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# Understanding the crosslinking processes of a peroxide/TAIC cured FKM

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**ABSTRACT:** The network structure developed during the curing process will greatly define the mechanical response of a rubber. Nonetheless, crosslinking mechanisms commonly admitted for non-fluorinated rubbers may not be applicable for fluoroelastomers due to the steric hindrance of fluorine. The aim of this experimental study is to apprehend the crosslinking processes of a fluoroelastomer cured by peroxide in presence of triallyl isocyanurate (TAIC). TAIC is commonly used as coagent to increase the crosslinking efficiency of numerous rubbers by reducing undesirable reactions. Several formulations based on FKM/peroxide/TAIC were prepared, varying the amount of TAIC. The cure characteristics and physico-mechanical properties were determined using Moving Die Rheometer (MDR), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), swelling tests and tensile tests.

## 1 INTRODUCTION

Fluoroelastomers (FKM) are commonly used in various industries such as automotive, aeronautic and aerospace, requiring both high temperature properties and chemical resistance (Berthier 2018). Depending on the curing system, the final thermomechanical properties exhibited by a rubber can be different (Basfar 2002). Peroxide curing is recommended regarding the thermal resistance due to the high bonding energy of C-C crosslinks ( $\approx 350$  kJ/mol) compared to sulphidic bonds ( $\approx 275$  kJ/mol) (Kruželák 2016). Due to the steric hindrance of fluorine, conventionally crosslinking mechanisms established for non-fluorinated elastomers may not be applicable (Kruželák 2017). One option is to introduce a functional reactive monomer (CSM) during the polymerization which allows to create a crosslinking site (Améduri 2001). This CSM, most often containing iodine or bromine, brings a functional group sensitive to a radical attack.

Moreover, crosslinking of elastomers with peroxide can be enhanced by using multifunctional organic molecules, named coagents (Alvarez Grima 2007, Kruželák 2017). Nonetheless, crosslinking mechanisms taking place between FKM, peroxide and coagent are not yet clearly understood as well as the final structure developed by the elastomer

(Henning 2007). The specific role of the coagent in this reaction needs to be defined.

The aim of this work is to have a better understanding of the mechanisms occurring during a peroxide crosslinking of a FKM, in the presence of TAIC as a coagent. TAIC is a tri-functional molecule commonly used for thermoplastics and rubbers displaying high thermal stability (Liu 2020, Muroga 2021). Thus, several amount of TAIC have been introduced in a FKM matrix in presence of peroxide in order to characterize its influence on the curing mechanisms.

Then, the rubber structure was determined both before and after curing with the view to apprehend the arrangement of the polymer network using FTIR experiments. Furthermore, mechanical tests (uniaxial tensile tests and DMTA) were used as a probe of the crosslinking density by means of the theory of rubber elasticity and compared to swelling experiments.

## 2 EXPERIMENTAL SECTION

### 2.1 Material

This study was carried out on several rubber formulations containing different amount of coagent. The proportions of each constituent are listed in Table 1. Small amount of carbon black was added to the rubber compounding to ease the processibility during the mixing stage.

Table 1. Rubber compounds formulation (in phr)

	Gum	Peroxide	TAIC	CB*
F-T0	100	3	0	5
F-T1	100	3	1.4	5
F-T2	100	3	2.8	5
F-T3	100	3	4.3	5
F-T5	100	3	7.2	5
F-T10	100	3	14.3	5

\* CB = carbon black

The fluoroelastomer used is a FKM terpolymer (HFP–TFE–VDF) provided by DuPont© (Wilmington, DE, USA). A fourth and unknown monomer called Cure Site Monomer (CSM) is added to promote the crosslinking. The crosslinking system is composed of peroxide and triallylisocyanurate (TAIC). The free radicals initiator was 2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexane (DBPH), commercially named Luperox101XL45, provided by Arkema (Colombes, France). This commercial grade contains calcium carbonate and silica as phlegmatizer up to 65%. The TAIC used is Norlink TAIC70CS from Nordmann, Rassmann (Hamburg, Germany). This commercial reference includes 30% of silica. The chemical structures of these three components are summarized in Fig 1.

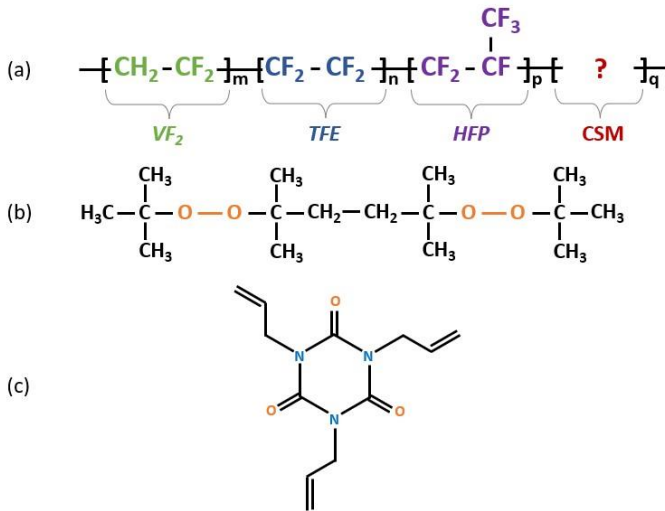


Figure 1. Chemical structures of: (a) FKM macromolecule, (b) DBPH peroxide and (c) triallyl isocyanurate (TAIC).

Rubber compounds were prepared using an external mixer (two roll rubber mill). Then, the masterbatches were cured at 150°C during 45 min in a compression mold using a heated press. Finally, a post-vulcanization of 6 h at 180°C is performed.

## 2.2 Curing processes

The curing characteristics were investigated at 150°C during 120 min using a moving die rheometer (MDR 2000E) at a frequency of 1.7 Hz and an oscillatory amplitude of  $\pm 0.5^\circ$ .

Curing processes were also characterized by DSC using a Netzsch instrument (DSC 200 F3) at 20°C/min under a flowing nitrogen atmosphere from room temperature to 300°C.

In order to have a better understanding of the different curing mechanisms, FTIR experiments were performed both before and after curing on a Perkin Elmer Spectrum One spectrometer in ATR mode using a diamond crystal. Spectrum were recorded between 600 and 4000  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ .

## 2.3 Mechanical properties

The tensile properties were determined on a Zwick/Roell Z010 tensile test machine at three different temperatures using an initial strain rate  $\dot{\epsilon}_0 = 10^{-2} \text{s}^{-1}$ . Elastic properties were calculated using the Mooney-Rivlin constitutive relation to fit the experimental data between  $\lambda = 1$  and 1.8:

$$\sigma_n = 2 \cdot \left( C_{10} + \frac{C_{01}}{\lambda} \right) \cdot \left( \lambda - \frac{1}{\lambda^2} \right) \quad (1)$$

where  $c_{10}$  and  $c_{01}$  = Mooney-Rivlin parameters. Then, assuming incompressibility, the Young modulus in the rubbery plateau was related to the crosslinks concentration by:

$$E = 3\nu RT \quad (2)$$

where  $\nu$  = number density of elastic chains;  $R$  = ideal gas constant;  $T$  = the absolute temperature.

The viscoelastic properties were measured in tensile mode by dynamic mechanical analyses between -60 and 250°C (Metravib 4400) for a frequency of 1 Hz and a heating rate of 1°C/min. The rubbery plateau and the principal relaxation provide information about the rubber network.

## 2.4 Equilibrium swelling experiment

The crosslinking density of the cured samples was also evaluated by equilibrium swelling experiments. Using the phantom model rather than the affine deformation one (Vieyres 2013), the classical Flory-Rehner equation is:

$$\ln(1 - V_{r0}) + V_{r0} + \chi \cdot V_{r0}^2 = -\nu \cdot V_S \cdot \left( 1 - \frac{2}{f} \right) V_{r0}^{1/3} \quad (3)$$

where  $V_{r0}$  = rubber volume fraction at swelling equilibrium or equivalently  $Q = 1/V_{r0}$  = degree of swelling;  $V_S$  = solvent molar volume;  $\chi$  = Flory-Huggins polymer-solvent interaction parameter; and  $f$  = crosslink functionality;  $\nu$  = number density of elastic chains.

Experiments were performed at room temperature using Methyl Ethyl Ketone (MEK) as a “good” sol-

vent for FKM. Samples were weighed initially ( $m_i$ ) and immersed during 24h in the solvent at constant room temperature ( $m_{sw}$ ) before being dried at 50°C during 24h ( $m_d$ ). From these masses, the swelling ratio was calculated, taking into account the weight of insoluble components like carbon black.

### 3 RESULTS AND DISCUSSION

#### 3.1 Curing mechanisms

MDR experiments (Fig 2) performed on all the samples indicate that whatever the TAIC amount between 1 and 10 phr, FKM is crosslinked.

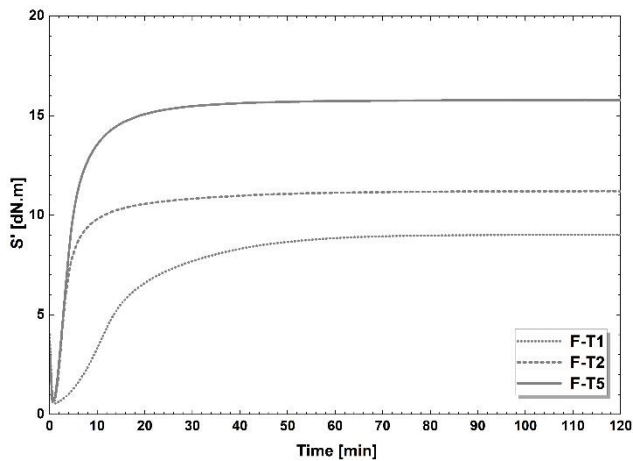


Figure 2. Rheological torque measured during curing of FKM rubbers containing different amount of TAIC.

The torque difference  $M_H - M_L$  is determined for each sample, where  $M_L$  is the torque measured prior to crosslinking and  $M_H$  the maximum torque when the curing is completed. It is commonly accepted that the torque difference is related to the shear modulus of the cured rubber which is proportional to the crosslinking density as suggested by Eq (2) (Sotata 2022).

DSC curves are shown in Fig 3.

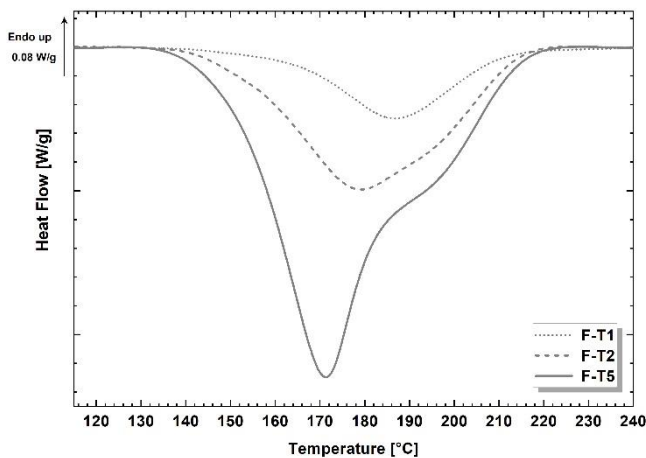


Figure 3. DSC curves of uncrosslinked FKM rubber containing different amount of TAIC.

The analyses of the crosslinking mechanisms highlight a two-step process except for the sample

containing the least amount of coagent. Indeed, for F-T1 sample, the curing step starts at higher temperature explaining the smaller cure rate index (CRI) observed in MDR at 150°C. Moreover, the first exotherm seems to be dependent on the TAIC content contrary to the second one.

#### 3.2 Mechanical behaviour

Figure 4 displays the global mechanical behaviour of three samples containing different amounts of TAIC.

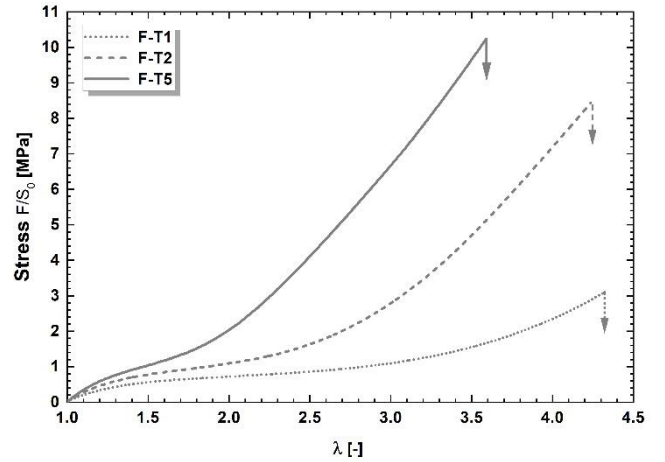


Figure 4. Tensile curves of uncrosslinked FKM rubber containing different amount of TAIC.

It must be emphasized that the mechanical behaviour of FKM strongly depends on the coagent ratio. At small elongations, the Young modulus increases with TAIC content. The strain hardening stage begins at smaller elongations and is more pronounced for high amounts of TAIC. Concerning the ultimate properties, the stress at break increases and the strain at break decreases as the coagent ration increases. These results are classically attributed to an increase in crosslink density.

Swelling experiments at equilibrium revealed that the degree of swelling decreases with the TAIC content suggesting once again an evolution of the crosslinking density with the amount of coagent.

### 4 CONCLUSIONS

The role of the coagent in a fluoroelastomer/peroxide/coagent vulcanization was investigated by coupling several experimental approaches. This study reveals that the coagent seems to be essential to cure the FKM in presence of peroxide. Moreover, all experiments highlight that a higher amount of TAIC generates a higher crosslinking density (for identical conditions of curing and amount of peroxide). From the comparison of these experiments, a general scheme will be proposed to explain the crosslinking mechanisms and the final structure of the FKM rubber.

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