FLUORINATION AND END-CAPPING OF PERFLUOROPOLYETHERS

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SUMMARY

This work present some results obtained in the perfluoropolyether fluorination with elemental fluorine and temperature range from 100 to 270°C.

The preliminary tests of fluorination reaction showed acid group neutralization. However, was observed high degradation and mass loss.

INTRODUCTION

Perfluoropolyethers (PFPE) form a class of fluids completely characterized by high thermal resistence and chemical inertness. These fluids have special characteristics, such as high specific weight, low surface tension, inertness towards all plastics and elastomers, compatibility with most metals over wide temperature ranges, immiscibility with all organic solvents except some fluorinated fluids.

These fluids comercially known as Fomblin are oligomers with the structure of perfluorinated polyethers and consist of carbon, oxygen and fluorine atoms only. The chain structure:

$$-(O\text{-}CF(CF_3)\text{-}CF_2)_n-(O\text{-}CF_2)_m-$$

has been demonstred for them. The monomeric units with indexes m, n are random distributed along the chain of the perfluoropolyether; m and n are integers from 0 to 200.

In the production of raw perfluoropolyethers, is obtained a product having an inert perfluoropolyether chain but with one or more chemically reactive groups. They are end groups of acid and ketonic nature.

The most convenient procedure for obtaining oils with extreme chemical inertness, is through fluorination. For the pratical realization of the reaction, the technique consists of sending a gaseous current of fluorine, either pure or diluted with an inert gas, into a liquid phase of raw perfluoropolyether kept at the temperature selected for the reaction, preferabily taking care of obtaining good contact between the gaseous phase and the reacting

liquid phase. The reaction is carried on until a complete or at least satisfactory disappeareance of the original acids terminal groups.

EXPERIMENTAL

Fluorination reactions were performed using a comercially fluorine/nitrogen gas cylinder from Air Products Company. The raw perfluoropolyether used in the reaction, was obtained at IPEN (Instituto de Pesquisas Energéticas e Nucleares) in liquid phase photooxidation of hexafluoropropene under atmospheric pressure at - 70 °C.

The viscosity was obtained from Ostwald viscosimitry. The molecular weight was calculated by follows formula: $\eta = 5.3 \times 10^{-7} \times mw^{2.474}$. Being η= viscosity at 20°C and mw= molecular weight.

Fluorination were performed in glass reactors where the stirred polyether was heated (from100 to 270° C) while bubbling a slight excess of fluorine. Under these conditions, the reactions were completed in about 24 hours.

One fluorination reactor with capacity of 1000 mL enclosing a Fomblin mass from 100 to 1000g with molecular weight from 2900 to 7400 and was carried out at temperature range from 100° to 270° C during 24 hours.

After this time the oil viscosity was measured and the infrared spectrum was obtained.

RESULTS AND DISCUSSIONS

The spectrum that before showed two peaks in region of 1780 to 1887 cm^{-1} that was relative to the -COOH and -COF groups no more appears, this means that had a neutralization of these groups. However, was observed high degradation and mass loss.

Table 1 shows more degradation when the temperature is high and is independent of the molecular weight from outlet polymer.

Table 1: Data from reactions in a differents temperatures of four photooxidation conditions.

MW-raw product	MW-fluorinated product	% degradation (MW	Temperature (°C)
3238	2654	18	170
7335	6087	17	220
7142	5293	26	250
4260	2543	40	270

Table 1 also shows the percentage of the polymer degradation in function of the molecular weight. These results are diferents from Lopergolo, L. et al. [1], in the study of the polymer degradation, in presence of Lewis acid. There the polymer degradation percentage increase when increase the molecular weight. This is in disagreement with the observed results. In the degradation polymer in presence of Lewis acid, the Fomblin degradation is given by the presence of acetal unities (-O-CF -O-) in the polymeric chain.

In the fluorination reactions the degradation occurs in diferent way. According to Sianesi et alli [2], the mechanism for the fluorination reaction is possible to be as following:

$$-O\text{-}CF_2\text{-}CO\text{-}CF_3 \xrightarrow{F_2} [-O\text{-}CF_2\text{-}CF(OF)\text{-}CF_3] \longrightarrow -O\text{-}CF_3 + CF_3CFO$$

However, the reactions above did not explain the big extension of degradation observed. The mecanism show the fluor bond in the carboxil carbon with β-carbon splithing. The decrease of the chain is limited by light groups outlet, that did not affect considerably decrease of the viscosity observed.

The main degradation is being associated to the presence of the peroxidics bonds that form in the polymeric chain on the photooxidation process.

The peroxidics bonds removal occurs easily when increase the temperature. According to Sianesi et al. [2], the decomposition process involve a sequence of elementary reaction where begins with homolytic cleavage of O-O bonds.

The so formed perfluoroalkoxy radicals undergo a fragmentation reaction, β-scission with chain degradation until that cleavage of a C-C bond occurs with formation of perfluoroalkyl radicals [2]. These carbon radicals undergo differents reactions: the induced homolysis of peroxide bonds and the coupling with other carbon radicals.

REFERENCES

[1] LOPERGOLO, L. C.; ALFARO, E. F.; SILVA, L. G. A.; LUGÃO, A. D.. Degradação térmica de perfluoropoléter catalizada por ácido de Lewis. Anais do 2 Congresso Brasileiro de Polímeros, São Paulo-SP, 5 - 8 de outubro, 1993, p.307-12.

[2] SIANESI, D.; PASETTI, A.; FONTANELLI, R.; Bernardini, G. C.; Caporiccio, G.; Perfluoropolyethers by photooxidation of fluoroolefins, **La Chim. L'Ind.**, 55 (2): 206-21, 1973.