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Elasticity Recovery of Crosslinked EPDM: Influence of the Chemistry and Nanofillers

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Abstract:

The objective of this work was to study the elastic recovery of EPDM samples crosslinked either by a phenolic resin (resol) or by a radical peroxide (dicumyl peroxide). From compression set experiments, it was observed that radically crosslinked EPDMs have better elastic recovery properties. On the other hand, for the same crosslinking density, radically crosslinked EPDM shows better compression set than EPDM crosslinked with phenolic resins. The Chasset-Thirion equation was then used to successfully fit the experimental relaxation curves. As a notable result, the preferential statistics of a peroxide-crosslinked network over a phenolic resin (resol) showed that better elastic recovery properties were obtained.

Finally, the influence of fillers (carbon black and silica) was also studied. Carbon black with DCP crosslinking was shown to improve elasticity recovery whereas silica fillers lead to worse properties. It was then assumed that the interaction between particle surface and crosslinking agents induced crosslinking gradients in the inter-particle volume.

Introduction

Ethylene-propylene-diene terpolymers (EPDM) are well known and used in industrial applications such as sealing in automotive materials. In fact, these terpolymers combine a saturated polymer chain with pendant residual unsaturated groups. As a result, they are more resistant to oxygen, ozone, UV and heat than basic polydiene elastomers (Ning et al. 2018). However, in terms of viscoelasticity, the property of recovering elasticity after a long period of application is required. Therefore, most EPDM applications require its chemical crosslinking in order to give it permanently elastic properties. In addition, nanofillers such as carbon black are often added to increase the mechanical properties.

Very few dienes are currently used in commercial EPDM: 5-ethylidene-2-norbornene (ENB), dicyclopentadiene and 5-vinylidene-2-norbornene. The chemical crosslinking reaction is then achieved using mainly three types of crosslinking agents: sulphur, peroxides and alkylphenol-formaldehyde resins (resols). Peroxide is gradually gaining importance mainly due to the high thermal stability of the C-C intermolecular bonds formed during the crosslinking of EPDM. Resols also offer high thermal stability and are preferably used in thermoplastic vulcanisates (TPVs), which usually include a polypropylene phase that would deteriorate by chain reactions if peroxides were used.

The mechanisms of the different reaction schemes used for the crosslinking of EPDM were derived from studies aimed either at modelling the crosslinking chemistry of rubber using low molar mass olefin models or directly analyzing the crosslinked material. With respect to the resol crosslinking reaction, few studies have been published, most of which are based on model systems (Van Duin 2000, 2002). In practice, resol curing is usually activated in order to achieve sufficiently high cure rates and degrees of crosslinking. This involves the introduction of an acid species (e.g. stannous chloride or an acid released by another chemical) that increases the rate of crosslinking by a carbo-cationic mechanism (Van Duin 2002). For the crosslinking reaction of EPDM by organic peroxides, the

chemical mechanisms were obtained using ^{13}C MAS NMR spectroscopy and ^{1}H T2 NMR relaxometry (Palmas et al. 2001 ; Orza et al. 2005). From an academic point of view, the chemistry of EPDM crosslinking is now satisfactorily understood. However, the influence of fillers and their interactions with these reactive molecules are poorly described in the literature in terms of resulting elasticity recovery.

In terms of industrial applications one of the most important property is the recovery property after long time under a constant strain. This mechanism of long-time relaxation is well known as the compression set (or tension set). The compression set test is intended to measure the ability of rubber compounds to retain elastic properties after prolonged action under compressive stresses.

From a viscoelastic point of view, the compression set experiment is a stress relaxation test under compression followed by an elastic recovery test. The linear viscoelastic behaviour of such an experimental system is based on Boltzmann's principle of superposition and has been discussed (Joubert et al. 2003) in order to understand the mechanisms of relaxation within the long time limit. A molecular interpretation of the long-term relaxation of elastomers was given for the first time by Curro and Pincus (Pincus and Curro 1983). Their model is based on the retraction of dangling chains in a crosslinked network with topological constraints (entanglements). They predict that a polymer network containing a random distribution of dangling chain ends leads to a relaxation modulus with a time-dependent power law as in the phenomenological equation of Chasset and Thirion (Chasset and Thirion 1965). Indeed, Chasset and Thirion postulated in the 1960's that an excellent representation of the isothermal relaxation modulus data for many rubbers can be given by:

$$E(t) = E_{\infty}\left[1 + \left(\frac{t}{\tau_0}\right)^{-m}\right] \qquad (1)$$

for long times t. E_{∞} is the equilibrium modulus, and m and τ_0 are material parameters. So, Curro and co-workers (Pincus and Curro 1983) provided an *a posteriori* theoretical background to this empirical equation and supported the conjecture of Ferry (Ferry 1980) that dangling chain ends lead to extremely long viscoelastic processes.

With regard to industrial developments, relaxation mechanisms within the long time limit are of great importance as they define elastic properties such as compression set. Despite its intensive use in industrial applications, network-based EPDM is a complex material due to its structure, crosslinking chemistry and the addition of fillers and plasticizing oils.

Thus, the main objective of this paper is to characterize the structure of oil-extended EPDM networks, crosslinked either by organic peroxides or phenolic resins, by performing swelling equilibrium, viscoelastic measurements and long-term stress relaxation. The final objective is to demonstrate that the peroxide crosslinking reaction is more efficient than that achieved with a phenolic resin in terms of compression set properties for the same crosslinking density. This important result is discussed and explained on the basis of the crosslinking statistics generated by the nature of the crosslinking agent (organic peroxide or phenolic resin). The influence of nanofillers, such as carbon black (CB) and fumed silica, on the elasticity recovery has been also investigated.

Experimental

Materials:

Experiments were carried out with EPDM Vistalon 8600 (ExxonMobil Chemical), in which the diene species is ethylidene norbornene (ENB). The molar content of each component in the terpolymer was determined by our NMR platform by ^{1}H NMR: 71.6 mol % ethylene, 26.4 mol % propylene and 2.0 mol % ENB. Vistalon 8600 has a specific gravity of 0.86 g.cm^{-3} at 15 °C and a Mooney viscosity $ML_{(1+8)}$ of 81 at 125 °C according to the supplier information. The following values of molar mass were measured in our lab from Size Exclusion Chromatography with a conventional calibration in trichlorobenzene at 150°C: $\overline{M}_n$ = 31000 g.mol^{-1} and $\overline{M}_w$ = 107 000 g.mol^{-1}. Additional paraffinic oil (Nypar 330, Nynas) was incorporated to Vistalon 8600 to mimic industrial compositions. The specific gravity of this plasticizer is 0.875 g.cm^{-3} at 15 °C. Its proportion in the binary EPDM/plasticizer mixture was set to the classical industrial standard, i.e. 60 phr (grams per hundred grams of EPDM).

Crosslinking reaction of EPDM was carried out by means of either organic peroxide (Dicumyl peroxide (DCP) from Aldrich, 99% purity) or by an activated octylphenol-formaldehyde resin (Nures 2055, Newport Industries) called resol in the following text. In order to vary the degree of crosslinking, the EPDM samples were prepared with diverse amounts of curing agent up to 3.9 wt.%. According to the supplier information, the carbon black N550 (Lehvoss) has a specific surface area of 40 m^2/g and the hydrophilic fumed silica Aerosil® 200 (Aerosil) has a specific surface area of 189 m^2/g

Samples preparation

The blends of the polymer, processing oil and curing system were prepared in an internal batch mixer (Haake Rheomix 600, Thermo Electron), at the temperature of 180°C. The following protocol was adopted: first, the polymer and the plasticizer (around 40 g overall) were introduced (at time t = 0) into the chamber and sheared for 5 minutes under 80 rpm in order to ensure thermal homogenization. Prior to introducing the curing system, the temperature and rotation speed were decreaJsed (80 °C and 50 rpm, respectively) and torque stabilization was waited. The curing system (DCP or resol resin) was then introduced and mixing could go until torque started to increase. The blend was rapidly removed in order to prevent the crosslinking reaction from occurring inside the mixer. All the mixtures were prepared with an equivalent volume of 48 cm^3.

Test samples of every composition were compression molded into 2 mm-thick sheets for 5 minutes at 110 °C (no crosslinking occurred during this operation). The samples were then crosslinked during molding in plates press at 200 °C for 20 minutes under the pressure of 200 bar.

For samples filled with CB or fumed silica, the filler is introduced in the mixer at the same time than the polymer and the plasticizer and the protocol in the internal batch mixer is the same. To have a better dispersion of the filler, the blend undergoes an additional step in the two-roll mill (Scamex, France) for 5 minutes at 50°C and 20 rpm before being compression molded in the same conditions than the unfilled samples.

EPDM soluble fraction and swelling equilibrium

The total soluble weight fraction in the crosslinked samples was extracted with p-xylene over 24 hours. Since this soluble fraction includes all the plasticizer initially present in the sample, the soluble polymer weight fraction could be expressed with respect to the mere sample polymer content, after subtraction of the plasticizer amount.

The swelling equilibrium was determined as following:

$$\mathrm{Se} = 1 + \frac{\rho_{\mathrm{polymer}}}{\rho_{\mathrm{solvent}}}\left(\frac{\mathrm{m_s} - \mathrm{m_i}.\theta - \mathrm{m_d}}{m_{\mathrm{d}}}\right) \quad (2)$$

$\mathrm{m_i}$ is the initial mass of polymer, $\mathrm{m_s}$ is the swollen polymer mass, $\mathrm{m_d}$ is the dry polymer mass and θ is the polymer volume fraction in the compound.

In the case of fillers additions, the swelling equilibrium as determined according to the following equation:

$$\mathrm{Se} = 1 + \frac{\rho_{\mathrm{polymer}}}{\rho_{\mathrm{solvent}}}\left(\frac{\mathrm{m_s} - \mathrm{m_i}.\theta - \mathrm{m_d}}{m_{\mathrm{d}}}\right)\left(\frac{1}{1 - \mathrm{wt\%_f}}\right) \quad (3)$$

$\mathrm{wt\%_f}$ is the weight fraction of the filler in the compound.

The Flory-Rehner expression for the swelling of a rubber network, based on the assumption of additivity of the free energy of mixing and the free energy of elasticity, has been used for the calculation of crosslinking density ν_S:

$$\ln(1 - \nu_2) + \nu_2 + \chi\,\nu_2^2 = \mathrm{V_1}\nu_S\left[\frac{\nu_2}{2} - \nu_2^{\frac{1}{3}}\right] \quad (4)$$

Where ν_2 is the polymer volume fraction at equilibrium swelling (ν_2 = 1/Se), χ is the Flory-Huggins polymer-solvent interaction parameter (χ = 0.4) (Briceño Garcia et al. 2014), and V_1 is the molar volume of solvent.

Complex shear modulus (G*(ω))

The complex shear modulus in the linear viscoelastic regime ($G^*(\omega) = G'(\omega) + j\,G''(\omega)$, $J^2 = -1$) was determined on a ARES rheometer (TA Instruments). All samples were tested in the form of 2 mm-thick disks) under nitrogen atmosphere, using 8 mm parallel plate geometry. The extent of the linear viscoelastic domain was determined from strain sweep experiments.

The value of the equilibrium modulus G_e was determined from the low frequency plateau exhibited on G' plots ($G_e = \lim_{\omega \to 0} G'(\omega)$). The density of elastically active chains ν_R can be then calculated according to the following equation derived in our previous work (Martin et al. 2008) from model developed by Langley (Langley 1968) and Dossin and Graessley (Dossin and Graessley 1979).

$$G_e = \nu_R \; R\,T\,\theta^{\frac{1}{3}} + G_e^{max}\,T_e\,\theta^{2.25} \qquad (5)$$

R is the gas constant and T the absolute temperature. T_e is the fraction of trapped entanglements in the network, i.e. the proportion of the maximum concentration of topological interactions that contribute to the modulus. G_e^{max} is the maximum topological contribution and it is expected to be very close to G_N^0, the plateau modulus of the un-crosslinked, high molar mass polymer. θ is the polymer volume fraction in the compound. Indeed, from a practical point of view, EPDM networks also contain large amount of plasticizer and are thus swollen by this extractable component which acts as a diluent.

Stress relaxation at long times

EPDM networks were submitted to a stress relaxation experiment using a compressive machine from Shimadzu (AGS-X, force sensor: SSM-DAK-5000N) equipped with an oven. The protocol was the following: the oven was preheated at the temperature of T = 100°C. A 13 mm-diameter, 6 mm-high cylindrical sample, prepared by stacking 3 discs of 2 mm thick, was placed between the plates and submitted to a compression strain of 25 % ($\varepsilon_{0,n}$ = 0.25) for 24 hours (sample initial height and deformation were controlled very precisely on the apparatus), while recording the stress relaxation $\sigma(t)$. It should be noted that the strain of 0.25 was chosen because it is the deformation used in the standard tests practiced in the industry. Finally, we defined: $E(t) = \sigma(t)/\varepsilon_{0,n}$.

Compression set

The elastic capacity of a crosslinked EPDM sample to recover its initial size after being subjected to constant deformation for a specified time at a given temperature is evaluated by the compression set test. This test is standardized by ASTMD 395 standards (ISO 815-1).

The cylindrical sample, 13 mm in diameter and l_0 = 6 mm thick, is 25 % compressed ($\varepsilon_{0,n}$ = 0.25) in an oven for 24 hours at 100°C and then removed and left to cool for 30 minutes. The compression set is then expressed by:

$$Cs\ (\%) = \frac{1}{\varepsilon_{0,n}}\left(1 - \frac{l_1}{l_0}\right).100 \qquad (6)$$

l_0 and l_1 are respectively the sample height at t = 0 and after having undergone the deformation imposed on it and $\varepsilon_{0,n}$ the nominal deformation imposed to 0.25. The residual deformation or elastic recovery of the material can then be known. The following limits of the compression set data under these experimental conditions (temperature and loading time) are then: Cs = 0 %, as $l_1 = l_0$, where the sample shows perfect elastic recovery and Cs = 100 %, as $l_1 = l_0(1-\varepsilon_{0,n})$, where the sample reflects no elastic recovery.

Transmission Electronic Microscopy (TEM)

The samples are first ultra-microtomed into thin pieces of about 70 nm in thickness using a Leica UC 7 apparatus under liquid nitrogen atmosphere at - 160 °C. The lamellae are then deposited on copper grids (Mesh 300). Observation is carried out using a Philips CM 120 TEM transmission electron microscope. The EPDM phase appears dark on the images, while the polypropylene is very light in appearance.

Results and discussion

As explained in the experimental part, the density of elastically active chains can be calculated from either the swelling equilibrium or the equilibrium modulus, i.e ν_S and ν_R according to equations (4) and (5) respectively. Concerning the ν_R calculation, it must be point out that the best fit was obtained with G_e^{max} = 2.0 x 10^5 Pa in agreement with the value of G_N^0= 2.1 x 10^5 Pa. As expected it is observed (see the **Table 1** and supporting info) for the variation of the storage modulus G'(ω)) that both equilibrium modulus and equilibrium swelling increase with increasing the concentration of the crosslinking agents (resol or DCP).

Table 1 : Density of elastically active chains (ν_S and ν_R) calculated from equations (4) and (5) respectively for resol and DCP crosslinking agents.

Resol (%wt)	Resol (mol.m^{-3})	G_e (x10^5 Pa)	ν_R (mol.m^{-3})	ν_2	ν_S (mol.m^{-3})
0.6	11	0.8	9	0.08	12
1.7	31	1.4	31	0.11	26
2.4	44	1.9	49	0.11	27
2.9	53	2.4	64	0.11	28
3.3	62	2.4	65	0.14	40
3.9	72	2.6	70	0.15	50
5.9	110	3.2	91	0.18	78
DCP (%wt)	**DCP (mol.m^{-3})**	**G_e (x10^5 Pa)**	**ν_R (mol.m^{-3})**	**ν_2**	**ν_S (mol.m^{-3})**
0.6	20	0.9	14	0.08	14
1.7	54	2.0	52	0.12	32
2.4	78	2.3	62	0.19	87
2.9	93	3.0	86	0.20	95
3.3	108	3.4	102	0.21	115
3.9	126	3.9	117	0.25	171

Actually, the **Fig 1** shows that there is a good agreement between the two methods because all the values are quite well placed on the ideal line (ν_R=ν_S). Furthermore, it can be observed, that a higher crosslinking density is reached with DCP than with resol. From a chemical point of view, the resol resin can react only with ENB so that the maximum of crosslinking density is limited by the molar concentration of ENB, i.e 80 mol.m^{-3}. On the contrary, the organic radicals generated by the decomposition of DCP can also react with aliphatic (hydrogen abstraction) and recombine to form a crosslink point. Of course, the reactivity of ENB is greater than that of aliphatic groups but the

concentration of the latter is much greater so that crosslinking reaction can exceed higher densities than those expected for ENB alone. Such results have been already reported by Orza (Orza 2008).

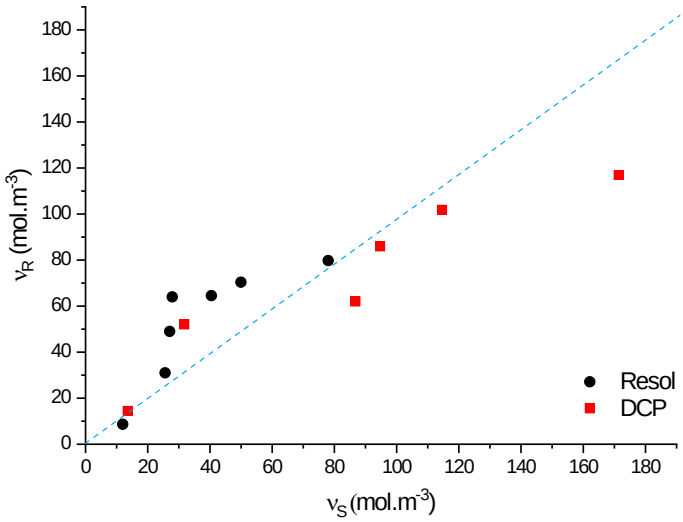


Fig 1: Plot of ν_R versus ν_S. Comparison between elastically active chains calculated from the equilibrium shear modulus and the swelling equilibrium.

More quantitatively, the variation of the density of elastically actives chains can be expressed versus the molar concentration of resol and DCP. For this purpose, **Fig 2** shows the variation of the density of elastically active chains (ν_R and ν_S) versus the molar concentration of crosslinking agents. According to the molar mass of the crosslinking agent, M_{DCP} = 270 g.mol^{-1} and $M_{resol} \approx$ 470 g.mol^{-1}, the efficiency of these crosslinking precursors has been calculated. Concerning EPDM crosslinking with DCP and according to **Fig 2** the efficiency of DCP is about 0.4, the other 60 % of the peroxide functions reacts to side reaction leading to non-elastically active products. Orza (Orza 2008) reported that 50 % of the original peroxide functions is effectively used for EPDM crosslinking whatever the ENB content. Then, our results show a lower efficiency of the DCP which could be explained by the presence of plasticizer or other additives in such industrial formulation. Concerning EPDM crosslinking with the resol, **Fig 2** shows that its efficiency is about 0.3.

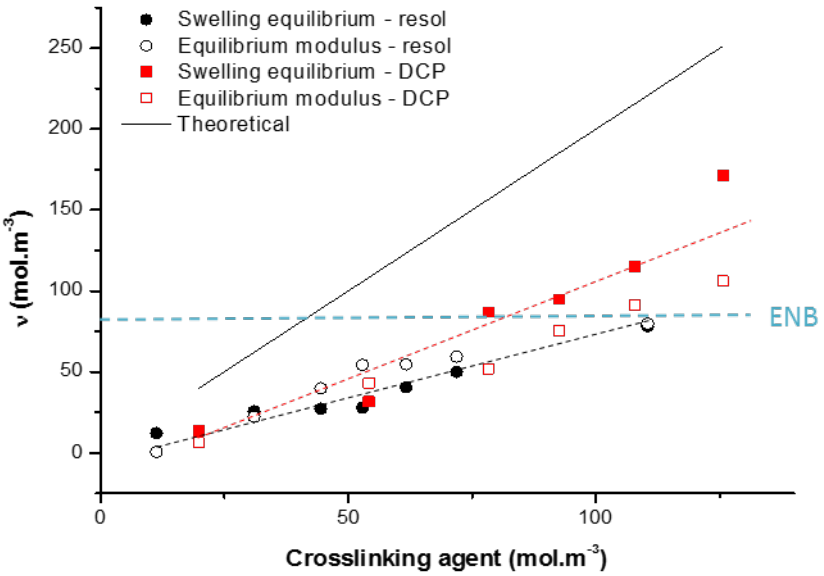


Fig 2: Variation of the density of elastically active chains (ν_R and ν_S) versus the molar concentration of crosslinking agents. The density has been measured from equilibrium shear modulus (open symbols) and swelling equilibrium (full symbols).

In the following, only the data from swelling equilibrium will be considered. The **Fig 3** shows the variation of the compression set versus the density of elastically active chains. As expected, the compression set decreases with increasing the crosslinking density which means that the elasticity recovery tends towards the property of a pure elastic material (Cs = 0 %). However, it can be observed that two different behaviours differ significantly depending on the nature of the crosslinking agent. From a general point of view and as explained previously, DCP allows obtaining higher crosslinking densities and therefore lower compression set. However, it must be pointed out that for the same crosslinking density, the compression set is lower for an EPDM crosslinked with DCP compared to an EPDM crosslinked with resol. Furthermore and by extrapolating the trend curves, it is obvious that the compression set of the EPDM/resol samples will never tend towards zero (pure elasticity) even for a higher resol concentration. In other words, crosslinking density is limited to 80 mol.m^{-3} with the resin and in addition the DCP as crosslinking agent is more efficient in terms of EPDM recovery elasticity.

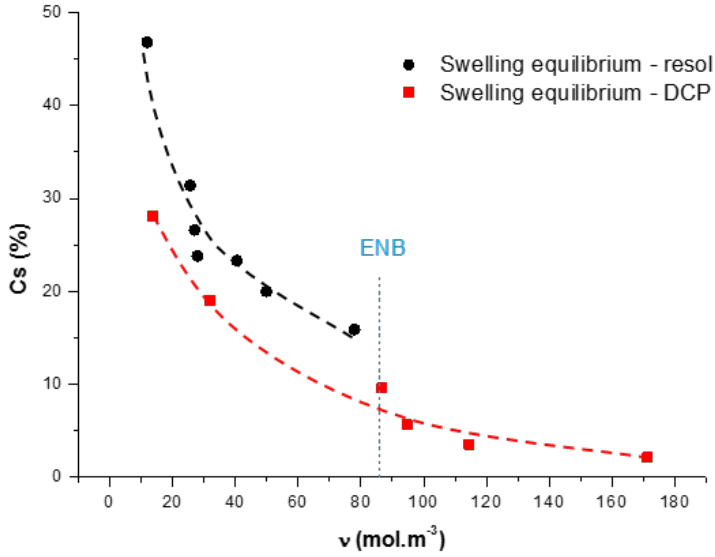


Fig 3: Variation of the compression set (Cs%) of crosslinked EPDM samples versus the density of the elastically active chains for the two types of crosslinking agents. The density has been measured from swelling equilibrium experiments

To go further in understanding this phenomenon, we performed some experiments of stress relaxation as depicted in the experimental section.

Ferry (Ferry 1980) suggested that the molecular mechanism responsible for the long relaxation process is the diffusion of dangling chain ends in the presence of entanglements. Indeed, an imperfect rubber network necessarily contains dangling chain ends as network imperfections. A molecular interpretation of the viscoelastic behavior of rubbers at long times was developed by Curro et al (Pincus and Curro 1983; Curro 1985). This theory was based on the concept of de Gennes regarding the reptation of branched molecules in the presence of topological constraints which is in qualitative agreement with the experimental observations of Chasset and Thirion (4) as they derived the following equation:

$$E(t) = E_{\infty}\left[1 + \left(\frac{t}{\tau_a}\right)^{-\frac{q}{\alpha}}\right] \qquad (7)$$

where α is a material constant and $q=\nu/\rho$ with ρ the chain segments per unit volume. By analogy with Eq 1 : $m = q/\alpha$ and $\tau_o = \tau_a$, τ_a is the characteristic time of relaxation of the dangling end chain so

that it should decrease with increasing the crosslinking density as this dangling end chains becomes shorter.

Fig 4 shows the stress relaxation experiments at T=100°C and the values of E_∞, τ_o and m are reported in **Table 2** for EPDM crosslinked either by resol or by DCP (see supporting info **Fig S 2** for curves modelling).

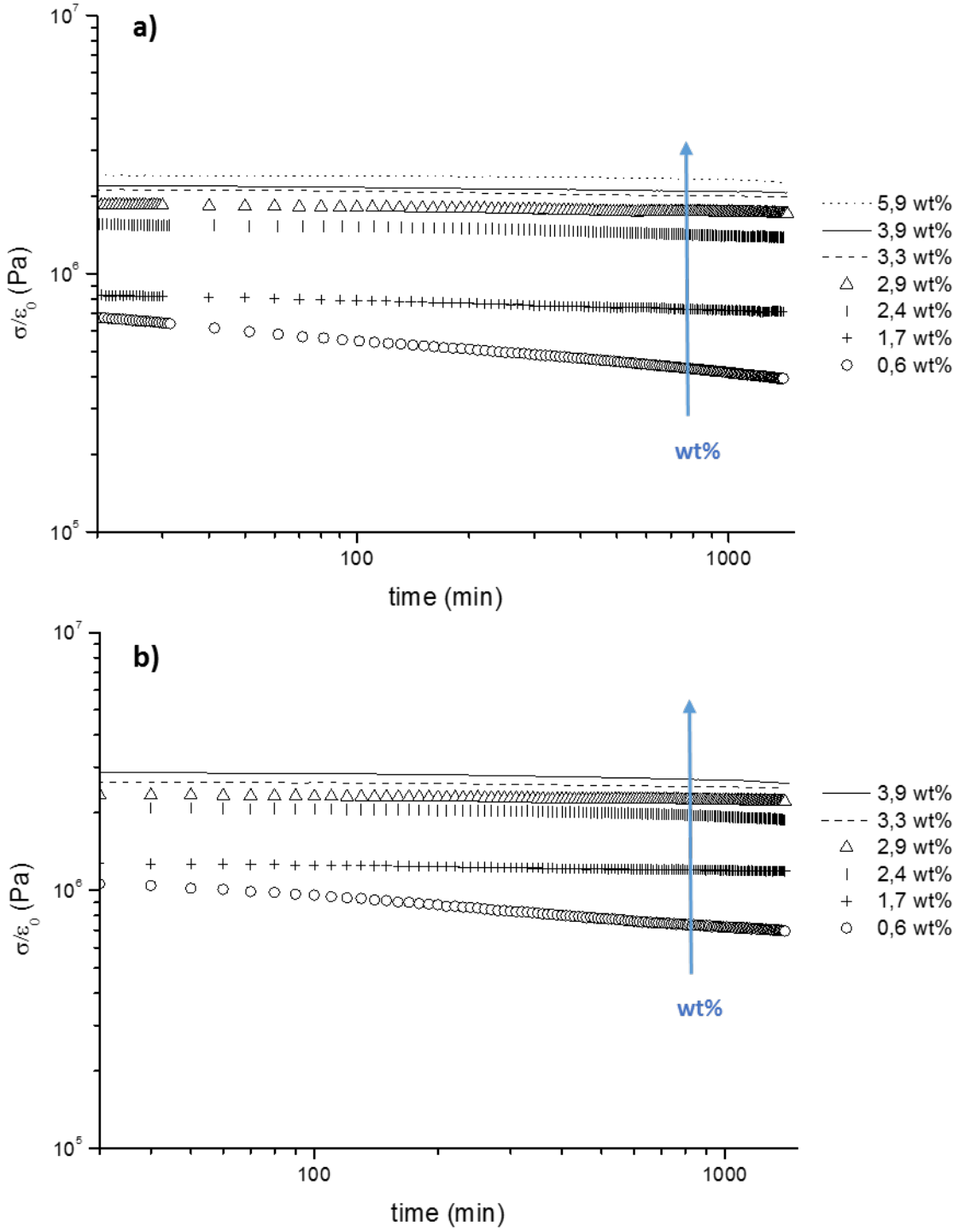


Fig 4: Variation of the stress relaxation versus the time. **a)** Networks crosslinked with the resol and **b)** crosslinked with the DCP

Table 2: Parameters of the Chasset-Thirion equation obtained from the best fit modelling of the stress relaxation experiment at T=100°C.

Resol (wt%)	E_∞ (x10^5Pa)	τ_o (min)	m
0.62	2.0	1 000	0.2

1.69	3.85	200	0.09
2.42	7.5	100	0.06
2.88	9.0	70	0.03
3.35	10	50	0.03
3.9	11	50	0.025
5.9	12	20	0.02
DCP (wt%)	**E_∞ (x10^5Pa)**	**τ_o (min)**	**m**
0.62	5	50	0.25
1.69	6.45	10	0.035
2.42	10.5	1.5	0.01
2.88	11.5	1	0.008
3.35	13	0.5	0.006
3.9	14	0.1	0.006

At the same crosslinking density, the **Fig 5** shows that the relaxation times are shorter for EPDM samples crosslinking by DCP compared with samples crosslinked with resol. Actually, this result is in agreement with the compression set dependence already discussed from **Fig 3**.

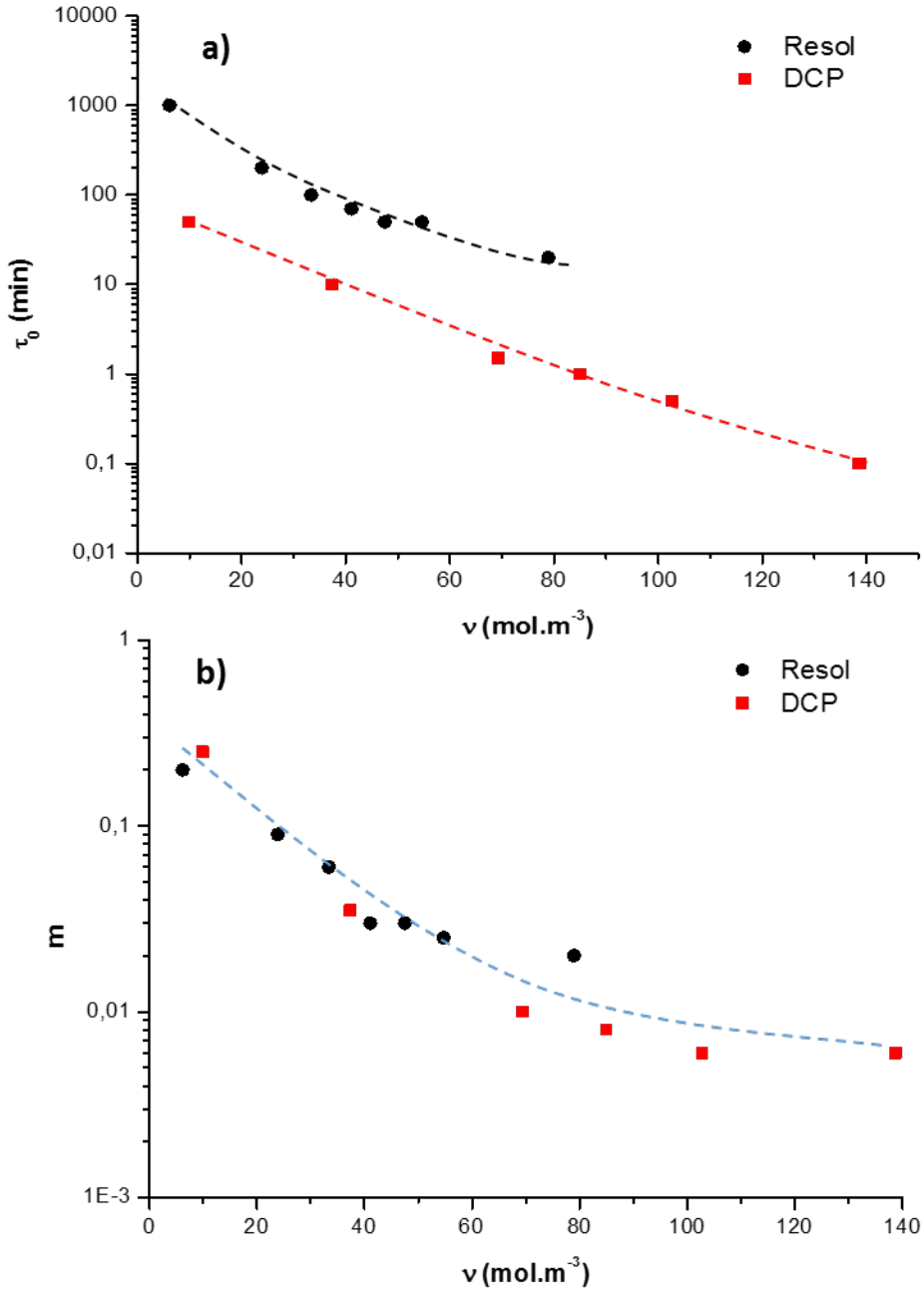


Fig 5: Variation of the exponents of the Chasset-Thirion equation. **a)** Variation of the relaxation time of the dangling end chains and **b)** Variation of m versus the density of elastically actives of EPDM crosslinked either by DCP or resol.

If we consider the crosslinking chemistry involved in the resol based systems, only the ENB functions statistically distributed over the EPDM chain are active in an assumed cationic mechanism (Van Duin 2000, 2002). Concerning the crosslinking reaction by DCP, this reaction also takes place on the ENB functions but radical reactions by hydrogen abstraction of aliphatic H-atom of the polymer chain are not to be excluded. Although the reactivity of ENB functions is much higher than that of aliphatic

groups, the molar ratio of CH_2/ENB is extremely high (CH_2/ENB ≈ 40) so that the crosslinking reaction induced by hydrogen abstraction and radical recombination is probable. The consequence of such a crosslinking statistic is that for the same crosslinking density, the dangling end chain segment is shorter in the case of crosslinking by DCP than by resol, which is shown in terms of elastic properties into a better elastic recovery property. Concerning the exponent, m, *a priori* it depends only on the crosslinking density and is constant whatever the crosslinking chemistry, it does not in fact depend on the crosslinking statistics but only on the density of elastically active chains. Such results are qualitatively consistent with the results (Zaborski 2003) on the PDMS model network in which it has been reported that m becomes almost independent as the polydispersity of the pendent chain length increases. Actually due to the random crosslinking nature of EPDM, a broad polydispersity is inherent to such network (imperfect network).

Influence of fillers:

The objective of this part is to study the influence of fillers on the compression set properties. To carry out this study, we considered two fillers (see experimental part): a carbon black and a hydrophilic silica at three different concentrations (3, 6 and 12 wt%). In addition, we considered only two crosslinking formulations resol and DCP at respective concentrations of 4 wt% (ν = 72 mol.m^{-3}) and 2 wt% (ν = 87 mol.m^{-3}). These fillers are of course different in nature but these fillers are in the form of aggregates made up of elementary particles of a few nanometres. On the other hand, their surfaces are of an extremely different chemical nature and therefore interactions with crosslinking additives can lead to crosslinking modifications or even crosslinking gradients in the inter-particle volumes.

Fig 6 shows the influence of the concentration of carbon black N550 on the compression set of this crosslinked system. Without filler the density of the resol network is 72 mol m^{-3} and the density of the DCP network is 87 mol m^{-3} for respective compression set of 19 % and 10 %. Concerning the resol, a lower density of crosslinking is measured in the presence of CB and therefore poorer

compression set properties. On the other hand, in the case of DCP, the crosslinking density increases resulting in an improvement of the elastic recovery properties.

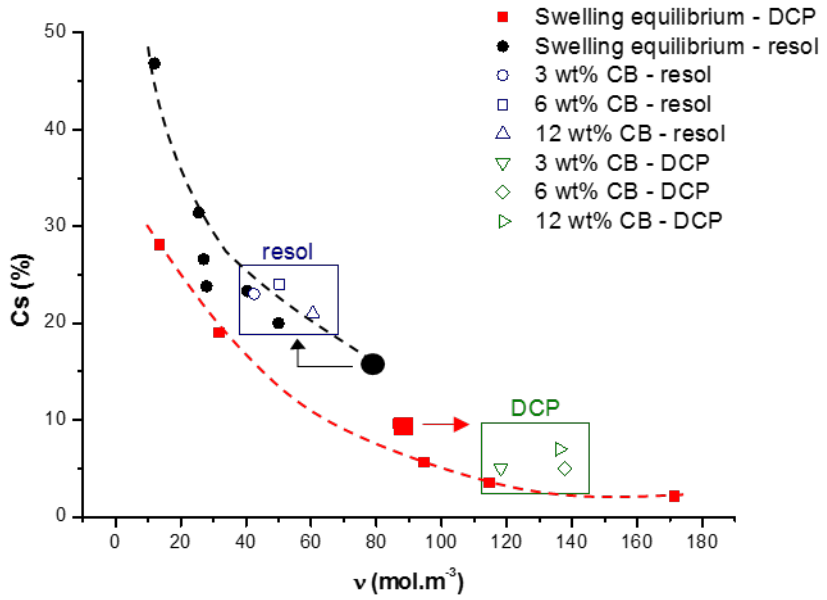


Fig 6: Influence of the carbon black filler (N550) on the compression set for the two types of crosslinking agents (resol and DCP). The trend curves are as shown in **Fig 3**. In the frame are the points obtained in the presence of CB filler.

Concerning silica fillers, the results are totally different. Indeed, the elastic recovery property is clearly degraded as shown in **Fig 7**, in fact the fillers contribute to an increase in compression set. In other words, and qualitatively, it can be concluded that carbon black fillers improve the compression set for a formulation crosslinked by DCP whereas silica fillers, and whatever the chemical nature of their surface degrade this elastic recovery property. What is then the origin of these phenomena? Transmission Electron Microscopy images in **Fig 8** show a good dispersion of carbon black and silica fillers in the EPDM matrix. As expected, the silica elementary particles are finer and form more aggregates than the carbon black fillers. But filler dispersion cannot be the first-order criterion to explain these elastic recovery properties which are in fact only improved in the case of CB dispersed in DCP crosslinked formulation.

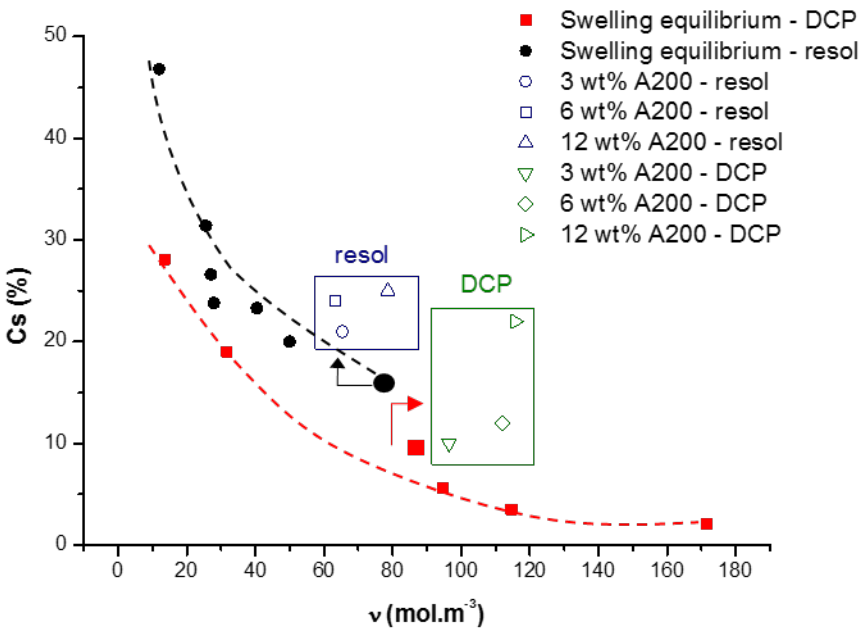


Fig 7: Influence of hydrophilic silica fillers Aerosil A200 on the compression set for the two types of crosslinking agents (resol and DCP). The trend curves are as shown in **Fig 3**. In the frame are the points obtained in the presence of theses silica fillers.

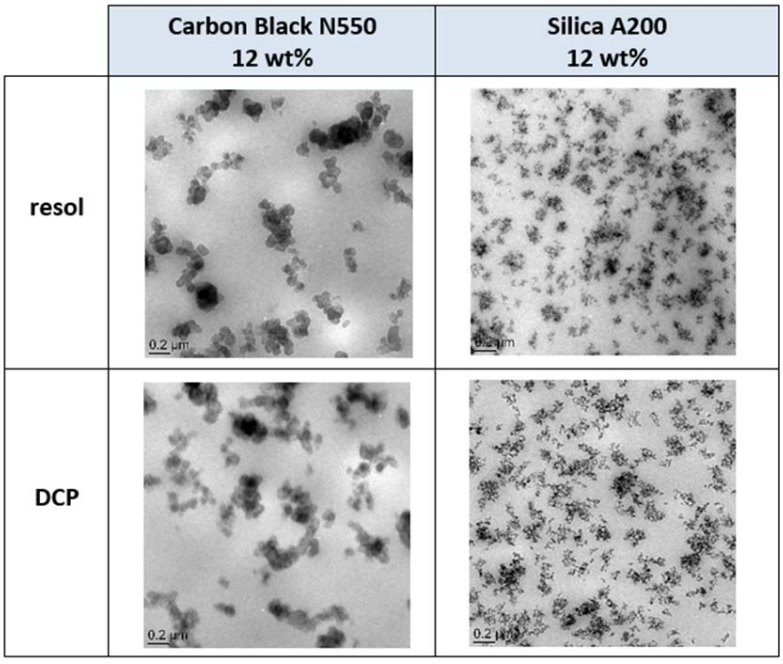


Fig 8: TEM images of carbon black and silica fillers dispersed in crosslinked EPDM samples. The crosslinking densities of these samples measured by swelling equilibrium are the following: resol/CB: 60 mol.m^{-3}; resol/silica: 79 mol.m^{-3}; DCP/CB: 136 mol.m^{-3}; DCP/silica: 116 mol.m^{-3}.

In fact, the explanation lies in the interactions between the particles and the crosslinking agents. These interactions have been described quantitatively by Zaborski and Donnet (Zaborski 2003). The conclusion of their work on model systems is that the reinforcement of elastomers by fillers depends on the type of crosslinking chemistry and the type of filler (CB or silica). Indeed, the crosslinking agents interact with the particles and adsorb on their surfaces and especially on the silica surfaces due to the Si-OH functions. This phenomenon results in a heterogeneous distribution of the crosslinking agents and thus in a crosslinking density gradient in the inter-particle volume. More specifically in the case of CB, the crosslinking reaction by decomposition of peroxides leads to another phenomenon which is that of a covalent grafting of polymer chains onto the filler. Actually, it was proved (Akbar et al. 2009) that ethylene-based polymer grafting takes place through radical addition onto unsaturated bonds located on the carbon nanotube surface using dicumyl peroxide as hydrogen abstractor. Such mechanism of EPDM grafting onto carbon black surface is also probable.

Conclusion

Ethylene-propylene-diene terpolymers (EPDM) are mostly chemically crosslinked to give the elasticity properties required for industrial applications. In the present work, the structure of oil-extended EPDM networks crosslinked either by an organic peroxide (Dicumyl peroxide) or by a phenolic resin was characterized by the achievement of a swelling equilibrium, viscoelastic measurements and long-term stress relaxation.

As a result, it was shown that crosslinking with resol does not allow crosslinking densities higher than the ENB concentration of the EPDM used (80 $mol.m^{-3}$). In fact, only ENBs are potentially reactive. On the contrary, higher densities up to 170 $mol.m^{-3}$ can be obtained by radical crosslinking. In fact, the radical reaction can also take place by abstraction of hydrogen from aliphatic groups and recombination of the radicals thus generated.

In addition, for the same crosslinking density, the compression set is lower for an EPDM network crosslinked with DCP than for an EPDM crosslinked with resol. In order to explain this interesting behaviour in terms of formulation and applications, long-term stress relaxation experiments (Δt = 24 h, T = 100°C) under a strain of $\varepsilon_{0,n}$ = 0.25 were then carried out. The Chasset-Thirion equation was then used to fit the experimental relaxation curves. It was deduced that the relaxation time of the dangling end chains is shorter in the case of radically crosslinked EPDM than in the case of crosslinked phenolic resin-based EPDM. These results highlighted the preferential statistics of a peroxide-crosslinked network compared to phenolic resin (resol) to obtain better elasticity recovery properties. Statistically, the pendant chain ends are statistically shorter in the case of DCP crosslinking than in the case of resol in accordance with the concepts of molecular dynamics developed by Curro and Pincus.

The presence of filler leads to different results depending on the nature of the filler, CB or silica. Indeed, the presence of silica fillers leads to poorer elastic recovery properties which are explained by interactions between fillers and crosslinking agents (DCP or resol). The result is an inhomogeneous crosslinking network in the inter-particle volume and/or inhibition of crosslinking agents. On the other hand, in the presence of carbon filler and crosslinking of the network with peroxide, an improvement of the compression set properties is observed. During the decomposition of DCP and the various radical reactions involved, EPDM chains (or chain segments) can be chemically grafted onto the surface of the filler, thus increasing the crosslinking density and thus improving the elastic recovery properties of the samples.

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Supporting information

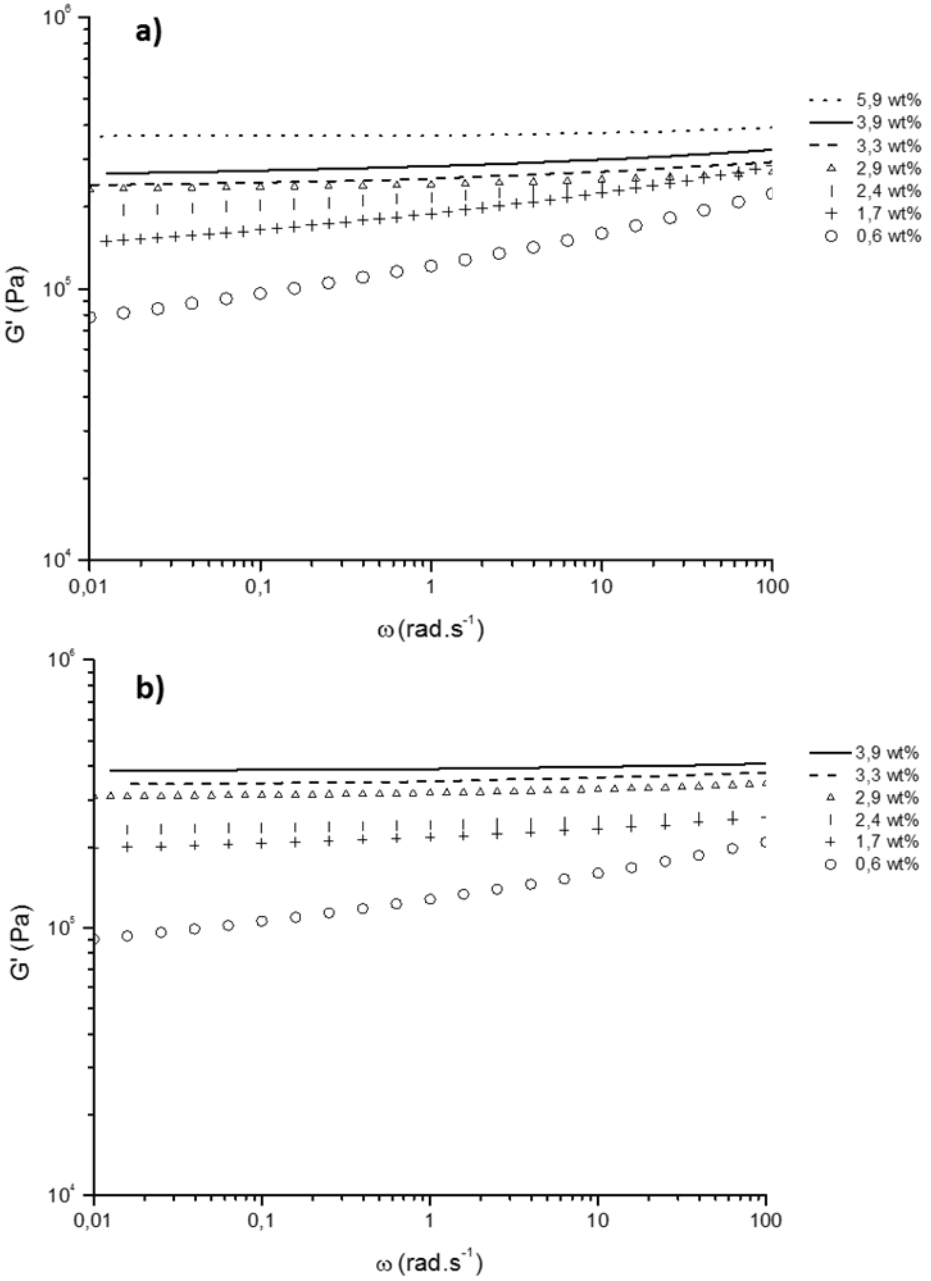


Fig S 1: Variation of the storage shear modulus versus frequency for crosslinked EPDM samples: **a)** EPDM crosslinked with resol, **b)** EPDM crosslinked with dicumyl peroxide.

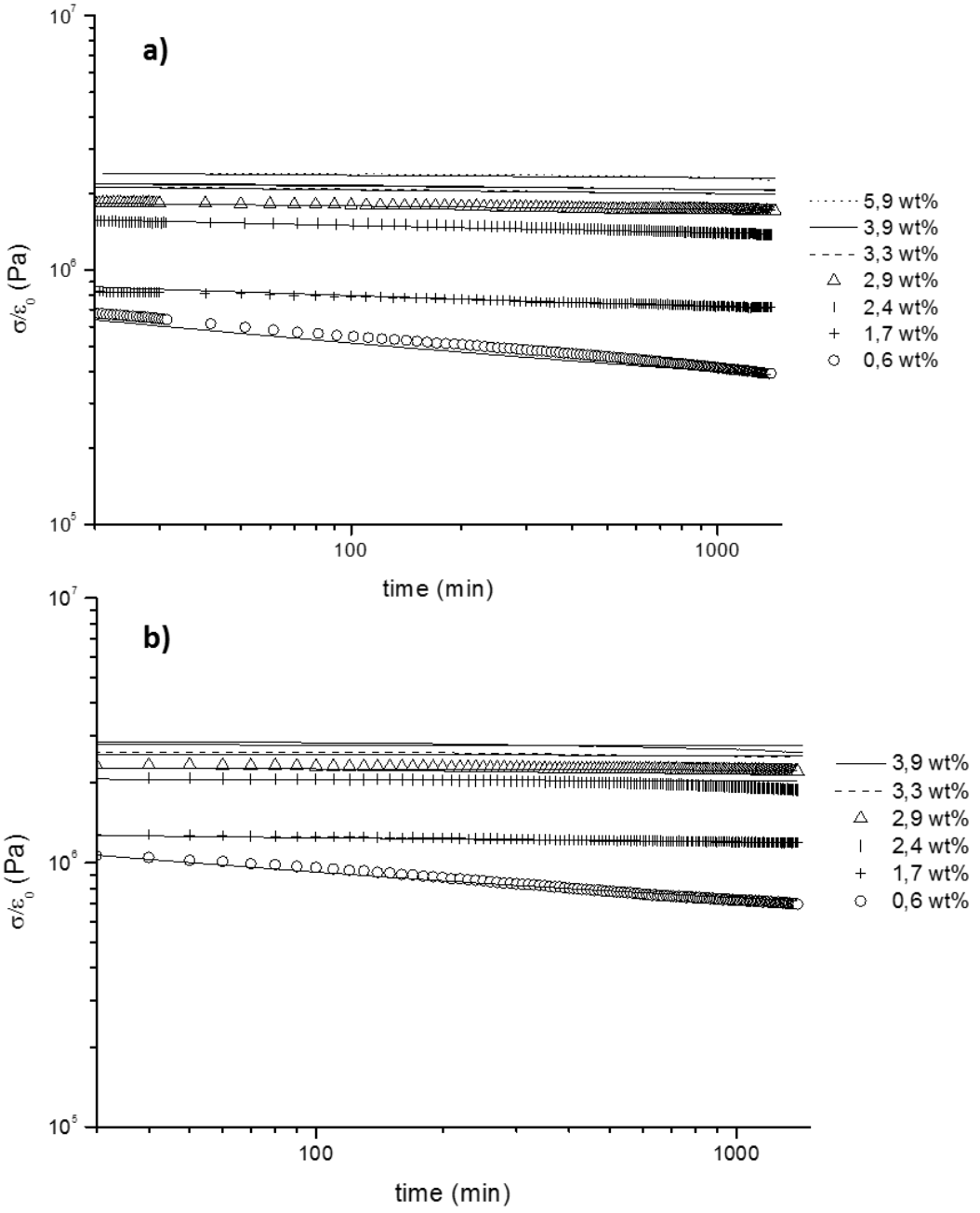


Fig S 2: Stress relaxation at the long time (Δt = 24hours, T = 100°C, $\varepsilon_{0,n}$ = 0.25), **a)** EPDM crosslinked with resol, **b)** EPDM crosslinked with dicumyl peroxide. The curves show the modelling from the Chasset-Thirion equation.