRACT

In this work was studied the effect of clay incorporation in the mechanical properties of fluoroelastomer (FKM). The polymer matrix that was used is a compound of the commercial terpolymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, with 70% of fluor content. This type of polymer is known for its resistance to high temperature and chemical products; it has low fuel permeation which allowing be used as sealant and especially as o-ring product. The incorporation of clay was carried to avoid excessive swelling and to observe the effect in the mechanical properties, for this application was used commercial clay, Cloisite® at 1 and 2% in weigh. The incorporation of clay into the FKM was carried out in a two roll cylinder. After that, the samples with and without clay loading were submitted to gamma radiation at 20 kGy in order to observe the changes in the polymer matrix. The characterization techniques used were: mechanical testes (stress – strain), rheometric properties and degree of swelling. After radiation process, was observed an increase in the swelling degree for the irradiated samples in relation to the pristine one. The incorporated samples with 1 and 2% of clay showed an increase in the elongation which can indicate a decrease in hardness of the polymer matrix.

1. INTRODUCTION

There many different kinds of elastomer natural and synthetic. The elastomer with Fluor are named fluorelastomer and due to the presence of C – F bonds, which are stronger than C - C and C – H bonds, this polymer has great mechanical and thermal stability, flame resistance and high oxidation resistance. Because of those properties and the acid resistance it's very usual to be used in aggressive chemical environment or when the exposition to oxidation is high. But this material cannot be used in basic chemical environment.

To transpose this poor property, many authors developed nanocomposites of elastomer and clay nanoparticle. The vulcanization behavior and mechanical properties of clay/fluoroelastomer nanocomposites produced by melt-mixing a terpolymer and montmorillonite (Cloisite15A and Cloisite20A) were studied by Lakshminarayanan et. al [1] . After characterization (XRD and TEM) the observed an increase in torque, modulus, hardness and tear strength in the clay/FKM nanocomposites. Another work that mixture clay anf fluoroelastomer by melt-mixing was reported by Gao et al [2], in this work the authors shown that the excellent tensile properties was reached with less than 12 wt% of clay, and was attributed to the nanometer scale dispersion.

Because of the chemical inertia, especially due to the C-F bonds, it is difficult to modify the surface and the bulk of the polymer with fluor content. The use of radiation process is a well-known technique used to modify a large number of fluor subtracts, including polymer. Fluoropolymer, fluorinated (PTFE, FEP and PFA) or partially fluorinated (PVDF and ETFE) polymers are well known to be sensitive to ionizing radiation [3]. Both chain scission and crosslinking reactions occur simultaneously during the radiation process and the final result will depend on the material chemical structure, type of radiation, dose rate and total absorbed dose. In the case of PTPE, FEP and PFA undergo predominant degradation reactions in this process.

The effects of ionizing radiation in polymers are chain scission, when occurs a decrease in molar mass; and crosslinking, when a tridimensional network is formed and consequently occurs an increase in a molar mass of the polymer. [4, 5].

In this work was studied the effect of dose irradiation in nancomposite of fluorelastomer and clay incorporated with 1 and 2%.

2. EXPERIMENTAL PART

2.1. Materials

The fluoroelastomer compound (FKM) used in this work was based on Viton® F (DuPont), which is applied in large scale in automotive industry; this compound was purchased by Croslin Ltda, Brazil. The FKM used was obtained from three monomers, vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, containing carbon black and inorganic fillers and the fluor content is 70%.
The clay used is the Cloisite® 15A (by Southern Clay) which is a natural montmorillonite modified with a quaternary ammonium salt with typical dry particles size about 13µm. The clay was incorporated at 1% and 2% (w/w).
The incorporation process of clay into FKM was made in a two roll cylinder at room temperature. All samples were vulcanized in a thermopress at 195°C for 5 minutes, in order to obtain a film of nanocomposite with 0.2mm thickness.
The nanocomposites were submitted to gamma radiation at 20 kGy at dose rate of 10 kGy h^{-1} under air atmosphere in order to evaluate the influence of this process in the polymer chain.

2.2. Characterization

The characterization techniques were applied before and after radiation, and also before and after clay incorporation.

The mechanical tests were carried out in a Texturometer with 50N load and samples in stripes format with dimensions: 10mm of length; 0.2 mm of thickness; and 30mm of height. The results were the averages of three readings.

The vulcanization behavior of the unfilled and clay filled FKM was determined using a Monsanto Rheometer. The torque and T_{90} were calculated from the torque–time curves.

Swelling of vulcanized samples was measured gravimetrically in methyl ethyl ketone (MEK), which act as a solvent for FKM. Samples were weighed before immersion, at room temperature, and when equilibrium swelling is reached, the samples were wiped dry and weighed again. For this test was used the averages of three samples. The degree of swelling was calculated using the following equation.

$$\%Swelling = \frac{(w_2 - w_1)}{w_1} * 100 \tag{1}$$

3. RESULTS

The radiation process is a large used technique to promote modification in polymers structures to apply them in different areas and is well known for its merits and potential in modifying the chemical and the physical properties of polymeric materials without cause drastic changes in their inherent properties, depend on the dose irradiated. The interaction of gamma irradiation and polymer material result in the formation and the breaking of chemical bonds, because of the intermolecular crosslinking and chain scission in the polymer. The chemical effect of high-energy radiation on fluoropolymer is degradation, mainly because of chain scission of C-O bonds in the backbone. To confirm this effect were carried out mechanical tests and swelling degree was calculated.

The results of mechanical tests are shown in Figure 1 and Table 1. The stress-strain curves for irradiated samples showed an increase in the elongation reaching almost 300%. This increase indicated the degradation effect of the irradiation process. The curves for non-irradiated films revealed lower values of elongation and stress at break when compared to irradiated ones, which means an increase of both material stiffness and strength by the amount of clay in the elastomeric matrix.

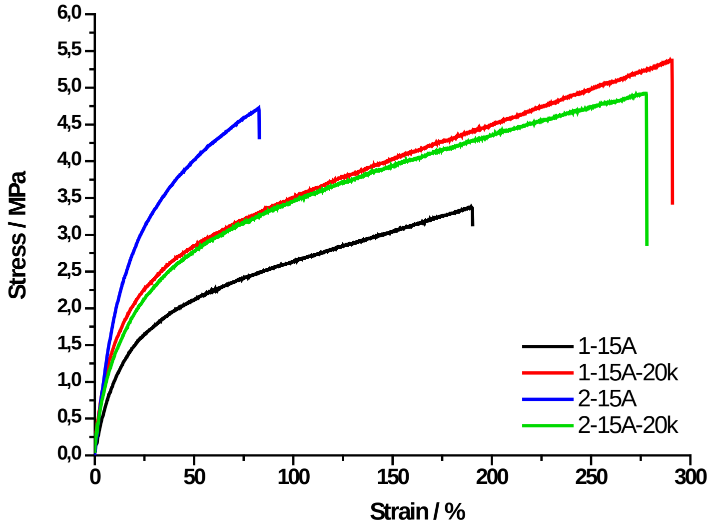

Figure 1: Stress-strain curves of irradiated and non-irradiated nanocomposites

Table 1: Numerical results of mechanical tests at break

Sample	Stress at break / MPa	Strain at break / %
1-15A	3,5 ± 0,9	190 ± 3,8
1-15A-20k	5,4 ± 0,8	290 ± 2,8
2-15A	4,7 ± 0,7	83 ± 1,2
2-15A-20k	5 ± 0,9	278 ± 3,7

The vulcanization parameters of nanocomposites reveals an increase in maximum torque (MH) and a decrease in minimum toque (ML), when was compared the irradiated and non-irradiated samples. The decrease of values of MH for non irradiated samples indicated an increase of the hardness; meanwhile for the irradiated samples was observed the opposite behavior an increase of MH with the increase of clay amount, which indicates a higher concentration of crosslinking reactions.

The ML parameter is related to the viscosity of the compound. For the sample with 1% of clay was verified a decrease in ML which meant a decrease in the viscosity; and for the sample with 2% of clay was observed an increase in the viscosity of the nanocomposite.

The ΔM, presented higher values for the irradiated samples, this fact indicated that for the irradiated nanocomposite the vulcanization process was completed lower than for the nanocomposite unmodified.

Table 2: Results of vulcanization behaviour

Sample	M_H lb.in	M_L lb.in	ΔM lb.in	T_{90} min
1-15A	28	2	26	1.3
1-15A-20k	33	9	24	1.3
2-15A	25	4	21	1.8
2-15A-20k	31	9	22	1.2

Besides the irradiation effect in the films, the swelling of the nanocomposite can be affected by the interfacial regions between the matrix and the inorganic filler. Another factor that affects this property is related to the aggregation of silicate layers which leads to a decrease of the aspect ratio of nanoparticles. The results of swelling (Figure 2) revealed similar values for non-irradiated and irradiated samples that indicate a same aspect ratio of nanoparticles, providing the same degree of delamination of the clay into polymer matrix.

The equilibrium was reached after 8 days of swelling proceedings. Both non irradiated films had lower solvent uptake than irradiated samples which corroborated the degradation reaction as directly effect of radiation process.

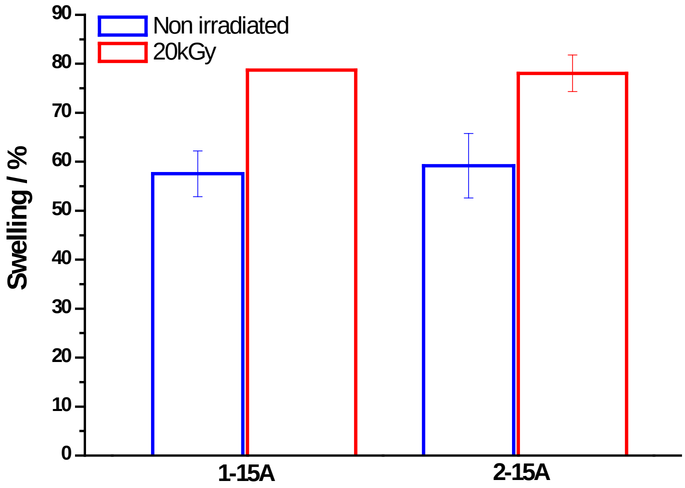

Figure 2: Swelling degree of nancomposites immersed in MEK

3. CONCLUSIONS

The presented techniques demonstrated degradation reactions as directly effect of irradiation process. This effect was confirmed by mechanical tests and the swelling degree that revealed an increase in the values for the irradiated samples.

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REFERENCES

1. S. Lakshminarayanan, B. Lin, G. A. Gelves, U. Sundararaj, "Effect of clay surfactant type and clay content on the rheology and morphology of uncured fluoroelastomer/ clay nanocomposites prepared by melt-mixing", *J. App. Pol. Society*, **112,** p. 3597-3604, (2009).
2. J. Gao , Z. Gu , G. Song, P. Li, W. Liu, "Preparation and properties of organo montmorillonite/ fluoroelastomer nanocomposite", *Applied Clay Science*, **42,** p. 272–275, (2008)
3. G Sharma, L Klintberg and K Hjort "Viton-based fluoroelastomer microfluidics", *Journal of Micromechanics and Microengineering*, **21,** (2011).
4. Y. A. Elabda and E. Napadensky, "Sulfonation and characterization of poly(styrene-isobutylene-styrene) triblock copolymers at high ion-exchange capacities", *Polymer*, **45**, p. 3037–3043, (2004).

5. A. Biswas, A. Bandyopadhyay, N. K. Singha, A. K. Bhowmick, “Sulfonation of metallocene-based polyolefinic elastomers and its influence on physicomechanical properties: Effect of reaction parameters, styrene grafting, and pendant chain length”, *Journal of Polymer Science: Part A: Polymer Chemistry*, **46**, p. 8023–8040, 2008.