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Industrial Production of Fluoroelastomer Nanocomposites by Microemulsion Polymerization followed by Co-Coagulation

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Summary: In this paper synthesis and properties of fluoroelastomer nano-composites are discussed. The production technology is based on two steps: first, high solid content nano-latex of a semi-crystalline perfluoropolymer is produced by means of a special microemulsion polymerization; then, co-coagulation of this latex with a fluoroelastomer latex leads to the formation of the nano-composite. When properly designed, fluoroelastomer nano-composites develop properties that are better than those of each individual polymer of the blend. This paper is particularly focused on the remarkable values of reinforcement and permeability that can be achieved with these nano-composites. A simple model is developed to better understand the origin of such properties. The model provides a possible explanation of the observed increase in nano-composite properties when the size of the dispersed phase is below 100 nm, that is in the nano-scale region. Finally, selected examples of industrial application of these nano-composites are briefly discussed.

Keywords: fluorinated elastomers; microemulsion; nano-composites; permeability; reinforcement

Introduction

Fluorinated polymers exhibit remarkable resistance to flame, chemicals, solvents and oxidative attack and, for this reason, they are extensively used in corrosive and high temperature environments[1]. Fluorinated elastomers in particular, are used in sealing applications in hostile environments in aircraft, aerospace, automotive, chemical, petroleum and energy industries[2].

The continuous request from the market of fluoroelastomer grades with improved properties has driven the development of new compounds based on blends of fluoroelastomers with semi-crystalline perfluoropolymers such as polytetrafluoroethylene (PTFE) and its copolymers (in the following referred to as ‘‘perfluoro-fillers’’). The introduction of semi-crystalline perfluoropolymers in fluoroelastomers improves many properties such as permeability, friction coefficient, purity and chemical resistance.

In a recent paper[3] it has been found that blend properties becomes outstanding when the size of the semi-crystalline perfluoropolymer particles is reduced to less than 0.1 microns, i.e. in the nano-scale region.

The synthesis of these nano-composites at the industrial scale has required the development of an innovative mixing procedure because by using the standard mixing technologies of fluoroelastomers (mechanical mixing in open or closed mixers) it is not possible to produce blends with such a small size of the dispersed phase.

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Nano-Blending Technology

Nano-blending technology improves the mechanical properties of the nano-composite by increasing the interfacial area between the fluoroelastomer and the semi-crystalline perfluoropolymer. This is obtained by reducing the perfluoro-filler particle size to values below 100 nm.

The nano-blending technology here described overcomes the limitations of the classic mechanical mixing techniques that are unable to reduce the size of the dispersed phase below 100 nm.

The concept that has driven the development of the nano-blending technology is based on the following idea: as the reduction of perfluoropolymer particles size to nano-scale by mechanical shear is almost impossible, it should be found a way to directly synthesize the particles at nano-scale and then blend them with the fluoroelastomer while keeping their size unchanged. Accordingly, the nano-blending technology here discussed is a two step process:

- nano-particles of fluoropolymers are produced by a special polymerization technology called "micro-emulsion"[4,5]. Fluorinated oil-in-water microemulsions are self-assembly systems that allow a much better control of particle nucleation. It has been found that the number of latex particles is controlled by the number of microemulsion droplets present at the beginning of the reaction. By increasing the amount of microemulsion fed to the reactor, latexes with number of particles of two-three orders of magnitude higher than the corresponding emulsion polymerization are produced. Thanks to the high number of polymer particles, latexes with particle size from 10 to 70 nm and with the high solid content typical of industrial latexes are easily obtained.
- the fluoropolymer nano-particles from step (i) are mixed in a fluoroelastomer by means of co-coagulum procedure. Co-coagulation is a delicate process: the two latexes should have the same colloidal stability so as to prevent perfluoropolymer particle aggregation that would preclude the nano-scale dispersion.

Nano-blending technology is extremely flexible as composition and molecular weight of both fluoroelastomer and semi-crystalline fluoropolymer can be freely chosen and the amount of dispersed phase can be easily varied. Usually, PTFE or its copolymers with monomers such as HFP and MVE are used as semi-crystalline fluoropolymer. The amount of dispersed phase is usually selected between 1 and 40 wt%. It should be pointed out that blends of semi-crystalline fluoropolymers in fluoroelastomers are well known in open literature[6] and the novelty of the approach here described resides in the nano-scale of the dispersion. More details on nano-blending technology can be found in Ref[7].

Fluoroelastomer Bano-Composites Reinforcement

The effect of the amount of perfluoropolymer nano particles on mechanical properties of fluoroelastomers has been investigated by using isochronal (1 Hz) dynamic mechanical analysis (DMA) to measure mechanical spectra as a function of temperature spanning from glassy to rubbery state of the continuous amorphous phase.

The results are shown in terms of reinforcement, defined as the ratio between the storage shear modulus of the nano-composite (G') and the storage shear modulus of the bare elastomer (G'_0), both measured at 50 °C.

Figure 1 shows the evolution of reinforcement with perfluoro-filler particle size. A sharp reinforcement increase is experimentally observed when particle size is below 100 nm: at same perfluoro-filler loading (30 wt%), a filler size of 165 nm produces a reinforcement of 3 times the value of bare fluoroelastomer, while particles of 40 nm produce a 7 times reinforcement increase.

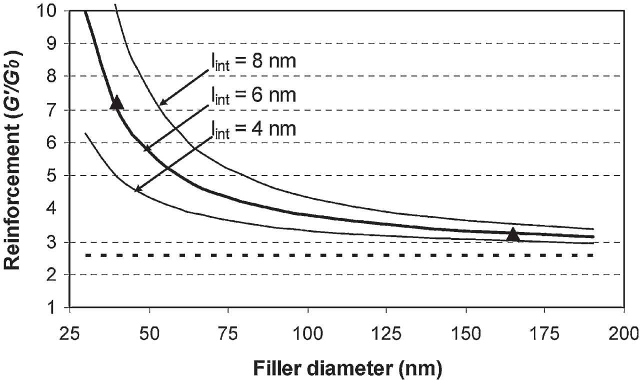


Figure 1.
Reinforcement (G'/G'_o) vs. perfluoro-filler diameter (nm). Filler content is 30 wt%. Solid lines = mathematical model (eq. 3) at various l_{int} values, dashed line = Guth and Gold model (eq.1); ▲ = experimental reinforcement data.

It is worth to note that the classic models for filler reinforcement (such as Guth and Gold[8], Mooney and Kerner equations[9]) are not able to predict the effect of particle size.

For example, Guth and Gold model calculates reinforcement as a function of filler amount, ϕ_F, neglecting any effect of its size:

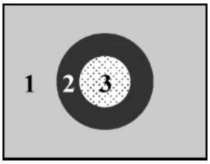
$$\frac{G'}{G'_0} = 1 + 2.5\phi_F + 14.1\phi_F^2 \qquad (1)$$

Figure 1 shows the reinforcement of composites with 30 wt% of perfluoro-filler as a function of filler size. Guth and Gold equation is the flat dashed line, with a calculated reinforcement of 2.7, no matter the filler size. Such a value is reasonable for filler sizes above 100 nm, but it is clearly underestimated when filler size is brought below 100 nm.

In order to introduce filler size effect, a simple model is here developed.

The model is based on the assumption that filler surface modifies the structure of the surrounding fluoroelastomer matrix up to a certain depth. In the following the thickness of this perturbed interfacial layer is indicated with the symbol l_{int}. The chain packing of the fluoroelastomer in the interfacial layer is different from that of the bulk, leading to a change in several properties of the nano-composite, like mechanical properties and permeation. According to this schematization, the nano-composite could be seen as a three-phases system:

1. "free" fluoroelastomer (continuous phase)
2. fluoroelastomer with denser chain packing (inter-phase)
3. semi-crystalline perfluoropolymer (filler)



The value of l_{int} is used to calculate the volume fraction of fluoroelastomer in the interfacial layer, ϕ_{int}, according to the following equation, derived from geometrical considerations:

$$\phi_{\text{int}} = \phi_F \left[\left(\frac{R_F + l_{\text{int}}}{R_F} \right)^3 - 1 \right] \qquad (2)$$

In the equation above R_F is the filler radius.

In order to take into account the role of the interfacial layer in determining the reinforcement of the fluoroelastomer, the Guth and Gold equation is modified as follows:

$$\frac{G'}{G'_0} = 1 + 2.5(\phi_F + \phi_{\mathrm{int}}) + 14.1(\phi_F + \phi_{\mathrm{int}})^2 \tag{3}$$

The equation has the same structure of the original Guth and Gold but ϕ_F is replaced with the sum $\phi_F + \phi_{\mathrm{int}}$. Equation (3) can now be used to determine the value of l_{int} by fitting the experimental data of Figure 1. Three simulations with different values of l_{int} are there reported. It turns out that the best fit is obtained with $l_{int} = 6$ nm. This value has been used in all the simulations shown in this paper.

As schematized above, the fluoroelastomer composite is actually a 3 components system, (i) perfluoro-filler, (ii) fluoroelastomer in the interfacial layer and (iii) ‘‘free’’ fluoroelastomer (i.e. the portion of fluoroelastomer not affected by filler surface).

Figure 2 shows the evolution of the 3 components of the fluoroelastomer composite by changing the perfluoro-filler size at constant filler amount. Inter-phase fraction is very small when filler size is above 100 nm but it grows rapidly when size is reduced to the nano-scale region and eventually it becomes the dominant phase when filler size is below 40 nm.

The evolution of reinforcement with perfluoro-filler amount is shown in Figure 3. Two experimental data sets are reported, one with perfluoro-filler diameter of 165 nm and the other one with diameter of 40 nm. Much higher reinforcement values are obtained when perfluoro-filler size is 40 nm, thus confirming the importance of inter-phase on fluoroelastomer composite properties.

The mathematical model here presented (solid lines) fits the data pretty well with both perfluoro-filler sizes. It should be noted that Guth and Gold model (dotted line in Figure 3) fits well enough the 165 nm data set but fail completely the data set at 40 nm. This confirms the accuracy of Guth and Gold model when filler particle size is in the usual range of microns or tens of microns but that model is no more valid when particle size is brought below 100 nm.

Thanks to the higher reinforcement obtained with nano-fillers, fluorinated nano-composites develop better mechanical properties, in particular much higher elongation and toughness[3]. This peculiarity is very useful for several industrial applications, for example in the oil drilling industry as will be shown later in this paper.

Fluoroelastomer Nano-Composites Permeability

Permeability is another property affected by the size of the filler. Maxwell model[10,11]

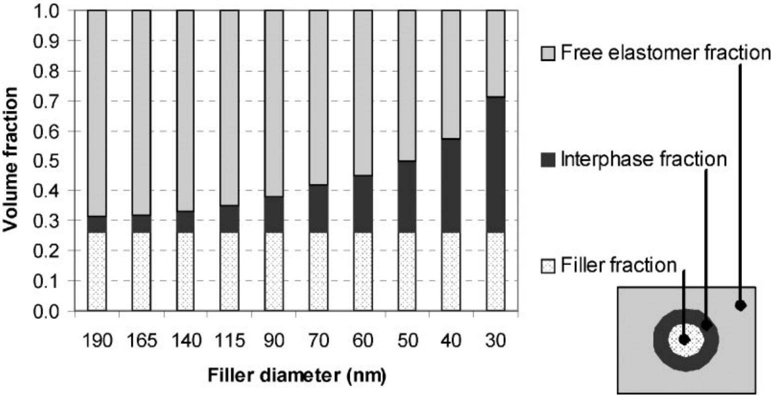


Figure 2.

Evolution of fluoroelastomer composite components vs. perfluoro-filler particle size. Filler amount = 26 vol%; interfacial thickness = 6 nm.

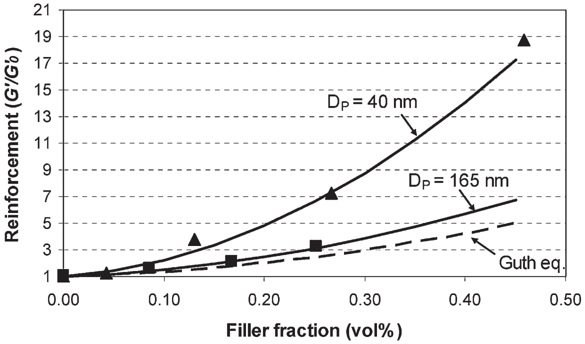


Figure 3.
Reinforcement (G'/G'_0) vs. perfluoro-filler content (vol%). Solid lines = mathematical model according to eq. (3) with $l_{int} = 6$ nm; dashed line is Guth and Gold model, eq. (1); ■ = experimental data with perfluoro-filler particle diameter of 165 nm ▲ = experimental data with perfluoro-filler particle diameter of 40 nm.

is often used to predict permeability, P, of composite materials:

$$\frac{P}{P_0} = \frac{P_F + 2P_0 - 2\phi_F(P_0 - P_F)}{P_F + 2P_0 + \phi_F(P_0 - P_F)} \tag{4}$$

Where P_0 is the permeability of the bare fluoroelastomer and P_F is the filler permeability.

Figure 4 shows the experimental permeability to oxygen of a fluoroelastomer loaded with different amounts of perfluoro-filler particles with diameter of 40 nm. Experimental results have been measured through ASTM D1434 test method. Permeability of the nano-composite goes down as perfluoro-filler amount increases. Actually this experimental trend is surprising because P_F is larger than P_0 (250 vs. 167 $\text{cm}^3 \cdot \text{mm/m}^2 \cdot \text{atm} \cdot \text{day}$), so, an increase of permeability with filler amount should be expected. This is exactly what Maxwell equation (dashed line in Figure 4) predicts, with an upward trend of permeability with filler amount.

As in case of reinforcement, the role of inter-phase could provide an explanation to such an experimental behavior. With reference to the sketch in Figure 2, the nano-composite is a three-phase structure with the inter-phase region separating the perfluoro-filler from the free fluoroelastomer. To calculate the permeability of the nano-composite, the approach described by

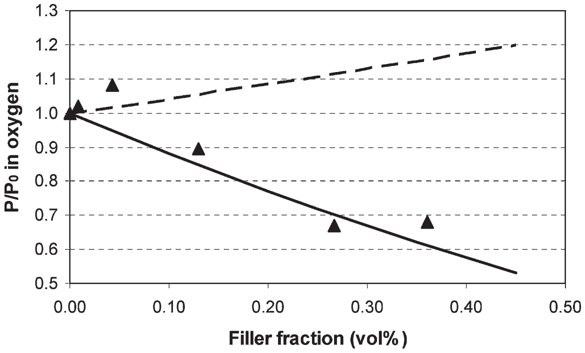


Figure 4.
Permeability ratio in oxygen, (P/P_0) vs. perfluoro-filler content (vol%). Solid lines = mathematical model according to eq. (7); dashed line = Maxwell model, eq. (4); ▲ = experimental data with perfluoro-filler particle diameter of 40 nm.

Chung et al.[12] is here applied. First, permeability of the combined perfluoro-filler and inter-phase structure, P_{eff}, is evaluated through the Maxwell equation applied to filler and inter-phase:

$$P_{eff} = P_{\text{int}} \frac{P_F + 2P_{\text{int}} - 2\phi_s(P_{\text{int}} - P_F)}{P_F + 2P_{\text{int}} + \phi_s(P_{\text{int}} - P_F)} \tag{5}$$

where P_{int} is the permeability of the inter-phase and ϕ_s is given by:

$$\phi_s = \frac{\phi_F}{\phi_F + \phi_{\text{int}}} \tag{6}$$

Then, the nano-composite permeability, P, is obtained applying Maxwell equation a second time:

$$\frac{P}{P_0} = \frac{P_{eff} + 2P_0 - 2(\phi_F + \phi_{\text{int}}) \cdot \left(P_0 - P_{eff}\right)}{P_{eff} + 2P_0 + (\phi_F + \phi_{\text{int}}) \cdot \left(P_0 - P_{eff}\right)} \tag{7}$$

The value of P_{int}, that is unknown, has been determined by fitting the experimental data of Figure 4. The best fit is obtained using a value of $P_{int} = 40\,\text{cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{atm} \cdot \text{day}$. It should be noted that such a value, considerably lower than that of the free fluoroelastomer, is consistent with a more dense chain packing in the inter-phase, thus affecting molecular transport.

Figure 5 shows an example of permeability to a liquid (methanol) measured with the Thwing-Albert Cup Test for liquids. Also in this case, Maxwell equation (dashed line) over-estimates permeability, while the modified Maxwell equation here proposed provides a better fit to experimental data. Permeability of inter-phase has been set equal to $1.5\,\text{ml} \cdot \text{mm}/(\text{m}^2 \cdot \text{day})$. As a comparison, permeability of bare fluoroelastomer is $5.3\,\text{ml} \cdot \text{mm}/(\text{m}^2 \cdot \text{day})$. Also in case of liquids, inter-phase shows a significantly lower permeability. This is coherent with the expected higher chain packing density at the inter-phase caused by filler surface proximity.

Equation (7) can now be used to predict the effect of perfluoro-filler particle size on permeability. Results are shown in Figure 6. A relevant decrease of permeability to methanol is obtained when perfluoro-filler particle size is reduced below 100 nm. This is particularly interesting for the development of more performing fuel hoses for automotive industry as will be shown in the next paragraph.

Industrial Exploitation of Fluorinated Nano-Composites

Fluoroelastomers are designed for high demanding applications in hostile environments characterized by high temperature ranges and contact with aggressive fluids.

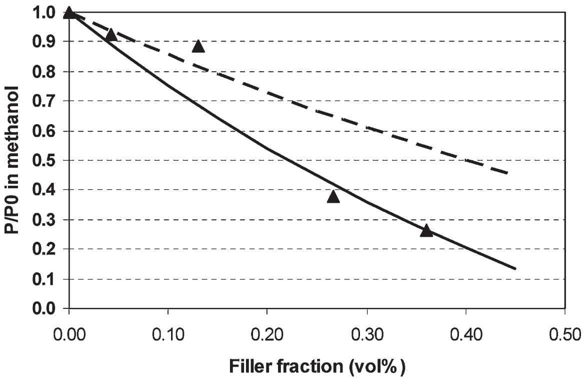


Figure 5.
Permeability ratio in methanol, (P/P_0) vs. perfluoro-filler content (vol%). Solid lines = mathematical model according to eq. (7); dashed line = Maxwell model, eq. (4); ▲ = experimental data with perfluoro-filler particle diameter of 40 nm.

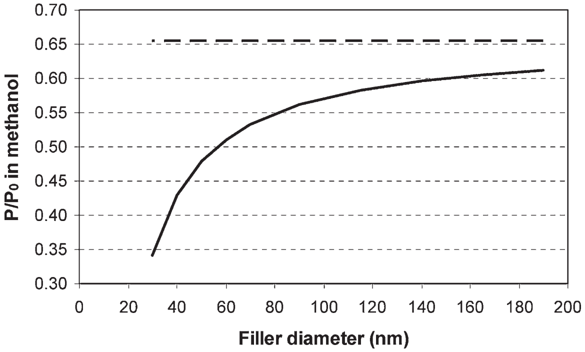


Figure 6.
Permeability ratio in methanol, (P/P_0) vs. perfluoro-filler particle size (nm). Filler content is 30 wt%. Solid lines = mathematical model according to eq. (7); dashed line = Maxwell model, eq. (4).

However, traditional fluoroelastomers are no more able to satisfy the stringent requirements of modern applications: for example, high chemical resistance in harsh environments like plasma chambers, very low permeability to aggressive fluids used in new automotive engines, outstanding mechanical properties requested in oil drilling. The fluoroelastomer nano-composites described in this paper provide an innovative answer to satisfy these new and severe needs. As shown in the previous paragraph, the use of perfluoro-fillers with particle size below 100 nm improves many properties ranging from mechanical properties to molecular transport. Among other properties that are positively affected by usage of perfluorinated nano-fillers there are chemical resistance, friction, hardness, elongation, and high purity. More details can be found in Ref[3].

The main application fields of these nano-composites are Semi-con (plasma etching), Petrochemical (oil field applications, oil drilling) and Automotive (fuel hose).

A brief overview of these applications is here below presented.

Semi-con

Wafers, chips and micro-electronic components are manufactured by using plasma, a versatile and powerful tool for etching, cleaning, stripping, ashing, and especially for the deposition process. To obtain good process efficiency, high purity conditions in the plasma chamber must be granted. Seals deterioration is a major source of contamination, by releasing particles, metal ions and gasses. Special grades of perfluorinated nano-composites are used to produce seals for plasma chambers because they grant high purity conditions even when very aggressive plasma are used. Thanks to the outstanding performance of these nanocomposites, maintenance downtime of plasma chambers is reduced, improving their productivity.

Oil Field Applications (petrochemical)

To fulfill oil drilling requirements, sealing elements must have high chemical and thermal resistance, high tensile properties, especially elongation at break, high hardness and, above all, adequate resistance to ‘‘explosive decompression’’. Indeed, elastomeric seals and liner materials subjected to high pressure hydrocarbon environment may exhibit blistering on sudden release of gas pressure. This phenomenon, known as explosive decompression, may occur for example when a high pressure valve is opened rapidly or a flexible gas hose is disconnected. The damage to the elastomer is brought by the rapid expansion of absorbed gas. Thanks to the reinforcement effect of filler nano particles, fluoroelastomer nano-composites show very good performance in explosive decompression test and can be conveniently used to develop sealing elements for oil drilling.

Automotive (fuel hose)

During the past 20 years the driving force for automobile development has been reduction in environmental pollution and improving operating efficiency. In order to optimize car performance, engines operate at high temperature and the fuel is added with chemicals to improve combustion efficiency. Combination of high temperature and aggressive chemicals is forcing car producers to look for new fuel hose with outstanding performance. Besides, the fuel hose must guarantee low permeation rates, so as to fulfill the stringent emission regulations. Nano-composites here presented provide an interesting solution due to the very low permeation to fuels and outstanding chemical and thermal resistance.

Conclusions

Introduction of nano-particles of a semicrystalline perfluopolymer in a fluoroelastomer provides an unexpected increase in a variety of properties, ranging from mechanical properties to permeation and chemical resistance. According to the schematization here proposed, the increase in properties like reinforcement and permeability is due to a modified packing of the elastomer chains around the filler surface. This effect becomes relevant only when filler particle size is below 100 nm, i.e. in the nano-scale region. A simple mathematical model confirms that this theory provides a good explanation of the experimental evidences.

The properties profile of these nanocomposites is of interest in severe applications in automotive, semi-con and oil drilling industries. A few examples have been briefly illustrated.

In conclusion, fluorinated nano-composites could provide a solution to the ever increasing performance profile asked by modern applications, taking advantage of the substantial enhancement of several properties when filler particle size is brought below 100 nm.

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