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CROSSLINKING OF VINYLIDENE FLUORIDE CONTAINING FLUOROPOLYMERS

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ABSTRACT

Fluoropolymers are well-known for their good properties in terms of chemical, thermal and electrical stabilities, inertness to acids, bases, solvents and oils, and high resistance to ageing and oxidation. Polyvinylidene fluoride (PVDF) is useful as homopolymer endowed with interesting characteristics. It contains a high cristallinity rate, but is base sensitive. In addition, VDF can be co- or terpolymerised with several fluorinated monomers, rendering them suitable as elastomer and various examples of synthesis of VDF-copolymers are also presented. This review also focusses on binary and tertiary systems containing VDF. Several curing systems for these VDF-containing copolymers have been investigated, especially diamines and their derivatives, aromatic polyhydroxy compounds, peroxides with coagents, such as triallylisocyanurate, radiations, and thiol-ene systems.The best vulcanisate properties are obtained by a two-step process. First, the material is press cured at different times and temperatures, then, it is post cured in air or under nitrogen at higher temperature and time, and under atmospheric pressure. Poly(VDF-co-HFP) copolymers can react with primary, secondary or tertiary monoamines, but they are mainly crosslinked by diamines such as hexamethylene diamine (HMDA), their carbamates (HMDA-C), and derivatives. A mechanism of crosslinking is identified by Infrared and ^{19}F NMR spectroscopies, and was evidenced to proceed in three main steps. First, a VDF unit undergoes a dehydrofluorination in the presence of the diamine, then the Michael addition occurs onto the double bonds to

form crosslinking, while HF is eliminated from crosslinks in the presence of HF scavengers.The crosslinking mechanism with bisphenols takes place also in three main steps (dehydrofluorination, then substitution of a fluorine atom by a bisphenol, and elimination of HF). The most efficient crosslinking bisphenol is bisphenol AF.
A fluoropolymer crosslinked with peroxide/coagent systems needs to be functionalized or halogenated to insure a free radical attack from peroxide. The peroxide is introduced with a coagent that enhances the crosslinking efficiency, and the most efficient one is triallylisocyanurate (TAIC). The crosslinking mechanism of peroxide/triallylisocyanurate system proceeds in three main steps. The crosslinking reaction occurs from a macroradical arising from the functional or halogenated polymer which is added onto the three double bonds of the TAIC. A fourth way to crosslink VDF-based fluoropolymers deals with high energy radiation, such as X and γ (^{60}Co or ^{137}Cs)-rays, and charged particles (β-particles and electrons). Three different reactions are possible after irradiation of a PVDF, and the one that leads to crosslinking is the recombination between two macroradicals. The irradiation dose on VDF-based copolymer has an influence onto the thermal and mechanical properties.
Finally, a crosslinking system also used to vulcanisate hydrogenated elastomers concerns a thiol-ene system which requires a mercapto function born by the VDF-based polymer. Crosslinking occurs via a non-conjugated diene. The mechanical properties (tensile strength, elongation at break, hardness, elongation modulus, compression set resistance…) of the three main crosslinking systems of fluoroelastomers are compared. Finally, the main applications of crosslinked VDF based fluoropolymers are summarised which include tubing in aircraft building industry, sealing, tube or irregular-profile items of any dimension, films with good adhesion to metallic or rigid surfaces, multilayer insulator systems for electrical conductors, captors, sensors, and detectors, and membranes for electrochemical applications.

KEYWORDS

Crosslinking, polyvinylidene fluoride, amines, bisphenols, peroxides/triallylisocyanurate.

List of ABBREVIATIONS and SYMBOLS

BTPPC	Benzyltriphenylphosphonium chloride
CTFE	Chlorotrifluoroethylene
DBU	1,8-Diazabicyclo[5-4-0]-undec-7-ene
DETA	Diethylene triamine
DMAC	Dimethylacetamide
d.o.g.	Degree of grafting
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EDA (-C)	Ethylene diamine (carbamate)
HBTBP	Hexamethylene-N,N'bis(tert-butyl peroxycarbamate
HFP	Hexafluoropropene
HMDA	Hexamethylene diamine
HMDA-C	Hexamethylene diamine carbamate
HPFP	1H-pentafluoropropene
MBTBP	Methylene bis-4-cyclohexyl-N,N'(tert-butylperoxycarbamate
ODR	Oscillating disc rheometer
PMVE	Perfluoro(methyl vinyl ether)
PVDF	Polyvinylidene fluoride
$t_{1/2}$	Half life
TAC	Triallylcyanurate
TAIC	Triallylisocyanurate
TFE	Tetrafluoroethylene
THF	Tetrahydrofurane
VDF	Vinylidene fluoride

1 INTRODUCTION

1.1 Introduction on fluoropolymers

Fluorinated polymers are particularly interesting and attractive compounds because of their properties. Indeed, the electronegativity of the fluorine atom implies a strong C-F bonds (about 110 kcal.mol^{-1}), and a higher strength of the C-C bonds in fluorinated compounds (97 kcal.mol^{-1}). It also supplies to fluoropolymers strong Van Der Waals forces between hydrogen and fluorine atoms [1-3], and it confers a lot of good properties to the fluorinated polymers such as:

- Chemical, thermal, electric stabilities [4-6],
- Inertness to acids, bases, solvents and oils,
- Low dielectric constant,
- Low refractive index,
- No flammability,
- High resistance to ageing, and to oxidation,
- Low surface tension.

Fluorinated polymers also range as a wide scope of thermoplastics, elastomers, plastomers, thermoplastic elastomers [7-14], and can be semi-crystalline or totally amorphous. Hence, fluorinated polymers have been used in many applications: building industries (paints and coatings resistant to UV and to graffiti), petrochemical and automotive industries, aerospace and aeronautics (use of elastomers as seals, gaskets, O-rings used in extreme temperature for tanks of liquid hydrogen for space shuttles), chemical engineering (high-performance membranes), optics (core and cladding of optical fibers), treatment of textile, stone protection (especially for old monuments), microelectronics [8-14], and for cable insulation.

As a matter of fact, the performance of fluoropolymers, especially insolubility and fusibility can be improved by crosslinking. Indeed, the crosslinking reaction takes advantage of the base-sensitive characteristic of the VDF-based polymer [15]. The crosslinking is a chemical reaction between the polymer backbone and an ex-situ agent that possesses both same fonctions in order to couple covalently the polymeric chains together, to produce a network structure, and to increase the molecular weight.
Sulphur has been the predominant curing agent in the rubber industry, and in 1840, rubber was with sulphur [16]. Many efforts have been devoted over the 40 years of existence of fluoroelastomers toward the development of practical crosslink systems.
Fluoroelastomers are now usually cured by nucleophiles such as diamines [17-31], or bisphenols [3,32-38], or with peroxides [3,35,39-43], by chemical reactions when the polymers based on VDF contain cure-site monomer, such as thiol function [44], by radiation, such as electron beam [45-52].
The cure chemistry of VDF based fluoroelastomers is connected with the strong polarity of the C-F bond and specific polarisation of molecules, which determine their selective ability to split off hydrogen fluoride under the influence of internal factors.

The first part of the review presents the generalities of the crosslinking of VDF-based fluoroelastomers, and especially the two steps of the cure (the press cure and the post cure). The second part deals with the crosslinking involving different agents: first, the aliphatic and aromatic amines and diamines, then the bisphenol-cure, third the peroxide-cure, fourth the crosslinking by irradiation, and finally the thiol-ene system-curing. Then, the third part compares all the crosslinking systems, by considering the main mechanical properties, and finally, the last part concerns the applications of the crosslinked VDF based fluoroelastomers.

1.2 PVDF

Among fluoropolymers, polyvinylidene fluoride (PVDF) is a semi-crystalline and thermoplastic polymer, with a glass transition temperature of –40°C [53,54]. This polymer exhibits interesting thermal, chemical and physical properties, especially when it is co- or ter-polymerised with a fluorinated alkene [14,35,50,55-59]. Its main drawback is its sensitivity to base that can degrade it by creating insaturations. PVDF homopolymer is a long chain macromolecule endowed with a high crystallinity rendering it unsuitable as elastomer, and unsuitable for curing. So, copolymers of VDF with various comonomers can fall into three categories: i) when the amount of comonomers in the copolymer is small about that of VDF, the resulting materials are thermoplastics with a lower crystallinity than that of the PVDF [60,61]; ii) for a bit higher content of comonomer, thermoplastic elastomers are obtained ; iii) for higher proportion of comonomers, the produced copolymers are elastomeric and amorphous with low intermolecular forces [35,50,57,58,62-66]. In the case of the poly(VDF-co-HFP) copolymer, when the molar percentage of VDF is higher than 85%, the copolymer is a thermoplastic, whereas for a smaller content, the copolymer is an elastomer [35,50].

1.3 Copolymers based on VDF

VDF has been involved in radical copolymerisation with many monomers [14,60,61,67], listed in *Table 1* [44,68-94].
Most common co- or termonomers of VDF [14,50] are hexafluoropropene (HFP) [80,82,83,95-97], tetrafluoroethylene (TFE) [78,80,81,98,99], chlorotrifluoroethylene (CTFE) [78,79,100-102], trifluoroethylene (and in that case, interesting piezoelectrical materials have been obtained) [75], perfluoro(methyl vinyl ether) (PMVE) [77,84,103-105], and 1H-pentafluoropropene (HPFP) [67,106,107]. Interestingly, functional fluoromonomers (also called cure site monomers) useful for further crosslinking, have been successfully used, bearing OH [86], CO_2H [71,89], $Si(OR)_3$ [94] functions, or bromine [87] and iodine atoms. *Table 1* supplies a non-exhaustive list of fluoromonomers that were copolymerised with VDF, and their reactivity ratios r_i, when assessed.

Insert Table 1

Although it is difficult to compare their reactivities (since i) the copolymerisations were not carried out under similar conditions, ii) certain articles do not mention if the kinetics of copolymerisation were realised at low monomer conversion, and iii) various kinetic laws were used), it was worth examining a reactivity series of fluorinated monomers with VDF. The traditional method for the determination of a reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the value $1/r_A = k_{AB}/k_{AA}$, as the ratio of rate constants of co-propagation (k_{AB}) to that of homo-propagation (k_{AA}). Thus, the higher the $1/r$ value, the higher the copropagation reactivity of the radical. Based on the data in *Table 1*, the increasing order of relative reactivities of monomers to ~VDF$^{\bullet}$ macroradicals is as follows :
$F_2C{=}CHC_6F_{13}$ < $F_2C{=}CHCF_3$ < HFP < PMVE < PPVE < $F_2C{=}CFC_2H_4Br$ < VDF < $F_2C{=}CFCH_2OH$ < $F_2C{=}C(CF_3)OCOC_6H_5$ < TrFE < CTFE (recent value) ≈ BrTFE < $H_2C{=}CFCF_2OR_F$ < $F_2C{=}CFCO_2CH_3$ < TFE < $F_2C{=}CFC_3H_6SCOCH_3$ < $F_2C{=}CFC_3H_6OAc$ < $H_2C{=}CHF$ ≈ CTFE (old value) < $H_2C{=}CH_2$, although numerous kinetics still deserve to be investigated.

2 GENERALITIES

In order to improve their properties, poly(VDF-co-HFP) copolymers or poly(VDF-ter-HFP-ter-TFE) terpolymers can be crosslinked by bisnucleophiles, such as diamines or bisphenols, or by irradiation. On the other hand, poly(VDF-ter-HFP-ter-termonomer containing an iodine or bromine atom) terpolymer can be crosslinked by peroxides/coagent systems. Those three main ways of crosslinking exhibit two main crosslinking mechanisms (ionic and radical mechanisms) and different properties.

2.1 Different crosslinking agents

Several curing systems have been investigated or developed for the crosslinking of fluoroelastomers. Some of them are [35,108]

- high energy radiation [19, 45-52],
- peroxide with or without coagent [3,35,39-43],
- dithiols in combination with amines [19],
- aromatic polyhydroxy compounds [3, 32-38],
- diamines and their derivatives [17-31],
- thiol-ene systems [44,50].

Each curing system exhibits a different crosslinking mechanism, and results in different mechanical properties and crosslinking densities. Indeed, *Table* 2 [35] shows different mechanical properties for bisphenols and peroxides cured systems.

Insert Table2

The comparison of the mechanism is comprehensively described in section III, while sections IV and V are devoted to the study of mechanical properties and the applications of each system.

2.2 Compounding

In order to improve the properties of the raw elastomer, many materials that enable to facilitate mixing or processing may be compounded with the vulcanising agent [28,55], (i) accelerators and accelerator activators to increase the rate of vulcanisation and to improve product properties; (ii) fillers to enhance physical properties and /or to reduce costs; (iii) softeners enable to aid processing or to plasticize the product; (iv) antioxidants and other materials which slow down decomposition of the product by oxidation; (v) heat and/or radiation; (vi) pigments and blowing agents.

For the main additional materials, the proportions (in part per hundred of polymer) are [55]:

Raw polymer	100
Curing agent	1-6
Basic metallic oxide	6-20
Filler	>60

2.3 Press cure and post cure steps for crosslinking

The best vulcanisate properties are obtained by a two step-process [35,58,109]. Fluoroelastomers and additives are generally molded in a press and then post cured in an oven [28].

First, the materials are press cured at different times and temperatures, depending on the size of the product, the structure of the polymer, the curing systems, and on end-use requirements (paints, O-rings, membranes, seals) [28]. Press cure conditions vary from 4 minutes at temperatures approaching 200°C for thin cross sections, to 30 min at 150-170°C for thick sections [28,110]. The purpose of this step is to develop sufficient crosslinks in the sample to prevent the formation of bubbles due to the release of trapped air during the early stages of the subsequent oven cure [111].
Then, the second step (post cure or oven-cure) is carried out in air or under nitrogen at higher temperature than that of the press cure, and under atmospheric pressure[35,58].
This post cure step is required to reach the best vulcanisate properties (tensile strength, modulus at 50 or 100% elongation, compression set resistance, elongation at break) [28,40,108,111]. *Table 3* [35] shows the improvement of compression set resistance with post curing, for four samples containing poly(VDF-ter-HFP-ter-TFE) terpolymer crosslinked with a peroxide [2,5-bis(t-butylperoxy)-2,5-dimethylhexyne] in the presence of triallyl/isocyanurate [35,108,112,113]. *Table 2* [35] presents the improvement of some mechanical properties of bisphenol and peroxide cured systems with post cure.
An improvement in compression set resistance is observed after post cure under nitrogen compared to that realised under air (*Table 3*). The C=C double bond of the polymeric backbone undergoes an oxidation from the oxygen of air atmosphere, that prevents from good compression set resistance. *Table 2* shows a 50% increase in modulus at 100% elongation (M_{100}) and tensile strength at break, and a 50% decrease in elongation at break.

Insert Table 3

During the step of crosslinking of fluoroelastomers, water is formed, and post cure removes this water, whose presence prevents from full development of the diamine cure and causes reversion of the bisphenol cure [3,23,40,114]. Indeed, during press cure, water is formed from the reaction between the acid acceptor and HF, caused by dehydrofluorination.

For thick sections, the temperature of the post cure oven is usually raised in several steps to prevent from fissuring of the part. Generally, 12-24h reaction time at a temperature of 200-260°C is used [28,35,58,110]. Typically, 200°C is sufficient for amines [59,111], whereas bisphenol and peroxide cures need higher temperatures (230 to 260°C).

All these results suppose a difference in the crosslinking mechanism of bisphenols, peroxides and diamines cured systems, that are the most important crosslinking agents for VDF-based fluoroelastomers. The crosslinking mechanisms and the properties of the resulting crosslinked polymers are the subject of the following parts.

3 CROSSLINKING OF VDF-BASED FLUOROELASTOMERS

3.1 CROSSLINKING WITH AMINES AND DIAMINES

The curing by diamines, originally introduced in late 1950ies, was a predominant way of crosslinking of raw fluoroelastomers until late 1960ies, when bisphenol curing was introduced [55,58]. The polyamine system is the best for general use because of easier processing [96]. Indeed, it only needs the presence of hydrogen atoms in the polymer backbone. Moreover, the mechanism of crosslinking can be a simple addition on this backbone [96].
The diamine curing system generally results in relatively poor processing, safety concerns, thermal and ageing resistance, and compression set resistance. However, this cure system has demonstrated specific properties, such as excellent adhesion to metal [115].
The curing of elastomer with an amine or a diamine usually takes place in the three following steps [24,114,116,117]:

(1) an elimination of HF (dehydrofluorination) from VDF segments adjacent to HFP in the main chain to generate internal double bonds,
(2) a Michael addition of the diamine onto the resulting double bonds to form crosslinks,
(3) an elimination of HF from the crosslinks, during post cure to form further double bonds.

These steps are detailed below.

3.1.1 Dehydrofluorination of the fluoropolymer

The dehydrofluorination of a solution of Viton® poly(VDF-co-HFP) copolymer treated with several amines, or heated at high temperature can be monitored by measurement of hydrogen fluoride elimination (titration of the HF in the solution) [5,15,19,116], infrared study [19,24,118], viscosity [19], solubility and determination of the gel content [5].

3.1.1.1 Evidences of dehydrofluorination

Solutions of Viton® in tetrahydrofurane were treated with primary, secondary and tertiary monoamines for periods of several weeks at room temperature. The reaction was followed by the measurement of HF elimination by a titration of the hydrogen fluoride in the solution.
Figure1 [19] shows the evolution of the quantity of HF in the solution of THF as a function of time for primary, secondary and tertiary monoamines. All of the monoamines used caused dehydrofluorination of the polymer to some degree. Tertiary amines are the least efficient, primary amines by far are the most active.

Insert Figure 1

Figure2 [24,118] shows the infrared spectrum of uncured poly(VDF-co-HFP) copolymer (FKM gum), before and after a thin film of polymer is heated in air at 300°C. Two new bands centered at 1580 and 1750 cm^{-1} appeared after heating, which are assigned to the conjugated double bonds and to the $-CH=CF_2$ end groups, respectively. Unsaturation is likely to be caused by elimination of HF from PVDF block of the FKM chain, in particular from the head-to-tail position of the structure.

Insert Figure 2

So, in the presence of a base or under heating, the VDF-based fluoroelastomers are submitted to dehydrofluorination.

3.1.1.2 Consequences of the dehydrofluorination

The conjugated double bonds evidenced by infrared measurements allowed us to interpret a new mechanism. *Figure 2* [118] exhibits the presence of isolated double bonds (1710 cm^{-1}), and the presence of conjugated double bonds (1580 cm^{-1}). It is proposed that the initial double bond (1710 cm^{-1}) activates the elimination of HF from neighboring atoms leading to conjugated double bonds (1580 cm^{-1}). This process would lead to the formation of a brown color [20,24,118] .
Such a conjugate site would then be expected to react with a double bond, in an adjacent chain by a Diels Alder reaction, leading to a fluorinated cyclohexene which should readily loses HF to form an aromatic ring (*Scheme 1*) [19,119].

Insert Scheme 1

The observed absorption at 1580 cm^{-1} could be ascribed to such a site.

The evolution of the solubility of a raw poly(VDF-co-HFP) copolymer heated in air at 250°C is shown in *Table 4* [24]. Indeed, there is an initial rapid decrease in solubility, and then it proceeds to rise slowly. This type of variation of solubility, together with the formation of a swollen gel, indicates the simultaneous occurrence of crosslinking and chain scission in the polymer [5,114] .

Insert Table 4

During heating or attack with a base, the polymer undergoes a dehydrofluorination, creating conjugated double bonds that can be involved in a Diels Alder reaction. But, at higher temperature or in the presence of a stronger base, it also creates degradation such as oxidation or scissions that can be evidenced by the measurements of the decrease in the intrinsec viscosity, caused by the decrease in molecular weight [19]. In order to avoid any degradation, the created double bonds can become the site of the addition of several agents like diamines, bisphenols or peroxides, that can increase the mechanical and chemical properties. The formation of the scissions in the network are explained in section III.1.4.

3.1.1.3 Sites of dehydrofluorination

In VDF-based fluoropolymers, and especially poly(VDF-co-HFP) copolymer, dehydrofluorination occurs on special sites.
Paciorek et al. [23] studied the crosslinking of amines on several fluoro-compounds models. The model of addition of butylamine onto 1,5,5-trihydro-4-iodoperfluorooctane and 4-hydroperfluoroheptene-3, in diethylether at room temperature, is the only one known. It proceeds according to the following scheme:

$$C_2F_5CFICH_2C_3F_7 + H_2NC_4H_9 \rightarrow C_2F_5C(=NC_4H_9)CH_2C_3F_7 + C_2F_5C(NHC_4H_9)=CHC_3F_7$$

The reaction occurs mainly on the carbon adjacent to the iodine atom, because dehydrofluorination is the main process under the selected conditions.

From ^{19}F NMR characterisation, Schmiegel [3,15,32,33] showed that a polymer based on VDF units with HFP, TFE, PMVE co- or ter-monomers in solution of DMAC can undergo dehydrofluorination from the n-Bu_4N^+ ^-OH in specific sites.
Figure 3 [33] represents the 294.1 MHz ^{19}F NMR spectra of poly(VDF-co-HFP) copolymer before (top) and after (bottom) treatment with hydroxylic base in DMAC at 20°C. Peaks A and B are assigned to CF_3 group, peaks C, D, E, F, G, H, I, J, K,and L are attributed to CF_2 of VDF, peaks M and N are assigned also to CF_2 of the HFP, and finally peaks O and P are assigned to CF. The small resonances A, G and O correspond to HFP inversions, whereas F, J, K, and L are attributed to VDF inversions. Spectrum at the bottom exhibits selective intensity reduction of resonance B, H, I, M, N and P after addition of Bu_4N^+ ^-OH. A peak assigned to CF_3 groups of –C=C(CF3)-C-appears also at -55 ppm. These observations can be accommodated to the highly selective dehydrofluorination of isolated VDF units, i.e. HFP-VDF-HFP structures [3,32-34]. The concentration of this site in a 3.5 poly(VDF-co-HFP) copolymer is about 0.6 mol/kg. The same results was observed in poly(VDF-co-TFE) and poly(VDF-co-PMVE) copolymers, and poly(VDF-ter-HFP-ter-TFE) and poly(VDF-ter-PMVE-ter-TFE) terpolymers [33]. For example, in poly(VDF-co-TFE) copolymer, dehydrofluorination occurs on VDF units having a TFE-VDF-TFE triad, or in poly(VDF-ter-HFP-ter-TFE) terpolymer, it occurs on HFP-VDF-TFE structure.

Insert Figure 3

A reaction scheme of dehydrofluorination of poly(VDF-co-HFP) copolymer in the presence of a base was given by Schmiegel (*Scheme 2*) [32,33].
First, the attack of hydroxide creates a double bond on VDF units in VDF-HFP diad. Then, a fluoride ion rearrangement of the initial double bond occurs. The resulting allylic hydrogen is abstracted by fluoride, followed by an elimination of a second fluoride. So, a bifluoride and a formally conjugated non-coplanar diene are formed. Then, a nucleophilic attack by the hydroxide on the diene forms an enone and subsequent attack of fluoride ion onto the highly acidic hydrogen of the tertiary carbon atom. The final product is the dienone [32,33].

Insert Scheme 2

3.1.1.4 Role of the acid acceptor

An acid acceptor of metal oxide type is a necessary ingredient of all VDF-based polymer curing formulations. No cure is obtained without any metal oxide which did not contain magnesium oxide, and the state of cure developed is directly related to the amount of MgO [111,114,120].
Figure 4 [111] represents the evolution of the tensile strength and the modulus versus the quantity of MgO, for a trimethylamine hydrochloride cured poly(VDF-co-HFP) copolymer.
Indeed, there is an evidence by infrared that MgO contributes to the elimination of HF from the polymer during irradiation, and probably also in the course of the chemical cures.

Insert figure 4

Figure 5 [116] shows the variation of the amount of fluoride ions at 200°C with MgO content. The presence of MgO does not prevent from HF elimination; it merely reduces its rate of

evolution from the elastomer, a 15% addition giving a result comparable with that of the raw polymer alone.

Insert Figure5

The reaction between MgO and HF is given in the following scheme [114]:

$$MgO + 2HF \rightarrow MgF_2 + H_2O$$

Several metal oxides can be used as HF scavengers for VDF-based polymers. The relative efficiencies of a number of basic oxides, hydroxides and carbonates as HF acceptors at approximately 275°C are illustrated in *Figure 6* [116]. It is apparent that there are many variations in the efficiencies of the different compounds. The decreasing order of efficiencies is as follows:
$CaO >> Li_2O \approx B_2O_3 \approx BeO > Al_2O_3 > MgO > TiO_2$
The hydroxides are significantly better acceptors than their analogous oxides. The decreasing order of efficiencies is [116]:
$Ca(OH)_2 > Mg(OH)_2 > LiOH > Al(OH)_3$
Finally, the decreasing order of efficiencies for carbonates is [116]:
$CaCO_3 > Li_2CO_3 > MgCO_3 > Na_2CO_3 > K_2CO_3$
The most commonly used acid acceptor is MgO.

Insert Figure 6

Thus, dehydrofluorination of VDF comonomer in the diad is the first step of crosslinking mechanism with diamine. The second step consists in the addition of the amine or the diamine onto that unsaturation.

3.1. 2 Second step: the Michael addition of the amine

After the dehydrofluorination of the poly(VDF-co-HFP) copolymer, the amine can add across the unsaturated center. Addition can be carried out with primary and secondary diamine, and less readily with primary and secondary monoamines. Vulcanisation of VDF-based fluoroelastomers is induced by secondary and tertiary monoamines [20].
Paciorek et al.[20] studied the treatment of Viton-A® (poly(VDF-co-HFP) copolymer) and Kel-F® (poly(VDF-co-CTFE) copolymer) with different primary, secondary and tertiary mono- and diamines. It appears that Kel-F® elastomer required specific crosslinking conditions according to the nature of the (di)amine, at room temperature from primary mono- and diamines, at 50-60 °C by secondary mono- and diamines, at 90-100°C by tertiary diamines, and at 180-190°C by tertiary monoamines.

3.1.2.1 Mechanism with monoamines

The general mechanism of grafting of a primary or a secondary monoamines onto a model compound is given in *Scheme 3* [22]. The different steps of this mechanism are identified by infrared spectroscopy. The primary monoamine (butylamine), such as a secondary monoamine, dehydroiodinates the model compound creating CF=CH double bonds. Then, the amine can add onto the unsaturation thanks to Michael addition. Finally, as it has been shown

by Pruett [17], a structure containing -NH-CF(X)- group readily eliminates hydrogen fluoride, leading to –N=C(X)-, or C=C(N)-X.

Insert Scheme 3

In addition to difunctional curing agents, strong basic primary, secondary and tertiary amines create also crosslinking of Viton-A®, even if they require rather high press temperature to obtain successful cures when used alone [19,111]. Indeed, those basic components can help to the dehydrofluorination of the polymer backbone. Further, mono tertiary amines are potential cocuring agents for all diamines. Tertiary amines show a good efficient as cocuring agent in combination with dithiols [111]. Indeed, dithiols do not crosslink Viton® when used alone, but in combination with tertiary amines, well-cured vulcanisates can be formulated by their use [19].
At higher temperature or time (12 days at 25°C with 72% of amine) a primary monoamine such as butylamine can crosslink a poly(VDF-co-HFP) copolymer or a poly(VDF-co-CTFE) copolymer [20]. The mechanism of crosslinking of the butylamine onto a poly(VDF-co-CTFE) copolymer [20] is given in *Scheme 4*. In a first step, the amine dehydrochlorinates the VDF/CTFE diad. Then, according to a Michael addition, the amine adds onto the CF=CH double bond, creating a secondary amine. Finally, in the last step of the mechanism, the secondary grafted amine can add again onto an unsaturation creating a bridge between two polymeric chains.

Insert Scheme 4

The addition of the butylamine can occur either at the carbon atom bearing a hydrogen as postulated in sequence (b), or at the fluorine-bearing carbon atom as postulated in sequence (a), although controversial, it was also found in the literature [17,121].

3.1.2.2 Mechanism with diamines

The mechanism of crosslinking with diamine is slightly the same as that involving monoamines. The mechanism of crosslinking with hexamethylenediamine onto a poly (VDF-co-HFP) copolymer is given in *Scheme 5* with R=$(CH_2)_6$ [19,21]. This mechanism occurs in the course of the press cure treatment of the polymer (150-170°C, 30 min). As above, in a first step, the diamine dehydrofluorinates the VDF/HFP diad, creating a double bond. Then, by Michael addition the diamine adds onto two CF=CH unsaturated backbones, creating bridges between polymeric chains. The CF-NH bonds are sensitive to oxygen atmosphere and heating, so it can submit a further dehydrofluorination leading to –C=N- bond that can degrade into a C=O bond.

Insert Scheme 5

3.1.3 The different amines and diamines

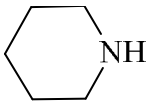
Although the crosslinking mechanism of amines and diamines onto VDF-based fluoropolymers proceed in three main steps and are slightly the same, the reaction conditions (temperature and time) and the physical properties obtained using aliphatic and aromatic mono or diamines are different.

3.1.3.1 Reaction with aliphatic and cycloaliphatic monoamines

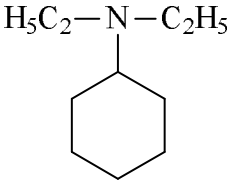
As mentionned above, Paciorek et al. [22] studied the addition of butylamine, dibutylamine and triethylamine on model fluoro-compounds. He also studied the reaction between a Viton-A® poly(VDF-co-HFP) copolymer and a Kel-F® poly(VDF-co-CTFE) copolymer with monoamines [20], in solution of diglyme, at different times and temperatures, and for different amounts of amines:

- butylamine $C_4H_9NH_2$

- dibutylamine $C_4H_9NHC_4H_9$
- piperidine



- triethylamine $(C_2H_5)_3N$
- diethylcyclohexylamine



Only one model of addition of amines on partially fluorinated molecules was studied. Indeed, the study of addition of equimolar quantities of monoamines (butylamine, dibutylamine and triethylamine) onto 4,4-dihydro-3-iodoperfluoroheptane as a model molecule, in diethylether at room temperature [22] afforded 80, 94 and 81% of the amine hydroiodides, respectively. But, by determining the time required for a given reaction mixture to reach a pH value of 6, it is concluded that the reaction with butylamine is faster than that using dibutylamine. This latter system is faster than that involving triethylamine.

The reaction between several monoamines and VDF-based fluoropolymers like Viton-A® and Kel-F® [20] evidences a crosslinking mechanism.
Tables 5 and 6 [20] exhibit the weight percentage of added amine, the temperature of reaction, the formation of a gel, the reaction time, the initial and final pH, and finally the color of the solution.
The presence of a gel from butylamine, dibutylamine, piperidine and diethylcyclohexylamine-cured Kel-F® polymer, and the piperidine-cured Viton-A® evidences a reaction of crosslinking between the polymer backbone and those monoamines [20].

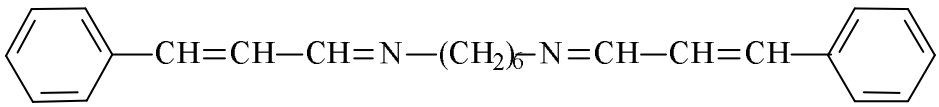
Insert Tables 5 and 6

Thus, the following mechanism can be postulated as a crosslinking from primary monoamines. This is explained in *Scheme 4*.
Poly(VDF-co-CTFE) copolymers are crosslinked more easily in the presence of monoamines than poly(VDF-co-HFP) copolymer are, because HF elimination should proceed more readily with tertiary fluorine than from difluoromethylene group [20]. Hence, dehydrofluorination proceeds at much lower rate with Viton-A® than with Kel-F® elastomer.

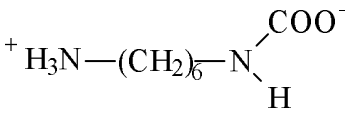
3.1.3.2 The aliphatic diamines and diimines

Several diamines are used as curing systems for fluorocarbon elastomers: acyclic diamines, cyclic diamines, and in some times aromatic diamines [28].
Diamines give effective vulcanisates, but those leading to the best properties are very scorchy [19,21]. Derivatives of diamines designed to stiff the amine function, so as to reduce the scorching tendency, are by far the most widely used curing agents [19,21]. The most common examples are the carbamate and bis-cinnamylidene derivatives of the hexamethylene diamine (HMDA):

- bis-cinnamylidene hexamethylene diamine [19,108]



- hexamethylene diamine carbamate (HMDA-C) [108]



- The bis-cinnamylidene hexamethylene diamine [19,108] :

A Viton-HV® poly(VDF-co-HFP) copolymer with a molar percentage of HFP of 28.5%, in the presence of 5 parts of MgO per hundred parts of rubber (phr), was vulcanised with different phr of Diak No3 (N,N'-dicinnamylidene-1,6-hexanediamine) [27].
Table 7 [27] gives the C_1 constant in the Mooney-Rivlin equation [122-124]:

$$2C_1/gRT = 6.1\times10^{-5}\ D$$

where g is the fraction of gel rubber, R is the gas constant, and D the amount of curing agent expressed in phr.
Table 7 also supplies the gel fraction (g), and crosslinking density of the different samples (A-1 to A-8) called ν_e and ν_e^*, where $\nu_e=\nu_e^*\times g$. The higher the amount of Diak No3, the greater the gel fraction, and the higher the crosslinking density. Indeed, for example in sample A-8 (8 phr of curing agent), all the polymer is in gel fraction (no soluble fraction), so it is completely crosslinked, and evidences the good effiency of Diak No3 as crosslinking agent for poly(VDF-co-HFP) copolymer.

Insert Table 7 and 8

Moreover, the study of crosslinking with Diak No3 shows an increase of the glass transition temperature (Tg) of the vulcanisate with the amount of crosslinking agent [27].
Table 8 [27] shows that the Tg increases from sample A-1 (0.2 phr of Diak No3, and Tg = -29°C) to sample A-7 (4.0 phr and Tg= -23.5°C). This increase of the glass transition temperature value is attributed to the increase of the crosslinking density.

Finally, crosslinking and decomposition temperatures of a Viton A-HV® cured by Diak No3 were studied by differential thermal analysis (DTA) [23].
Figure 7 [23] represents the variations of temperature *versus* temperature for four different samples. Curve (B) (Viton A-HV + MgO + Diak No3, mill-mixed) exhibits an exotherm

centered in 200°C, which is due to the crosslinking reaction occurring in the course of the press cure. Indeed, curves (C) and (D) that correspond to the same samples as curve (B), press cure and post cure, respectively, do not exhibit such an exotherm.

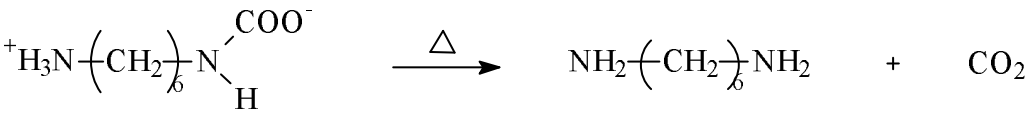
Insert Figure 7

Paciorek [23] also studied the evolution of decomposition temperature of different post cured systems by DTA. Thermograms of three Viton A-HV® vulcanisates crosslinked by press cure (30 min at 150°C) and post cured for 24h at 200°C are shown in *Figure 8* [23].
Both (A) and (C) curves indicate a final exothermic reaction initiated in the vicinity of 285°C, whereas elastomer cured by Diak No3 shows some reaction as low as 200°C. In contrast, the untreated Viton A-HV® starts to decompose from 430°C. Hence, vulcanisation results in decreasing the thermal stability of fluorinated elastomer.

Insert Figure 8

- <u>Reaction with HMDA and ethylenediamine:</u>

HMDA-C is the ionic form of HMDA, which is unreactive at room temperature, but decomposes rapidly in the range of 130 to 170°C, to produce the free reactive diamine [18,35], as shown in the following Scheme:



A solution of Viton® poly(VDF-co-HFP) copolymer in tetrahydrofurane, mixed with HMDA, at room temperature for one day produces gel formation [20], proving that the HMDA adds onto unsaturations created by dehydrofluorination, and creating crosslinks [26,29,125].
Different amounts of HMDA-C are added to a poly(VDF-co-HFP) copolymer, and *Figure 9* [21,114] shows the amount of water evolved in a given time for different amount of curing agent. This water could have arisen from an HF elimination from the polymeric chain, that reacts with MgO (coagent), according to the following reaction:

$$MgO + 2HF \rightarrow MgF_2 + H_2O$$

Hence, the higher the amounts of HMDA-C, the higher the HF elimination, thus the higher the amount of addition [21,114].

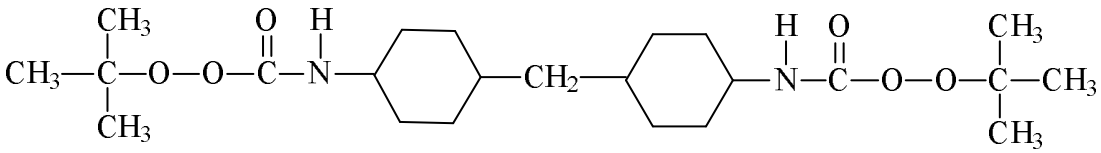
Insert Figure 9

Ethylenediamine carbamate of (EDA-C) is particularly advantageous. Results of stress-strain tests and compression set of a poly(VDF-co-HFP) copolymer cured by EDA-C show that 0.85 part of EDA-C produces a state of cure equal to that obtained with one part of HMDA-C (*Table* 9 [111]).

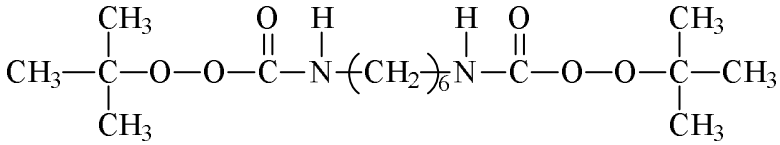
InsertTable 9

The crosslinking mechanism of the HMDA-C is the same than that with HMDA (S*cheme 5, with R=$(CH_2)_6$)* [21,114].

- Bis-peroxycarbamates (hexamethylene-N,N'bis(tert-butyl peroxycarbamate) or HBTBP, and methylene bis-4-cyclohexyl-N,N'(tert-butylperoxycarbamate), or (MBTBP) [30] have the following formula, respectively:



HBTBP



MBTBP

There are two possible crosslinking mechanisms which occur in the presence of those peroxycarbamates (*Schemes 6 and 7*) [30]. One is different from the usual mechanism of diamine crosslinking, while the second one is the classic one where the diamine adds onto the polymeric backbone by nucleophilic Michael addition. Indeed, those peroxycarbamates can undergo a thermal decomposition creating radicals (*Scheme 6*), and so the crosslinking mechanism can be a nucleophilic addition.

Insert Scheme 6 and 7

HBTBP and MBTBP were mixed with a poly(VDF-ter-HFP-ter-CF_2=CF-R-Br) terpolymer (Viton GF® or FKM-G®) -where R is a fluorinated methylene spacer- in the presence of MgO. The typical formulation is given in *Table 10* [30]. The samples were then press cured (15 min at 170°C) and post cured (24h at 250°C).

Insert Table10

Figure 10 [30] represents a comparison between the ODR cure traces of both samples. HBTBP (curve C) is noted to possess a higher state of cure than that of MBTBP (curve E). Although there is a significant structural similarity between both crosslinking agents, they have different cure responses with FKM-G copolymer.

Insert Figure 10

Figure 11 [30] exhibits the crosslinking density *versus* the amount of HBTBP (in phr), and the extrapolation of this plot shows that a minimum quantity of HBTBP is required before any formation of crosslinks can occur. In the crosslinking formation by HBTBP, there is a thermal

decomposition of the peroxycarbamates to give free radicals in a suitable medium. This thermal decomposition is represented in *Scheme 6* [30,126-129].

Insert Figure 11

Two possible routes of crosslink formation have also been proposed. *Scheme 7* [30] leads to the first one [30]. The hexamethylene diradical abstracts the hydrogen atoms of two polymeric chains creating two macroradicals, and regenerating the hexamethylene diamine. Both macroradicals form carbon-carbon crosslinks.

Hexamethylene diamine (intermediate products of the mechanism given in *Scheme 7)* can then form additionnal crosslinks. This mechanism is given in *Scheme 8*. It is the classical Michael addition of the HMDA onto the fluoropolymer.

Insert Scheme 8

From those crosslinking mechanisms, it can be understood that the radical of HBTBP is more reactive than that of MBTBP. That is why HBTBP-cured system possesses a higher state of cure.

- Piperazine, triethylene diamine, tetramethylethyldiamine, and diethylene triamine :

Different diamines (piperazine, triethylene diamine, and tetramethylethyldiamine), given in *Scheme 9* were also used as crosslinking agents for two copolymers: poly(VDF-co-HFP) copolymer (Viton A®) and poly(VDF-co-CTFE) copolymer (Kel-F®) [19,20,111,130]. Those curing agents were mixed with both copolymers in a solution of diglyme, at different temperatures and for different reaction times. Results are summarised in *Tables 11 and 12* [20]. Kel-F® exhibits a gel formation when vulcanised with piperazine at 57°C for one day, while the same behaviour occured when it was crosslinked with triethylene diamine and tetramethylethyldiamine at 97°C for one day. Poly(VDF-co-HFP) copolymer exhibits gel formation only with piperazine at 55°C for 1 day, or at 25°C for 20 days.

Insert Scheme 9, Tables 11 and 12

So, piperazine is less efficient as curing agent for poly(VDF-co-HFP) copolymer, whereas 2,5-dimethyl piperazine [18] produces well-cured vulcanisates from stocks which are less toxic than those containing HMDA-C.

Insert Figure 12

Compression set resistance at 200°C was compared between a TecnoflonT® (poly(VDF-ter-HFP-ter-1-hydropentafluoropropene) terpolymer) vulcanised with HMDA-C, and TecnoflonT® vulcanised with piperazine carbamate [131]. The results are included in *Figure 12* [131]. Curves 3 and 4 are both poly(VDF-co-HFP) copolymer vulcanisates with piperazine carbamate in the presence of trimethylenediamine carbamate and MgO for curve 3, and bisphenol in the presence of MgO for curve 4. The compression set resistance is better for curve 4, than curve 2, which is better than curve 3, and finally the worst compression set resistance is obtained for Tecnoflon T® vulcanised with HMDA-C.

The reaction between PVDF and diethylene triamine (DETA $H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$) at various temperature (25-80°C) was monitored by infrared spectroscopy [25,31].

Figure 13 (a and b) [31] represents two infrared spectra. The first one (a) illustrates the spectrum of PVDF and DETA when no reaction occured, whereas spectrum (b) represents PVDF film after heating in DETA for 16h at 70°C. For spectrum (a), the absorption bands at 3350 cm^{-1} and 1590 cm^{-1} are assigned to the NH stretching and to NH_2 deformation in the primary amine DETA, and the additional absorptions are from PVDF. In spectrum (b), the bands of primary amine at 3350 and 3270 cm^{-1} are replaced by that of a secondary one at 3240 cm^{-1}. Two strong bands also appear at 1630 and 1560 cm^{-1} which are also attributed to secondary amide. A shoulder at 1738 cm^{-1} is characteristic of C=N streching. Thanks to infrared spectroscopy, a crosslinking mechanism was proposed [31] and is likely the same as that of *Scheme 5.*

Insert Figures 13

Reaction between PVDF and diamine curing agent produces alterations in the polymer's surface, which enables the formation of strong adhesive joints without prior surface modification [31].

3.1.3.3 Aromatic and aromatic containing amines and diamines

Aromatic containing diamines have been explored at various times, because it was assumed that the aromatic ring structure built into the polymeric network, during the curing process, would be more stable to high temperature oxidation than the aliphatic hydrocarbon crosslinks derived from aliphatic diamines. However, little success has been achieved [17,28,132].

Recently, the grafting of aromatic containing amines (benzylamine and phenylpropylamine) onto poly(VDF-co-HFP) copolymers was investigated [133]. First, the ^{19}F NMR spectrum of a benzylamine grafted onto poly(VDF-co-HFP) copolymer was studied, and is represented in *Figure 14*. *Figure 14* shows the evolution of the peaks centered at –108.5, -110.4, -112.3, -113.6, -115.2, -115.9, and –117.9 to –118.5 ppm, assigned to fluoride groups (given in *Table 13*) of a benzylamine grafted copolymer (containing 20% in mol of HFP). This spectrum shows the disappearance of the peaks at –108, -115.2 and –117.9 ppm of the copolymer. This result confirms Schmiegel's conclusions [33] that stated that the addition of the crosslinking agent first occurs onto VDF between two HFP units.

Insert Figure 14
Insert Table 13

Then, the evolution of the molar percentage of grafted benzylamine as a function of time was studied at different temperature, with different molar percentages of HFP (ranging from 10 to 20 % in mol) in the copolymer. *Figure 15* plots the molar percentages of grafted benzylamine at 80°C for a 10% in mol of HFP containing copolymer. It proves that in the first 300 minutes, all the HFP/VDF/HFP sites were crosslinked. Finally, phenyl propylamine seems to add faster onto copolymer than benzylamine does, that latter amine containing one spacer only.

Insert Figure 15

So, aromatic containing amine can graft onto poly(VDF-co-HFP) copolymer if it exhibits a spacer between the amino group and the aromatic ring. As expected, the higher the number of

methylene goups in the spacer, the faster the kinetics of grafting. As in the cases above, the grafting is carried out first onto VDF between two HFP units.

Finally, it was deduced that the crosslinking mechanism for aliphatic and aromatic containing amine and diamine was slightly the same and took place in three steps. Aliphatic diamines are more reactive than aliphatic amines; and the most used diamine is HMDA-C and its derivatives (N,N'-dicinnamylidene-1,6-hexanediamine and bis-peroxycarbamates). During the post cure treatment, two different mechanisms of bond making and bond breaking were evidenced, as explained in section III.1.4.

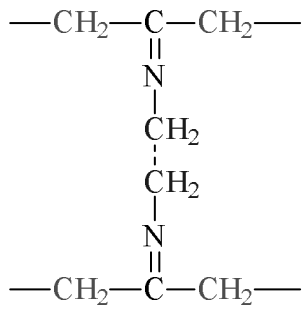
3.1.4 Formation of two networks during post cure

The study of the heat ageing of bisphenols- peroxides- and diamines- cured systems shows the formation of different networks more or less stable.
First, a Size Exclusion Chromatography (SEC) study of untreated and unheated FKM gum showed an average molecular weight of 250,000 g/mol. The gum heated at 325-375 °C for 3h gave a molecular weight of 96,000 g/mol, suggesting chain scissions. Seven to ten percent part of this sample could not be dissolved in tetrahydrofurane (THF), showing that crosslinking took place [118].
Second, the infrared spectrum of heated FKM-gum (§ III.1.1.2) shows the presence of HC=O groups at 1745 cm^{-1} [24]. Those aldehyde functions were identified in the last step of the crosslinking mechanism (*Scheme 5*), and result from the oxidative scissions of the bridges created by the diamine. These scissions induce the decrease in molecular weight.
The compression set percentage of a cured poly(VDF-ter-HFP-ter-TFE) terpolymer, press cured and post cured under nitrogen or air (*Table 3*) was studied [35]. The authors noted first that post cure drastically improves the compression set resistance of the press cure sample, and second a nitrogen atmosphere leads to better post cure results than air atmosphere. It can be concluded that post cure improves compression set resistance all the more it is carried out under nitrogen in order to avoid oxidative scissions. Consequently, the scissions in or at the crosslink are due to oxygen [35].

Kalfayan [118] and Thomas [24] studied the stress relaxation of poly(VDF-ter-HFP-ter-TFE) terpolymers crosslinked with N,N'-dicinnamylidene-1,6-hexanediamine, and of a poly(VDF-co-HFP) copolymer crosslinked with HMDA-C, respectively.
Figures 16 [118] and *17* [24] exhibit the evolution of f/fo *versus* time, where f and fo represent the tensile forces at t and to times, respectively.
In *Figure 16*, [118] stress relaxation is measured for three samples that contain different amounts of diamine at 200 and 250°C in air. In *Figure 17* [24], stress relaxation is measured at 250°C in air for different amounts of diamine. Those figures show that stress relaxation is independent of both the amount of diamine and of the crosslinking density.

Insert Figures 16 and 17

The most readily oxidizable groups in both structures are the methylene groups in α position to the C=N bond.



It suggests that scissions occur at the crosslinking group (i.e., the grafting group) rather than in the polymeric chain [24,118].

Hence, in order to avoid this oxidative chain scissions at the crosslink, the sample must be post cured under nitrogen [24].
Post cure contributes to a thermally induced bond-breaking and bond-making process that results in a thermally and mechanically more stable network [35,58,134].

3.2 CROSSLINKING WITH BISPHENOLS

Bisphenols are presently the predominant crosslinking agents for curing fluorocarbon-based elastomers. Bisphenols curing was developed in the late 1960ies and started replacing the diamine cure in the early 1970ies [109,135-138]. Because of processing and property advantages, the most commonly used compound is bisphenol AF (2,2-bis(4-hydroxyphenyl) hexafluoropropane). Others, like substituted hydroquinone, and 4,4'-disubstituted bisphenols also work well and are used commercially to a lesser degree [35,36,38,58]. As in cases above, crosslinking reaction was evidenced by ^{19}F NMR.

3.2.1 Crosslinking mechanism

The crosslinking mechanism takes place in three steps: elimination of HF creating double bonds, then reorganisation of the double bonds, such as in *Scheme 2*, and finally substitution of the bisphenol onto the double bond.
Crosslinking agent require accelerators to make that reaction more efficient. For example, to enable the dehydrofluorination of a VDF/HFP diad, bisphenols need to react with a metal oxide to give the phenolate ion, which in turn reacts with the phosphonium or tetraalkylammonium ion to give intermediates I and II.

$R_4P^+\ ^-OArOH$ *I* $\qquad$ $R_4N^+\ ^-OArOH$ *II*

These intermediates are strong bases [35]. The crosslinking mechanism proposed by Schmiegel is shown in *Scheme 10* [33,35,64,139].

Insert Scheme 10

In the first step (the dehydrofluorination) Viton® copolymer is attacked by the intermediate described below, creating diene. Then, the bisphenol-derived phenolate (^-OArOH) attacks the intermediate diene and finally leads to the dienic phenyl ether crosslinks [32,33]. This

reaction is a substitution. The resulting product surprisingly shows good properties, particularly with regard to oxidative and hydrophilic stability.

3.2.2 ^{19}F NMR study

The mechanism of crosslinking was evidenced by ^{19}F NMR, and Schmiegel et al. [3,32,33] studied the ^{19}F NMR spectra of poly(VDF-co-HFP) copolymer treated in dimethylacetamide (DMAC), with DBU (1,8-diazabicyclo[5-4-0]-undec-7-ene) and bisphenol AF. DBU is strong enough to enable a dehydrofluorination of the polymer and to ionise the phenol, but is sterically hindered for being an efficient competitor of phenoxide for the fluoroolefin [33].
Figure 18 [33,34] represents the ^{19}F NMR spectra of a base (DBU)-treated soluble polymer (upper spectrum), and the gel produced by base in the presence of bisphenol-treated polymer (lower spectrum). Both spectra exhibit two new peaks at –55 and –62 ppm, assigned to –C=C(CF3)-C- isomeric structure of the CF_3. So, poly(VDF-co-HFP) copolymers treated with DBU and with DBU/bisphenol system undergo at least dehydrofluorination and rearrangment, such as in *Scheme 2*. However, to prove the crosslinking of bisphenol-AF onto the copolymer, a ^{19}F NMR spectrum of the same sample after precipitation must be recorded.

Insert Figure 18

Figure 19 [33,34] shows two ^{19}F NMR spectra of poly(VDF-co-HFP) copolymers. The first one (top) deals with the spectrum of poly(VDF-co-HFP) copolymer treated with DBU and the bisphenol AF in DMAC, while the other one (bottom) represents the same sample but precipitated twice from an appropriate solvent for free phenol or any unreacted phenolate (acetonitrile). The ^{19}F NMR spectra of the washed polymer (bottom) clearly shows the presence of the geminal trifluoromethyl groups. So, after precipitation in acetonitrile of all the phenol and phenolate that did not react with the copolymer, the peak at –55 ppm was still noted. It proves that a part of the bisphenol-AF enabled the crosslinking of the copolymer. Under those conditions, about 40% of the phenolate were incorporated based on the internal p-fluoroanisole standard.

Insert Figure 19

Hence, ^{19}F NMR results allowed us to evidence that crosslinking was achieved.

3.2.3 Oscillating Disc Rheometer (ODR) response

Bisphenol-cured fluoropolymers are usually analysed by ODR. Reaction time and crosslinking density can be deduced from ODR curve .
This equipment can plot the evolution of the torque (in N.m) as function of time (in min), at a given temperature, for a crosslinkable mixing (copolymer, crosslinking agent, accelerators, coagent...). Usually, the torque starts to decrease (during an induction period), and when the crosslinking reaction occurs it increases rapidly, reaching a maximum when the reaction is finished.
Bisphenols curing systems are usually used for O-ring applications [26]. Indeed, they exhibit a high resistance to high temperature compression set. *Figure 20* [3,33,35] depicts the

evolution of a 177°C cure response by ODR, of a bisphenol AF (Bp-AF) curing poly(VDF-co-HFP) copolymer.

Insert Figure 20

The ODR response is characterised by an induction period, which depends on the amount of the accelerator (benzyltriphenylphosphonium chloride or BTPPC), or amount of bisphenol. High Bp-AF amounts increase the length of the induction period and lead to high cure states. The maximum cure state is the initial slope of the curve; t_{s2}, the time to initiation; t_{c90}, the time to 90% completion of cure; M_L, the minimum torque; M_H, the maximum torque; and M_H-M_L, the degree of state of cure [3,33,35]. In *Figure 20*, at 177°C, and after a 2.5 minutes induction period, the reaction of crosslinking is practically complete after 5 min. Only a 2% increase in cure state occurs between 13 and 60 min. The final state of cure does not change with increasing temperature [3,33,35]. When BTPPC is omitted from the standard recipe, no cure occurs within one hour at 177°C.
Figure 21 [3,33] shows the dependence of the ODR cure state versus Bp-AF concentration, in the presence of standard concentration of $Ca(OH)_2$, MgO, BTPPC and carbon black. It is noted that the greater the concentration in bisphenols, the higher the ODR cure state, so the higher the crosslinking density. The lower line shows that the accelerator BTPPC in the absence of the bisphenol can also lead to a substantial cure state, although only at very high concentrations [3,33].

Insert Figure 21

3.2.4 Limitations of the bisphenol-cured fluoroelastomers

Bisphenol-cure is a very rapid crosslinking system, as shown by ODR, but this system presents also some limitations.
The crosslinking mechanism between poly(VDF-ter-PMVE-ter-TFE) terpolymer and bisphenols generates elimination of a trifluoromethoxide and a fluoride ion, giving a CF=CF double bonds. The trifluoromethoxide reacts with hydrogen, giving trifluoromethanol that is further degraded in air to hydrogen fluoride and carbon dioxide, which results in the formation of a large amount of volatiles [3,33,35]. The cured system, therefore, shows excessive porosity and poor vulcanisate properties due to volatiles produced during the curing process. For this reason, it is advisable that VDF-based polymers containing perfluoroalkyl vinyl ethers have a special cure site with curing chemistry different from nucleophilic attack on the backbone. Such a chemistry is the peroxide induced crosslinking which was specially developed to bypass these kinds of problems.

3.3 CROSSLINKING WITH PEROXIDES

Another technique to crosslink VDF containing fluoropolymers requires peroxides.
The first peroxide cure agents were used in 1929. But the vulcanisates obtained had poor physical properties, and poor resistance to heat ageing when compared to sulphur-cured vulcanisates.
Braden and Fletcher [140] described the vulcanisation of natural rubber with dicumyl peroxide using different compounding ingredients and comparing it with sulphur-cured compounds.
Since 1950s, peroxides/triallylisocyanurate systems, which enable crosslinking of fluoropolymers through a free radical mechanism, have been established as the best-known non sulfurated crosslinking agent.

3.3.1 Reaction conditions

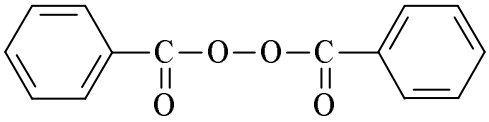
That kind of crosslinking is more easily achieved when the polymer bears specific group. This group or atom can be introduced into the polymer from the direct terpolymerisation of VDF and fluoroalkene.
A fluorinated monomer susceptible to copolymerise or terpolymerise vinylidene fluoride is needed to undergo free-radical attack to render peroxide curable the elastomeric co- or terpolymers of VDF [35]. So, this monomer must be functionalised or halogenated to ensure a free-radical crosslinking. The main used monomers are bromine-containing fluoroolefins such as [42,43]:

- Bromotrifluoroethylene, $BrCF{=}CF_2$ [42,141,142]
- 1-bromo-2,2-difluoroethylene, $BrCH{=}CF_2$ [143-145]
- 4-bromo-3,3,4,4-tetrafluorobutene-1, $CH_2{=}CHCF_2CF_2Br$ [146-148]
- 3-bromoperfluoropropylene, $BrCF_2CF{=}CF_2$ [149]
- Fluorobutylene $BrCF_2CF_2CF{=}CF_2$, $BrCF_2CF_2CH{=}CF_2$, $F_2C{=}CFOC_2F_4Br$ [150-152] or 1,1,2-trifluoro-4-bromobutene, $F_2C{=}CFC_2H_4Br$ [87]

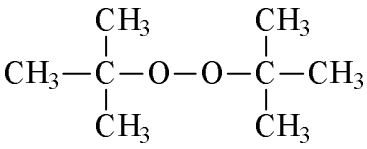
The VDF-based polymer containing the brominated monomer gives free radical intermediates on its polymeric backbone upon attack by peroxides [3,35,40,41,134].
Fluoroelastomers containing iodine or bromine atoms can be cured with peroxides. Indeed, modifications of fluorocarbon elastomers with perfluoroalkyl iodides allow to introduce iodine end groups on the polymeric chain [35,153-158]. These polymers also lead to free radical intermediates upon attack by peroxides, which in turn crosslink into a network in the presence of a radical trap. Thus, the peroxide needs a coagent to trap the polymeric radicals.

Aromatic as well as aliphatic peroxides can be used. Diacyl peroxides give low crosslinking efficiency and usually require 10 phr for adequate curing. Some dialkyl peroxides and peresters give high crosslinking efficiencies. However, mainly di-tertiary butyl peroxide and dicumyl peroxide are able to cure compounds containing reinforcing carbon black fillers [16].
The main used peroxides are:

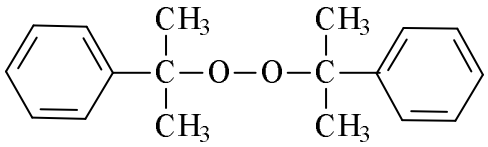
- dibenzoyl peroxide, $t_{1/2}$ = 1h at 92°C [16]:



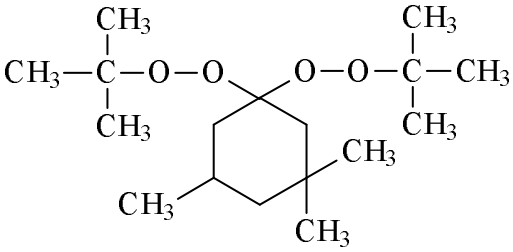
- di-t-butyl peroxide, $t_{1/2}$ = 1h at 141°C [16]:



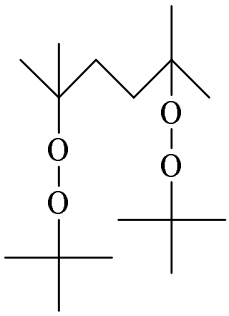
- dicumyl peroxide, $t_{1/2}$ = 1h at 132°C [16,159]:



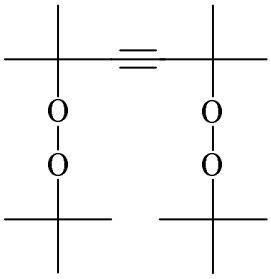
- 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, $t_{1/2}$ = 1h at 105°C [159]:



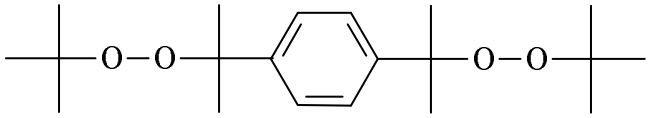
- 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane, $t_{1/2}$=1h at 134°C [40,159]:



- 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne, $t_{1/2}$ = 1h at 141°C [40,159]:

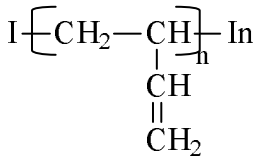


- α,α'-bis(t-butylperoxy)diisopropylbenzene, $t_{1/2}$ = 1h at 134°C [39,159]:

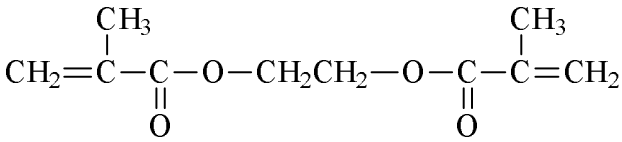


The coagents are used to enhance the crosslinking efficiency of peroxide cured compounds. They are generally di- and trifunctional vinyl compounds, such as:

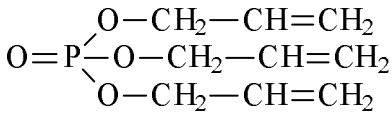
- 1,2-polybutadiene [16,159]:



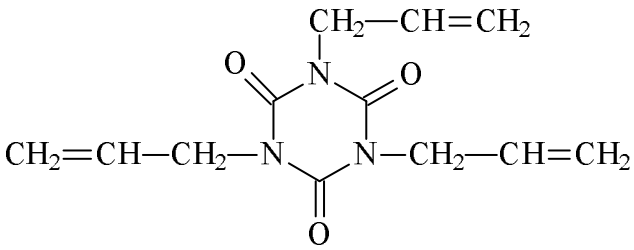
- ethylene glycol dimethacrylate [16,159]:



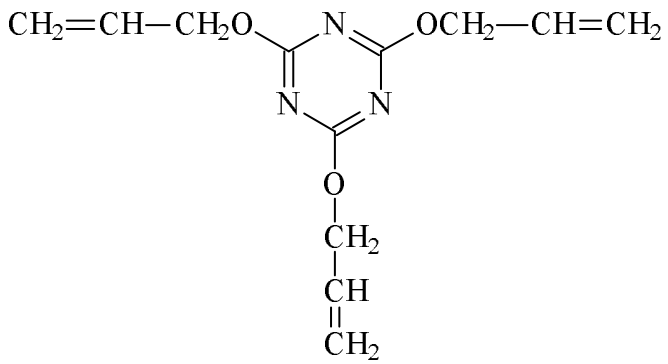
- triallyl phosphate [16]:



- the triallylisocyanurate (TAIC) or triallyl-1,2,5-triazine-2,4,6-(1H,3H,5H)-trione [35,40,95,97,160]:



- the triallylcyanurate (TAC), or 2,4,6-triallyloxy-1,2,5-triazine [16]:



The triazine ring is chemically and thermally stable. So, it reinforces the crosslinking network. But the best coagent is TAIC.
The crosslinking reaction also needs metal oxides such as $Ca(OH)_2$, CaO, MgO, ZnO, and PbO to absorb traces of HF generated during the curing process [35], MgO, being the most efficient one, as shown in a case above (see section 3.1.1.4).

3.3.2 Importance of the coagent

The coagent, whose most efficient one is TAIC, is essential in the peroxide-cure mechanism. Indeed, it permits the reaction of crosslinking and improves the compression set resistance.
A poly(TFE-alt-P) copolymer is mixed with the α,α'-bis(t-butylperoxy)diisopropylbenzene (5 phr), different coagents, such as divinylbenzene, N,N'-*m*-phenylenedimaleimide, 1,2-polybutadiene, trimethylolpropane trimethythacrylate, diallylmelamine, TAC, TAIC (3 phr), MgO as acid acceptor (10 phr), and carbon black (35 phr), to investigate the influence of the different coagents on the gel fraction and the compression set resistance [39]. Each sample is press cured at 160°C for 30 min, and oven cured at 200°C for 2h.
Table 14 [39] exhibits the effects of the coagent on peroxide vulcanisation. By considering the compression set percentage, TAIC is found to exhibit the lowest compression set, so it is the most efficient coagent. Basic metal also contributes to improve the compression set resistance. Indeed, the percentage of compression decreases from 75 to 62% thanks to calcium carbonate in the presence of TAIC.

Insert Table 14

Figure 22 [39,40] shows the gel formation as a function of the peroxide level. The gel fraction gradually increases with the peroxide level, when coagent is not present. The cure-promoting effect of the TAIC is remarkable, yielding a gel fraction of nearly 90% at low peroxide dose. So, the crosslinking density is not really influenced by the level of peroxide when coagent (TAIC) is introduced.

Insert Figure 22

The same result is obtained in the presence of the 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane [40]. A poly(VDF-co-HFP) copolymer was crosslinked by this peroxide in the presence of TAIC, by oscillating disk rheometer (ODR) at 177°C for 30 min. M_H-M_L represents the measured cure state (or crosslinking density in N.m).
Figure 23 [40] shows that cure state tends to be more drastically influenced by coagent concentration than peroxide concentration. Indeed, *Figure 23* shows that with an unchanged

amount of 3 phr for the coagent, and by increasing the quantity of peroxide, the cure state remains constant, whereas with a constant amount of 3 phr of the peroxide, and by increasing the amount of the coagent, the cure state increases. However, cure rate is influenced by both TAIC concentration and peroxide concentration.

Insert Figure 23

3.3.3 Influence of the nature and the amount of the peroxide

Lots of peroxides enable the curing of VDF-based fluoropolymers, but the nature of the peroxides, and the molar amount can influence many different factors such as the curing temperature and the gel fraction.
Identical cure systems are crosslinked, with either 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane, or 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne [35,40] . *Table 15* [35] shows the different cure state obtained when changing the peroxide and the temperature. For both peroxides, the cure state exhibits a maximum at a fixed temperature. For 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane, the cure state is maximum at 177°C, whereas with 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne, it is maximum at 182°C. Moreover, 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane is also more efficient than 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne. Indeed, the first peroxide reaches a cure state of 8.6 N.m, whereas it is 7.7 N.m for the second one.

Table 15

Gel fractions were measured from different poly(TFE-alt-P) copolymers cured by peroxide. In *Table 16* [39], 30 eq.mol^{-1} polymer of peroxide (acyl-, alkyl- or hydro-) are added to a poly(TFE-alt-P) copolymer and vulcanised in mold at 160°C for 30 min, and post cure at 200°C for 2h. Gel fraction results indicate that these peroxides achieve vulcanisation, except for the hydroperoxide which tends to decompose ionically. The best result was obtained with α,α'-bis(t-butylperoxy)diisopropylbenzene, but even in this case, the gel fraction was only 44% because of the absence of a coagent.

Insert Table 16

A rheometric study [159] was carried out by different tested poly(VDF-ter-HFP-ter-TFE) terpolymers cured by peroxides (dicumyl peroxide (40%) for P-1; 1,3-bis(tert-butylperoxisopropyl)-benzene (40%) for P-2; 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (40%) for P-3; 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane (45%) for P-4; 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne (45%) for P-5) with the same coagent (TAIC). *Table 17* [159] gives the composition of the compounds used in the study. Compounds (FP-1 to FP-5) differ only from the type and the amount of the peroxide.

Insert Table 17

Figure 24 [159] is the cure response of an oscillating disc rheometer of the compounds mentioned in *Table 17*. *Figure 24* demonstrates that the rate of crosslinking varies drastically for the industrial peroxides. Efficiencies of P-4 and P-5 are outstanding as compared to the three other peroxides, but in the presence of P-3, no crosslinking could be detected by rheometric curve.

So, the following decreasing activity series of the peroxides can be suggested: P-5 ≈P-4 >> P-1≈P-2.

Insert Figure 24

3.3.4 Mechanism of crosslinking

The crosslinking mechanism with peroxide/ TAIC system is slightly different from these of diamine or bisphenol ones.
Scheme11 [3,16,35] shows the most probable reaction taking place in a fully compounded stock. An initial process is the thermally induced homolytic cleavage of a peroxide molecule to yield two oxy radicals. The primary decomposition of the 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane leads to the formation of a t-butoxy radical, which may, in a minor reaction, abstract a hydrogen atom to give a t-butanol, and in a major reaction (usually from 120°C), decomposes into acetone and methyl radical. The methyl radical, in turn, can abstract a bromine atom from the polymer, to give methyl bromine, or add to the triallyl(iso)cyanurate to give a more stable radical intermediate. These intermediate radicals abstract bromine from the polymer to generate polymeric radicals. The driving force for the chain reaction during propagation is the transfer of a bromine atom from the electron-poor fluoropolymer to an electron-rich hydrocarbon radical on the coagent. Crosslinking takes place when the polymeric radicals add to allylic bonds of the trifunctional coagent. The coagent, therefore becomes the crosslinker.

Insert Scheme 11

The cure temperature chosen in peroxide formulations depends on the stability, and the half life of the peroxide. Peroxides with acid groups decompose at lower temperatures than these involving dialkyl or diaryl peroxide. Thus, dicumyl peroxide offers better processing safety than dibenzoyl peroxide does. According to Bristow [161], to obtain peroxide cured natural vulcanisates endowed with the best properties, cure times should not be less than one hour at 160°C, 3h at 150°C, and 8h at 140°C.

Peroxide and bisphenol or diamine- cured systems are differentiate by the type of reaction of crosslinking. Bisphenols or diamines exhibit a dehydrofluorination of the fluoropolymer backbone, followed by a Michael addition for the diamine, and a substitution of the fluorine atom for the bisphenols. Peroxide-cure reaction is a free radical attack, and so this system needs special cure site monomers. Another important crosslinking system that implies radical is the radiation crosslinking.

3.4 RADIATION CROSSLINKING

The last important way to crosslink VDF-based fluoroelastomers occurs by high energy radiation. This method only needs the use of specific radiation (without any agent or coagent), but can lead to the formation of others undesirable reactions.
VDF-based copolymers containing hydrogen can be crosslinked with different degrees of efficiency by high-energy radiation [50]. In 1957, Dixion et al. [96] were the first to disclose that poly(VDF-co-HFP) copolymers could be cured successfully with high-energy radiation. Then, Florin and Wall [162] performed further studies of VDF-based copolymers, and

Yoshida et al. [163] studied the stress relaxation of irradiated fluorocarbon elastomers. Moreover, many reviews and articles reported the radiation crosslinking of fluoroelastomers, published by Lyons [164-166], Logothetis [167], and Forsythe [168,169], respectively.
The mechanism of crosslinking by irradiation is the same as that of grafting. That is why grafting process is briefly explained.
Different types of high-energy radiation are available to be used for the grafting process [170-176]. This radiation may be either electromagnetic radiation such as X-rays and γ-rays (^{60}Co, ^{137}Cs) or charged particles, such as β particles and electrons.
The purpose of the use of γ-rays or electron beam is to generate radicals in the grafting system. Three different methods may be used to generate radiations [164,166,170-178]:

(a) simultaneous radiation grafting;
(b) pre-irradiation in air (hydroperoxide method);
(c) pre-irradiation in vacuum (trapped-radicals method);

In simultaneous radiation grafting, the polymer and the monomer are exposed to radiation at the same time. A chemical reaction of the monomer with the polymer backbone radical initiates the grafting reaction [177]. Alternatively, a two-step grafting procedure may be adapted. In the first step, the polymer is exposed to radiation which leads to the formation of radicals on the macromolecular chain. If the irradiation is carried out in air, radicals react with oxygen, leading to the formation of peroxides and hydroperoxides (hydroperoxide method). When in contact with a monomer, the irradiated polymer initiates grafting by thermal decomposition of the hydroperoxides.
In the absence of air, these macromolecular radicals remain trapped in the polymer matrix and initiate the grafting in the presence of a monomer (trapped radical method).
Simultaneous radiation grafting is, therefore, a single step process while the pre-irradiation method involves two steps [170,177]. The lifetime of irradiated PVDF at room temperature is about one year [179].
The free generated radicals can undergo several reactions, such as combination to form crosslinks [164,169], chain scission and recombination or disproportionation, and elimination with the formation of double bonds [170]. In the presence of vinyl monomers, the free radical centers can initiate graft copolymerisation [177].

3.4.1 Crosslinking mechanism by electron beam radiation

When irradiated by electron beam, a VDF-based fluoropolymer can undergo many radical reactions that are going to be detailed in this section. The crosslinking reaction is a particular one.
A PVDF polymer (0.08 mm of thickness, 1.76 mg/cm^3 of density) was electron beam irradiated at different doses (from 0 to 1200 kGy) [51]. *Scheme12* [45,51] proposes the radiation induced reaction in this PVDF.

Insert Scheme 12

It is shown that three different reactions are possible after irradiation. Both macroradicals can react together leading to a crosslinking structure as shown in reaction (2) [45,51,180]. The macroradicals can rearranged leading to a disproportionation end-mechanism, which is given in reaction (3) of Scheme 12. Finally, as shown in reaction (4), the macroradical can react with the oxygen atom leading to the formation of hydroperoxide. Those two last reactions (reactions (3) and (4)) do not lead to the formation of a crosslinked structure. These mechanisms are identified by FTIR.

Figure 25 [51] represents FTIR spectra of irradiated PVDF films with their corresponding unirradiated samples. The spectra of irradiated films do not show major changes in the main absorption band compared to the unirradiated film. However, two small adjacent bands, in the range of 1650-1750 cm^{-1} appear in the spectra of the irradiated films. The peak at 1654 cm^{-1} is assigned to the C=C bond resulting from the dehydrofluorination reaction in PVDF. Whereas the bands at 1739 and 3300 cm^{-1} represent the C=O group of hydroperoxide initiated by irradiation in air, and the OH group of hydroperoxides, respectively.

Insert Figure 25

Activated PVDF or poly(VDF-co-HFP) copolymer prepared by γ pre-irradiation (at 25 kGy/h with ^{60}Co source), underwent a grafting by styrene [52]. Indeed, styrene-grafted copolymers based on VDF find a wide range of applications. The degree of grafting (d.o.g.) is determined after assessing the weight of the membrane before irradiation (W_1) and after grafting (W_2):

$$d.o.g.(\%)=\frac{w_1-w_2}{w_2}*100$$

Table 18 [52] reports the d.o.g. (%) of different membranes under the same experimental conditions. The difference in d.o.g. between the homopolymer and the dense membrane copolymer is evident. A 100% grafting yield is detected in the case of the poly(VDF-co-HFP) copolymer, whereas 6% is the d.o.g. obtained in the case of the PVDF membrane. This difference can be due to the different compatibility of the two polymers with styrene, and the kinetics of grafting which is faster in the case of the copolymer. Hence, when irradiated VDF-based copolymers can give higher grafting densities than PVDF homopolymer can.

Insert Table 18

3.4.2 Influence of irradiation parameters on the properties of crosslinked fluoropolymers

The way of irradiation and the dose can influence several properties such as thermal properties (glass transition temperature T_g, decomposition temperature T_{dec}, crystallisation temperature T_c, and melting temperature T_m) and mechanical properties (tensile strength, modulus at 50% elongation, gel fraction...).

3.4.2.1 Thermal properties

A PVDF film was irradiated with doses of electron irradiation (ranging from 0 to 1200kGy). *Figures 26 and 27* [51] represent the evolution of the DSC melting thermograms, and cooling thermograms, respectively of irradiated PVDF films. The heat of melting which is obtained from the area under the peaks of curves noted in *Figure 26*, is found to increase for the lower melting peak, whereas that under the higher melting peak decreases with the increase in the irradiation dose up to 200kGy. *Table 19* shows that the heat of melting under both peaks together increases with the increase in irradiation dose. Moreover both melting temperature, T_m, (*Figure 26*) and the crystallisation temperature, T_c, (*Figure 27*) decrease with the increasing irradiation dose [180,181]. *Table 19* [51] summarises those results.

Inset Figures 26,
Insert Figure 27
and Insert Table 19

Those behaviours indicate that crosslinking and main chain scission reaction play an important role during irradiation of PVDF. Furthermore, the decreasing of T_c with the increasing irradiation dose indicates that crosslinking is the predominant reaction.
The evolution of the glass transition temperature (T_g) of a FKM [poly(VDF-ter-HFP-ter-TFE] terpolymer) crosslinked by electron beam irradiation in the presence of MgO, and HMDA-C is measured as a function of radiation dose. *Table 20* [48] represents the evolution of the T_g. The higher the radiation dose, the higher the T_g. Indeed, crosslinking hinders the macromolecular rotation, thus requiring a higher temperature for the inception of rotation. An increase in glass transition temperature at higher radiation doses are due to an increase in the extent of crosslinking.

Insert Table 20

3.4.2.2 Mechanical properties

The interaction of high energy radiation with partially fluorinated polymer causes various changes in its thermal properties, but also in its physical and mechanical properties, depending on the irradiation conditions.
Polyvinylidene fluoride and poly(VDF-ter-HFP-ter-TFE) terpolymer were irradiated in the presence or the absence of a crosslinking agent, and several mechanical properties were measured.
A PVDF film was exposed to high energy electron radiation in air with a 1Mev electron beam to different dose levels up to 10^6 Gy [46]. Gel fraction analysis was carried out on the virgin and irradiated films. The samples were extracted in dimethylacetamide (DMAC) at 75°C for 1h. The residue contents were then dried out in a vacuum oven at 80°C for 16h. According to Charlesby [182], the gel fraction analysis is a measurement of the degree of crosslinking, and is defined as the ratio of weight of the insoluble residue, to the weight of the original sample. The evolution of the gel fraction versus total absorbed dose is given in *Figure 28* [46]. The curve increases gradually of about 20% with an increase in total absorbed dose up to 10^4 Gy, and exhibits a larger increase to about 82% with a further increase in the radiation dose to 10^6 Gy. The presence of a gel is a clear evidence of extensive crosslinking.

Insert Figure 28

A PVDF and a poly(VDF-co-HFP) copolymer were irradiated by Kr ions at 6.2 Mev/amu energy [47]. The evolution of the insoluble F fraction versus the absorbed dose D, and the fluence is represented on *Figure 29* [47]. In both cases, an increase of the gel fraction F as the absorbed dose increases is observed.

Insert Figure 29

A poly(VDF-ter-HFP-ter-TFE) terpolymer was irradiated with an electron beam accelerator at different doses (0-200kGy) in air, and cured afterwards with 1 phr of HMDA-C. The gel fraction was carried out using the solvent methyl ethyl ketone at 25°C [48,49]. *Figure 30* [49] shows the gel fraction and the crosslinking density of the irradiated pure or vulcanised poly(VDF-ter-HFP-ter-TFE) terpolymer at different doses. It is observed an increase in

crosslinking density (- -) on irradiating rubber vulcanisates 50kGy dose and above. Both the control (pure rubber) and the rubber vulcanisate behave similarly. The increase in crosslink density is about 10-25 times, and the change in crosslink density is more important for the rubber vulcanisate.

Insert Figure 30

Nasef and Dahlan [51] investigated the irradiation of PVDF using an electron beam accelerator of 2.0 Mev. The effect of irradiation dose on the mechanical properties (tensile strength (a), elongation at break (b)) is given in *Figures 31 and 32* [51]. The tensile strength (*Figure 31*) of PVDF increases until a dose of 800kGy, then it slightly decreases as the irradiation dose goes higher.
The elongation at break (*Figure 32*) decreases gradually with the increase in the irradiation dose, due to crosslinking. This leads to an increase in molecular weight and to the formation of an insoluble three dimensional network [46,51]. The crosslinking progressively immobilises the insoluble oriented molecules and prevents them from moving laterally without breaking the bonds.

Insert Figure 31 and 32

These radiations inducing changes in the mechanical properties of a PVDF are permanent since crosslinking causes damage to the crystal structure which is unalterable [46]. A poly (VDF-ter-HFP-ter-TFE) terpolymer was irradiated by an electron accelerator (at energy of 2 Mev) in the presence of MgO (5 phr) and HMDA-C (1 phr). Mechanical properties (tensile strength, elongation at break and modulus at 50% elongation) were investigated and are presented in *Table 21* [48,49]. The modulus increases and the elongation at break decreases with an increase in irradiation dose. The tensile strength, however, stay slightly the same when increasing irradiation dose.
The radiation curing is the last main way of crosslinking for VDF-based fluoroelastomers. It is more efficient for copolymers and terpolymers than for PVDF.

Insert Table 21

3.5 CROSSLINKING WITH THIOL-ENE SYSTEM

There are few other methods to crosslink VDF-based fluoroelastomers, like the thiol-ene system, but those are very rare.
Although thiol-ene systems have easily led to vulcanise hydrogenated elastomers, this process has scarcely been used to cure fluoroelastomers because of the difficult availability of mercapto side groups. However, we have recently used an original trifluorovinyl ω-thioacetate monomer able to copolymerise with VDF [44,50] and the resulting copolymer was hydrolysed to generate elastomers bearing mercapto lateral groups. Curing was performed in the presence of nonconjugated dienes under radical conditions as in *Scheme 13* [44].

Insert Scheme 13

Other systems of crosslinking exist, but they are more adapted to TFE-containing elastomers. Although crosslinking in the presence of water from PVDF bearing trialkoxysilanes was efficient [94].A nitrile containing cure-site monomer with the same reactivity as perfluoromethylvinylether was copolymerised with TFE. Crosslinking was

brought about by the catalytic interaction of tetraphenyltin or silver oxide on the pendant nitrile groups. The structure of the crosslinks is assumed to be mainly triazine [35,183].

4 COMPARISON OF PHYSICAL AND MECHANICAL PROPERTIES

All the different cured systems mentionned previously differ from the crosslinking agents and mechanism, but also from the crosslinking density, and the mechanical properties, such as compression set resistance, elongation at break, modulus at 100 and 200%, tensile strength, hardness of the cured material, etc... The comparison of the crosslinking density and the different mechanical properties for the main cured systems (diamines, bisphenols and peroxides) is the subject of this part.
Regarding resistance to acids (H_2SO_4, HNO_3), to bases (NaOH, NaClO), and to water, by measuring the volume increase after immersion, it is clear that peroxide-cured elastomers are more resistant to acids, to bases and to water than those from diamine one. Indeed, this last system decomposes when immersed in a strong base or an acid solution.
Nevertheless, diamine-cured systems have a lower percentage of volume increase after immersion in oil and fuel oil than peroxide ones.

Figure 33 [3,35,134] compares the crosslinking density of post cure diamine, bisphenol or peroxide cured systems at 204°C under nitrogen. The vulcanisate crosslinking density of bisphenol and peroxide cured systems, before and after post curing remains the same, whereas that of the diamine vulcanisate increases substantially. This implies that diamine is a better crosslinking agent than bisphenol or peroxide regarding crosslinking densities.

Insert Figure 33

A Viton A-HV® (poly(VDF-co-HFP) copolymer) is crosslinked with a same amount of a diamine (biscinnamylidene hexamethylene diamine or LD-214) and a peroxide (benzoyl peroxide), in the presence of Maglite D (MgO) [23]. Different mechanical properties (tensile strength, elongation at break, and hardness) are evaluated for both press cure and post cure systems. *Tables 22 I and II* [23] shows that peroxide cure system leads to materials which exhibit higher tensile strengths, whereas diamine improves the elongation and hardness of the resulting crosslinked macromolecules. *Table 16 II* also shows that post cure step improves readily each mechanical property (tensile strength, elongation and hardness). So, this step is essential in the crosslinking mechanism.

Insert Tables 22 I and II

Other mechanical properties and resistance to bases and to acids are studied for a poly(TFE-alt-P) elastomer cured with a peroxide (α,α'-bis-(t-butylperoxy)-p-diisopropylbenzene), and a poly(VDF-ter-HFP-ter-TFE) terpolymer cured with a diamine (N,N' dicinnamylidene-1,6-hexanediamine) (*Table 23*) [39].
As in *Table 22 II*, peroxide-cured systems exhibit a better tensile strength, and a better compression set resistance, whereas diamines exhibit higher elongation at break and hardness.

Insert Table 23

Table 2 [35] displays different mechanical properties (modulus at 100%, tensile strength, elongation at break and compression set for O-rings and pellets) for bisphenol-cured and peroxide-cured poly(VDF-ter-HFP-ter-TFE)terpolymer, after press cure at 177°C for 10 min and after post cure at 232°C for 24h. As in *Table 22 II*, *Table 2* shows an improvement of the mechanical properties after post cure. Moreover, bisphenol-cured system has a better compression set resistance than peroxide-cured system, whereas peroxide-cured system has better modulus at 100%, better tensile strength, better elongation than those resulting from bisphenol crosslinking.

A study of several mechanical properties (100% Modulus, tensile strength, elongation at break, and compression set resistance) of bisphenol AF and peroxide (2,5-dimethyl-2,5-di-t-butyl-peroxyhexane)-cured poly(VDF-co-HFP) copolymers is supplied in *Table 24* [40]. First, the post cure step improves all mechanical properties. Then, bisphenol post cure systems exhibit a better compression set resistance than peroxide one, whereas peroxide-cured polymer exhibits better modulus at 100%, better tensile strength, and better elongation at break than bisphenol-cured polymer.

Insert Table 24

Flisi [131] studied the evolution of elongation at break and tensile strength for a poly(VDF-co-HFP) Tecnoflon N® copolymer cured with a bisphenol AF and diamines (melting of piperazine carbamate and trimethylene diamine carbamate). *Figures 34 and 35* [131] represent elongation at break and tensile strength versus time for those samples. This author showed that elongation at break (*Figure 34*) decreased continuously because the network chains became shorter. Moreover, crosslinking with bisphenol yielded materials with a higher elongation than those achieved from diamine. Tensile strength (*Figure 35*) decreased slowly in bisphenol vulcanisate during the whole period of 32 days, while the curve of the diamine vulcanisate presents an irregular trend. Indeed, the curve first decreased, then increased, and finally decreased again.

Insert figures 34 and 35

Flisi [131] also study the compression set resistance at 200°C versus ageing time for different diamine and bisphenol Tecnoflon T® (poly(VDF-ter-HFP-ter-TFE) terpolymer) vulcanisates (*Figure 12*).
First, the best compression set resistance was obtained for curve 4 (biphenol-AF cured poly(VDF-co-HFP) copolymer). Second, little improvement was obtained in Tecnoflon T® by changing the curing agent from HMDA-C (curve 1) to piperazine carbamate (curve 2). Finally, no practical difference was observed by changing the polymer with the same formulation, since curves 2 and 3 have the same behaviour.

Table 25 summarizes the efficiency of bisphenol, peroxide and diamine cure systems regarding each mechanical property. Bisphenols and peroxides-cured fluorinated polymer exhibit better tensile strength, and resistance to bases and acids than diamine-cured systems. However, diamine-cured VDF-based polymers show a higher hardness and resistance to oil than those of peroxide- and bisphenol-cured systems. Indeed bisphenol was shown to be the best crosslinking agent for a high compression set resistance. By regarding the thermostability of each cure system, the diamine (biscinnamylidene hexamethylene diamine) cure copolymer

decomposes at 457°C whereas the peroxide one decomposes at 472°C [23,184]. The diamine cure is thermally more stable than the hydroquinone one [29].

Insert Table 25

5 APPLICATIONS

The chemical, physical and mechanical properties mainly depend on the crosslinking agent. Those properties are crucial for the applications.
The thermal stability, sealing capability and chemical resistance of fluoroelastomers have lead to increase their use in a broad variety of industries. Applications for fluorocarbon elastomers in automotive, petroleum, and energy related industries illustrate the potential for those high-performance elastomer [115].
Fluoroelastomers are nowadays widely used in the industry as O-rings, V-rings, gaskets and other types of static and dynamic seals, as diaphragms, valve seals, hoses, coated clothes, shaft seals [185], expansion joints, etc [186]. They are also used in cars as O-rings for fuel, shaft seals and other components of fuel and transmission systems[35,58,63-66].
Moreover, some properties of fluoroelastomers, and especially those of VDF-based elastomers can be improved by crosslinking. Those better properties allow one to use cured fluoroelastomers in new applications as mentioned below.
The elastomeric poly(VDF-co-HFP) copolymers crosslinked with polyamine possess high temperature stability, good resistance to a wide variety of solvents, oils, and fuels [187]. So, these cured elastomers are particularly suitable for use in the manufacture of tubing employed as aircraft hoses, used to carry fuel lubricants, at high temperature and under high pressure [188]. Moreover, poly(VDF-co-HFP) copolymers crosslinked with aminosilane are used in the aircraft construction industry because they are also odorless [189].
Other applications of cured fluoroelastomers are sealings, O-rings [26] and oil seals [26,115,131,190]. It is mentioned above that a cured VDF-based copolymer has a better compression set resistance than a raw rubber. This property is essential for the sealing application.
Peroxide curable VDF-based copolymer and terpolymer offer improved extrusion characteristics. They can be vulcanised at atmospheric pressure and eliminates fissuring in thick sections. They have applications as cords, tubes or irregular-profile items of any dimension [40,191].
A poly(VDF-co-HFP) copolymer is applied to a metallic substrate, as coating composition and crosslinked with amine, diamine, or ethoxysilane [192]. This cured polymer used as thick or thin free standing films, or thick or thin films with good adhesion to metallic or other rigid surfaces [192]. Moreover, diamine-cured PVDF can be used as strong adhesive joints without prior surface modification [31].
Crosslinkable fluoropolymers based on TFE, TrFE, HFP, VDF, CTFE, and perfluoro(alkylvinylether) can form corrosion resistant structures [193].
Another application of cured fluoroelastomer is a multi layer insulator system for electrical conductors. This system possesses an extruded crosslinked fluoroelastomer outer layer with the fluoropolymer selected from copolymer or terpolymer of ethylene and TFE.
Irradiated PVDF and poly(VDF-co-TrFE) copolymer possess ferroelectric properties that allow the use of such fluorinated polymer in the domain of captors, sensors, and detectors [47,194]. Another interesting property of crosslinked poly(VDF-co-HFP) copolymer is their insolubility in oganic solvent [195]. Cured fluorinated polymers can be processed as

membranes for many electrochemical applications such as fuel cell and batteries [196]. For example, a poly(VDF-co-HFP) copolymer has been crosslinked with polyamines, polyols, by irradiation with electron beam or γ-rays in order to elaborate a solid polymer electrolyte for non aqueous lithium battery [197]. This electrolyte is particularly interesting for its ionic conductivity, its adhesion with an electroconductive substrate and also remarkably enhanced heat resistance.

6 CONCLUSION

A wide variety of copolymers containing VDF are either commercially available or prepared in laboratory scale.
VDF-based fluoropolymers are usually crosslinked by four main agents: diamines, bisphenols, peroxides/coagent systems and by radiation. Those ways of crosslinking differ from the polymer used, the mechanism, the conditions of reaction, the searched properties, and the desired applications.
First, it is observed that whatever the agent, the mechanism of crosslinking needs two steps, the press cure and the post cure, in order to activate the reaction, and to improve the physical, mechanical and thermal properties.
The oldest and the easiest processing system concerns the amine and diamine cure one, although the mechanical properties are the worst. The mechanism proceeds in three steps,: dehydrofluorination, then addition of the (di)amine onto a HFP/VDF/HFP triade, and finally elimination of HF from the polymer. Primary and secondary monoamines can crosslink poly(VDF-co-CTFE) copolymers. Primary amines are faster than secondary ones. They can be added at lower temperatures. The tertiary amines are potential cocuring agents for all diamines. Aliphatic diamines and diimines can crosslink VDF-based fluoropolymers, whereas diamines containing aromatic group must exhibit nucleophilicity and hence require always a spacer between the aromatic ring and the amino group to react with poly(VDF-co-HFP) copolymer, and they have lower reaction rate. The most common diamines are hexamethylene diamine carbamate that crosslinks poly(VDF-co-HFP) copolymer at 200°C, and bis-cinnamylidene hexamethylene diamine. Bis-peroxycarbamates, like hexamethylene-N,N'bis(tert-butyl peroxycarbamate), and methylene bis-4-cyclohexyl-N,N'(tert-butylperoxycarbamate, introduced in a minimum quantity, can add onto VDF-based fluoropolymers, thanks to a radical mechanism. HBTBP is more reactive than MBTBP.
Piperazine can crosslink poly(VDF-co-HFP) and poly(VDF-co-CTFE) copolymers at 57°C in one day, whereas triethylene diamine and tetramethylethyldiamine can crosslink poly(VDF-co-CTFE) copolymer at 97°C in one day. Finally, diethylene triamine crosslinks PVDF at 70°C for 16h.

Crosslinking with bisphenols in the presence of a metal oxide and phosphonium or tetraalkylammonium ions also proceeds in three main steps. A dehydrofluorination, then a double bond reorganisation, and finally the substitution by the bisphenol onto the double bond. This mechanism was identified by ^{19}F NMR. Interestingly, ODR measurements show that 98% of the bisphenol-AF –which is the most used bisphenol- is crosslinked in 5 minutes at 177°C. And, the crosslinking density, measured by ODR, can be improved by increasing the initial concentration in bisphenol-AF. But the bisphenol-cure of a perfluoroalkylvinyl ether exhibits limitations, like porosity or poor vulcanisate properties produced during the curing process. In that case, those VDF-based polymers must be crosslinked by peroxides/coagent systems.

However, peroxide/coagent systems need that the copolymer bears a bromine or iodine content to insure free-radical crosslinking. The monomer precursor must be co- or terpolymerised with VDF. Peroxide cure must be carried out in the presence of a coagent and a metal oxide with the most efficient ones are triallylisocyanurate, and MgO, respectively. 2,5-Bis-(t-butylperoxy)-2,5-dimethylhexane is more efficient than 2,5-bis-(t-butylperoxy)-2,5-dimethylhexyne because it reacts at a lower temperature and also leads to a better cure state. Both those peroxides have a higher rate of crosslinking (measured by ODR) than that of α,α'-bis(t-butylperoxy)diisopropylbenzene or dicumyl peroxide. The crosslinking mechanism is slightly different from the two previous ones. Indeed, the decomposition of the peroxide leads to a radical that adds onto the TAIC coagent. This intermediate radical, by abstracting a bromine from the polymer, becomes the crosslinker.

VDF-based fluoroelastomers can also be cured by different types of high energy radiation (X-rays, γ-rays, β-particles or electrons). However, the generated free radicals can undergo several reactions, different from the crosslinking reaction (e.g., they can cause chain-scission). This last one comes from the recombination between two macroradicals. Several properties vary with the radiation cure. For instance, the glass transition temperature, the gel fraction and the crosslinking density increase with the radiation dose.
Other systems, like thiol-ene systems are also efficient as crosslinking systems for VDF-based fluoroelastomers.

Finally, peroxide-cure fluoroelastomers are more resistant to acids, to bases and to solvents, than diamines-cure systems. But diamines exhibit a better crosslinking density. Regarding the mechanical properties, peroxide-cure leads to a high tensile strength, bisphenols to a high compression set resistance, and diamines are the best agents to exhibit a low elongation and a high hardness.

Fluoropolymers crosslinked with polyamines are particularly suitable for use in the manufacture of tubing employed as aircraft hoses, to carry fuel lubricants at high temperature and under high pressure, and in the aircraft construction industry. They can also be used as strong adhesive joints without prior surface modification.
Bisphenol-cure polymers are exploited for their compression set resistance.
Peroxide curable VDF-based polymers have found applications as cords, tubes or irregular-profile items of any dimension.
Irradiated VDF-based polymers are suitable in the domain of captors, sensors, and detectors.
Another application of cured fluoroelastomers is sealing, O-ring, oil seals, multi layer insulator systems for electrical conductors, and membranes for many electrochemical applications such as fuel cell and batteries.

However it can be assumed that other curing systems will be also found and should attrack the motivation of many academic and industrial researchers.

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SCHEMES CAPTIONS

Scheme 1 : Diels-Alder reaction during post-curing forms aromatic ring with loss of HF [19].

Scheme 2: Dehydrofluorination mechanism of poly(VDF-co-HFP) copolymer in the presence of base [32,33].

Scheme 3: Reaction between butylamine and a model compound [22].

Scheme 4: Reaction mechanism between butylamine and a poly(VDF-co-CTFE) copolymer [20].

Scheme 5 : Mechanism of crosslinking with diamine, in three main steps.

Scheme 6: The homolytic thermal decomposition of the hexamethylene-N,N'bis(tert-butyl) peroxycarbamate [30].

Scheme 7 : Crosslinking formation in terpolymer obtained through hydrogen abstraction [30].

Scheme 8 : Further interaction of the reactive intermediate (hexamethylene diamine) with a fluorinated polymer, bearing a bromine side atom[21,30,114].

Scheme 9: Piperazine, triethylene diamine, and tetramethylethyldiamine [20].

Scheme 10: Crosslinking mechanism with the bisphenol [33,35].

Scheme 11 : crosslinking mechanism with peroxide [3,35].

Scheme 12: schematic representation of the mechanism of electron radiation-induced reactions taking place in PVDF films [51].

Scheme 13: Crosslinking of VDF-containing copolymer by thiol ene systems [44].

FIGURES CAPTIONS

Figure 1 : Amount of elimination of HF from primary, secondary and tertiary amines cured-VitonA® (Reprinted with permission of Lippincott et Peto) [19].

Figure2: Infrared spectra of an uncured poly(VDF-co-HFP) copolymer before (A) and after (B) heating at 300°C for 20 min under air (Reprinted with permission of ACS) [118].

Figure 3: ^{19}F NMR spectra of a poly(VDF-co-HFP) copolymer before (top) and after (bottom) treatment with hydroxylic base (2,5-trifluorobenzotrifluoride internal standard). Changes in peak intensities are indicated (Reprinted with permission of Verlag Chemie) [33].

Figure 4: Effect of MgO on the mechanical properties of a formula comprising VitonA® cured with dithiol (Reprinted with permission of Lippincott and Peto) [111].

Figure 5: Evolution of the yield of fluoride atom of a VDF-based fluoropolymer heated at 200°C *versus* time and amount of MgO (acid acceptor) (Reprinted with permission of Wiley) [116].

Figure 6: Comparison of the efficiency of acid acceptors: metal oxide at 275°C (a), hydroxide acceptors at 275°C (b), and carbonate acceptors at 275°C (Reprinted with permission of Wiley) [116].

Figure 7: Differential Thermal Analysis of VitonAHV®cured with Diak No3 after various heat treatment: (A) Viton AHV®; (B) Viton AHV® + 15 phr Maglite + 4 phr Diak No3 (mill mixed); (C) Viton AHV® + 15 phr Maglite + 4phr Diak No3 (press cure); (D) Viton AHV® + 15 phr Maglite + 4 phr Diak No3 (oven cure) (Reprinted with permission of Wiley) [23].

Figure 8: Differential Thermal Analysis of VitonAHV®cured with Diak No3 after oven cure: (A) Viton AHV® + 15 phr Maglite; (B) Viton AHV® + 15 phr Maglite + 4phr Diak No3; (C) Viton AHV® + 15 phr Maglite + 4phr benzoyl peroxide; (D) Viton AHV® (Reprinted with permission of Wiley) [23].

Figure 9: Effect of the concentration (phr) of curing agent (HMDA-C) on the rate of elimination of H_2O from a VitonA® [21].

Figure 10: Comparison of ODR cure traces of a poly(VDF-ter-HFP-ter-CF_2=CF-RBr) terpolymer crosslinked with HBTBP (curve (c)), and MBTBP (curve (e)) at 170°C.
Formulation: terpolymer (100), MT Black (25), CaO (4), $Ca(OH)_2$ (6), and HBTBP (4) for curve (c); terpolymer (100), MT Black (25), CaO (4), $Ca(OH)_2$ (6), and MBTBP (4) for curve (e) (Reprinted with permission of ACS) [30].

Figure 11: Effect of HBTBP concentration (in phr) on the crosslinking density (Reprinted with permission of ACS) [30].

Figure 12: Compression set *versus* ageing time at 200°C for several vulcanisates: TecnoflonT®(poly(VDF-ter-HFP-ter-TFE) terpolymer) vulcanised with HMDA-C (curve1); TecnoflonT® vulcanised with piperazine carbamate (curve2); Technoflon® (poly(VDF-co-HFP) copolymer) vulcanised with piperazine carbamate and trimethyldiamine carbamate

(curve 3); Technoflon® cured with bisphenolAF (curve4) (Reprinted with permission of Hüthig Fach Verlag) [131].

Figures 13: Transmission infrared spectra of DETA on PVDF unreacted (a), and DETA – PVDF composite reacted for 16h at 70°C (b) (Reprinted with permission of VSP) [31].

Figure 14: ^{19}F NMR spectra (zone from –108 to –120 ppm of a poly (VDF-co-HFP) copolymer 20%$_{mol}$ HFP grafted with 200%$_{mol}$ of benzylamine at 80°C: the copolymer (curve a); after 115 minutes of reaction (curve b); after 475 min (curve c); after 2845 min (curve d); after 6835 min (curve e) [133].

Figure 15: Kinetics of grafting of the benzylamine (200%) onto a poly(VDF-co-HFP) copolymer Kynar® containing 10%$_{mol}$ of HFP. The grafting reaction is carried out in MEK at 80°C [133].

Figure 16: Stress relaxation of FKM (poly(VDF-co-HFP) copolymer) of various crosslink densities at 200 and 275°C in air.
• FKM + 1.5 phr of Diak No3
FKM + 3.0 phr of Diak No3
× FKM + 4.5 phr of Diak No3 (Reprinted with permission of ACS) [118].

Figure17: Continuous stress relaxation of poly(VDF-co-HFP) copolymer vulcanisates at 250°C in air, with :
• 2.0 % of HMDA-C
× 1.5 % of HMDA-C
o 1.0 % of HMDA-C (Reprinted with permission of Wiley) [24].

Figure 18: ^{19}F NMR spectra of a poly(VDF-co-HFP) copolymer treated with DBU in a solution of DMAC (top), and the gel which results from this reaction in the presence of Bp-AF (bottom) (Reprinted with permission of Verlag Chemie) [33].

Figure 19: ^{19}F NMR spectra of a poly(VDF-co-HFP) copolymer treated with DBU and Bp-AF in a solution of DMAC (top), and the same sample after several purification (bottom) (Reprinted with permission of Verlag Chemie) [33].

Figure 20: Cure response by Oscillating disc rheometer at 177°C of a VDF-based polymer cured with Bisphenol-AF (Reprinted with permission of Elsevier) [35].

Figure 21: Evolution of the ODR units (crosslink density) at 177°C :
(o) with variation of bisphenol-AF concentration (in phr), in the presence of BTPPC (benzyltriphenyl phosphonium chloride)
(Δ) with BTPPC concentration, in the presence of Bisphenol-AF (Reprinted with permission of Verlag Chemie) [33].

Figure 22: Evolution of the gel fraction as a function of peroxide dose (phr) for a peroxide-cured poly(TFE-alt-P) copolymer without any coagent (○); with 3 phr of TAIC (●); with 2.4 phr of divinylbenzene (◒); with 3 phr of TAC (◗) (Reprinted with permission of ACS) [39].

Figure 23: Interactions between peroxide and coagent, in the evolution of initial cure state (N.m) of a poly (VDF-co-HFP) copolymer, measured by ODR at 177°C for 30 min (Reprinted with permission of Sage) [40].

Figure 24: Rheometer curve of the compounds containing different peroxides (Reprinted with permission of Ferenc Wettl) [159].

Figure 25: FTIR spectra of irradiated PVDF films from 0 to 1200 kGy (Reprinted with permission of Elsevier) [51].

Figure 26: DSC melting thermograms of irradiated PVDF films from 0 to 1200 kGy (Reprinted with permission of Elsevier) [51].

Figure 27: DSC cooling thermograms of an irradiated PVDF film from 0 to 1200 kGy (Reprinted with permission of Elsevier) [51].

Figure 28: Gel fraction analysis in DMAC at 75°C of virgin and irradiated PVDF films (Reprinted with permission of Kluwer) [46].

Figure 29: Evolution of the insoluble fraction *versus* the absorbed dose and the fluence for a PVDF and a poly(VDF-co-TrFE) copolymer (Reprinted with permission of Elsevier) [47].

Figure 30: Variation of the gel fraction (full line ○) and the crosslink density ( ) of irradiated poly(VDF-ter-HFP-ter-TFE) terpolymer vulcanised with HMDA-C, and variation of the crosslink density of pure terpolymer rubber (broken – line) *versus* radiation dose (Reprinted with permission of Kluwer) [49].

Figure 31: Variation of the tensile strength of PVDF films *versus* irradiation dose (Reprinted with permission of Elsevier) [51].

Figure 32: Variation of the elongation percent of PVDF films *versus* the irradiation dose. (Reprinted with permission of Elsevier) [51] .

Figure 33 : Crosslinking density of cured gum stocks *versus* post cure time at 204°C, under nitrogen: (A) diamine cured system; (B) peroxide cured system; (C) bisphenol cured (Reprinted with permission of ACS) [134].

Figure 34: Dependence of elongation at break *versus* aging time of a TecnoflonN® (poly(VDF-co-HFP) copolymer) crosslinked with piperazine carbamate and trimethyl diamine carbamate (curve A), and a TecnoflonN® cured with a bisphenol AF (curve B) (Reprinted with permission of Hüthig Fach Verlag) [131].

Figure 35: Dependence of tensile strength *versus* ageing time of the same sample than Figure 24 (Reprinted with permission of Hüthig Fach Verlag) [131].

TABLES CAPTIONS

Table 1: Monomer reactivity ratios for the radical copolymerisation of VDF (A) with other fluoroalkenes (B) (and vinyl acetate and ethylene).

Table 2 : improvement of mechanical properties of bisphenol, and peroxide-cured poly(VDF-ter-HFP-ter-TFE)terpolymer with post cure step [35].

Table 3: Compression set resistance measured at 204°C for 70h, of a peroxide cured-poly(VDF-co-HFP-ter-TFE)terpolymer, after presscure in air at 177°C for 15min, and after postcure in air or under nitrogen at 232°C for 24h [35].

Table 4: Fraction soluble in acetone of a poly(VDF-co-HFP)copolymer heated in air at 250°C [24].

Table 5: Reaction of a Kel-F® poly(VDF-co-CTFE)copolymer with several amines [20].

Table 6: Reaction of a poly(VDF-co-HFP)copolymer Viton-A® with monoamines [20].

Table 7: Evolution of the gel fraction and crosslinking density (ν_e) of different cured poly(VDF-co-HFP) copolymers with increasing curing agent (N,N'-dicinnamylidene-1,6-hexanediamine) [27].

Table 8: Evolution of the glass transition temerature (T_g, °C) of samples A-1 to A-7 (indicated in Table 7) with the amounts of N,N'-dicinnamylidene-1,6-hexanediamine[27].

Table 9: Mechanical properties of HMDA-C, EDA-C or N,N'-biso-hydroxybenzylidene)-1,2-propylenediamine cured poly(VDF-co-HFP) copolymer of Viton A-HV® [18].

Table 10: Typical formulation of fluoroelastomers cured by bis-peroxycarbamate [30].

Table 11: Conditions of reaction of diamines with a Kel-F® poly(VDF-co-CTFE)copolymer [20].

Table 12: Conditions of reaction of diamine onto a Viton-A® poly(VDF-co-HFP)copolymer [20].

Table 13: Characteristic peaks in ^{19}F NMR between –108 and –120 ppm of fluorinated groups in VDF or HFP units of grafted poly(VDF-co-HFP) copolymer.

Table 14: Influence of the coagent onto the gel fraction and the compression set resistance of a peroxide-cured poly(VDF-co-HFP) copolymer (M_n = 100,000 g/mol) [39].

Table 15: Crosslinking of two peroxides (2,5-bis(t-butylperoxy)-2,5-dimethylhexane, and 2,5-bis(t-butylperoxy)-2,5-dimethylhexyne-3) onto poly (VDF-co-HFP) copolymer, and the influence of their cure temperature on ODR values (t_s2, t_s90, and M_H-M_L) [35].

Table 16: half life and gel fraction values of poly(TFE-co-P) copolymers (Mn = 100,000 g/mol) cured with acyl-, alkyl- or hydroperoxides [39].

Table17: Composition of different Viton GF compounds cured with peroxide [159].

Table 18: d.o.g. (degree of grafting) of starting membranes of PVDF and poly(VDF-co-HFP)copolymer [52].

Table 19: Variation of heat of melting , melting temperature and crystallisation temperature of PVDF films with the irradiation dose [51].

Table 20: Influence of electron beam irradiation on the glass transition temperature of a poly(VDF-ter-HFP-ter-TFE)terpolymer [48].

Table 21: Influence of electron beam irradiation on the mechanical properties of a terpolymer. [48].

Table 22 I: Composition of Vulcanisates I and II [20].

Table 22 II: Mechanical properties of vulcanisates I (diamine cure) and II (peroxide cure) after press cure at 150°C for 30min, and post cure from 120 to 200°C at a heating rate of 25°C/hr, then heat at 200°C for 24h [20].

Table 23: mechanical and chemical properties of a peroxide-cured poly(TFE-alt-P) elastomer, and a diamine-cured poly(VDF-ter-HFP-ter-TFE) elastomer [39].

Table 24: Mechanical properties for press cure and post cure poly(VDF-co-HFP)copolymer cured with bisphenol AF or peroxide (2,5-dimethyl-2,5-di-t-butyl-peroxyhexane) [40].

Table 25: Comparison of the three main cure systems regarding mechanical properties.