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**Extensional rheology and CO₂ foaming of Thermoplastics Vulcanizates:
Influence of the crosslinking chemistry**

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Abstract:

The objective of this study is to investigate the ability of TPV (materials based on PP/EPDM blend) to foam under CO₂ batch conditions. The EPDM phase, which is dispersed into the PP phase, was dynamically crosslinked either by a phenolic resin (Resol) or by a radical peroxide (dicumyl peroxide). The results show an influence of the crosslinking chemistry on the extensional viscosity of the TPV. Regarding radical chemistry, the peroxide induces polypropylene degradation by β -scission reaction during the dynamic crosslinking process. As a result, the ability of the TPV to deform under extensional flow (Hencky deformation at break < 0.5) is greatly reduced. On the contrary, the Resol-based TPV has demonstrated a non-linear viscosity behaviour (strain hardening) and a great ability to deform (Hencky deformation at break > 1.5). This unexpected result for a non-homogeneous system can be explained by the confinement of the PP phase between EPDM nodules which gives to the PP chains a gel rheological behaviour. In addition, the influence of the addition of carbon black filler has also been studied. Finally, the relationship between extensional viscosity and physical foaming has been investigated. As for a homogeneous polymer, the extensional viscosity has been proved to be a key factor to estimate the foaming behaviour of complex systems like TPV. Hence, the importance of non-linear viscosity for a multi-phasic polymer to ensure foaming ability has been demonstrated.

Introduction

In order to reduce plastic consumption, foams are being more and more used. Firstly, polystyrene and polyurethane have been developed and now are well understood. More recently, foams with nanoscale cell size have been developed from nanostructured polymethylmethacrylate (PMMA), they exhibit enhanced properties due to this nanoscale morphology, e.g., high thermal insulation, superior to air due to the Knudsen effect [1]. To be as eco-friendly as possible, foams research has focused on physical foaming because it is harmless to human and environment, unlike chemical foaming which can produce chemical species and pollute the foam reducing its recyclability. In fact, chemical blowing agent such as azodicarbonamide can be decomposed [2][3][4].

Due to the growing interest in designing greener polymer foams, the interest in foams based on thermoplastic elastomer (TPE) and thermoplastic vulcanizates (TPV) is increasing too. Thermoplastic vulcanizates (TPV) are a family of TPE although the rubber phase is dynamically crosslinked [5]. This induces a fine dispersion of crosslinked rubber particles on the thermoplastic matrix [6]. TPVs have highly improved mechanical properties as long as the rubber part is sufficiently crosslinked and therefore behave like a vulcanized rubber, but due to the thermoplastic phase, they can be processed just as thermoplastics [6][7]. These unique properties make them a greener and recyclable rubber. A widely used family of TPV is composed of a dispersed EPDM vulcanized phase and a polypropylene matrix [8][9]. Many physical foaming agents have been investigated like water, N₂, or CO₂ [3][6]. Supercritical CO₂ seems to be the most suitable agent for foaming TPV because of its high solubility in polymer and more particularly on polypropylene and EPDM [10].

The TPV and TPE foaming has been studied and it has been reported that low density foam with fine cell dispersion could be achieved [6][11]. In literature, using CO₂ as a foaming agent has been proven to be effective, but the elasticity of the polymer has a major role in the resulted foam. As the crosslinking level of the elastomeric phase influences the elasticity of the global polymer blend this would influence the foaming behaviour, a too crosslinked rubber induces a poor foaming capacity [12].

The significance of the strain hardening on the foamability is well known, especially for polypropylene[13] [14] [15–18], however, the influence of the non-linear extensional viscosity has not been investigated in many details for complex blend such as TPV. Nevertheless the importance of non-linear viscosity on TPE foaming has already been demonstrated by increasing the branching level [19] which resulted on increasing the strain hardening. Thus, the addition of filler on polymer matrix (having poor foamability) has proven to be a way of improving their ability to foam by create the strain

hardening phenomena [20][21]. These results indicate the importance of the macroscopic rheology and specifically strain hardening for the ability to foam complex polymer blend.

The rheological behaviour of TPV and its relationship to foaming has not been fully investigated [3] despite the necessity to understand how TPV foaming occurs to know how to design the polymer depending on its specific application. So, this work is focused on the influence of the crosslinking chemistry on the foaming and elongational viscosity and the relationship between them.

Experimental part.

Polymers and formulations

Polymers and chemical products used in the present study have been described in detail in our previous works ([22,23]). Firstly, the polypropylene used is an isotactic homopolymer purchased from TotalEnergies having a Melt Flow Index of 1.8 g/10min (measured at 2.16 kg/230°C) and molar masses $M_n = 70\,000$ g/mol and $M_w = 380\,000$ g/mol with the reference PPH3060. The EPDM used is provided by ExxonMobil Chemical (EPDM Vistalon 8600). The molar composition of the terpolymer are specified on previous works ([22,23]) which is 71.6 mol% ethylene, 26.4 mol% propylene and 2 mol% of ENB. The molar masses are $M_n = 69\,000$ g/mol and $M_w = 203\,000$ g/mol. Paraffinic oil used blended with EPDM is the Nypar 330 (Nynas) having a density at 15 °C of 0.875 kg/m³, fraction of oil depends on the blend of polymers studied, 60 phr for pure EPDM and 122 phr for EPDM/PP blend. Crosslinking reactions of EPDM are made using two different crosslinking agents: an organic peroxide, dicumyl peroxide provided by Aldrich (99% purity) abbreviated in our work as DCP and an activated octyphenol-formaldehyde resin (Nures 2055, Newport Industries) its abbreviation in this work is Resol. The carbon black is provided by Lehvoss (N550) with a specific surface area of 40 m²/g.

TPV preparation:

TPV samples were prepared using the same [method as](#) described in our previous work [23]. First the EPDM, paraffinic oil and the filler (carbon black) are mixed in a batch mixer (Haake Rheomix 600) at 60 °C and 50 rpm for 5 minutes in order to homogenize the blend. Then, the polypropylene phase is added and the blend is mixed for 5 more minutes with no change of temperature. Then, the temperature is set up to 180°C to crosslink the EPDM phase. The vulcanization time depends on the crosslinking agent nature.

The samples used for rheological measurement and foaming stage are made through compression molding at 180°C for 10 mn for DCP crosslinked systems and 20 min at 200°C for Resol systems.

Table 1: TPV samples composition. v^* is the crosslinking density determined in ref [22] for pure crosslinked EPDM. Cs are the compression set values. For all TPV samples, EPDM: 100 phr, PP: 75 phr and oil plasticizer: 122 phr.

Reference	Resol (phr/%wt)	DCP (phr/%wt)	Carbon black (phr)	$C_{\text{crosslinking agent}}$ (mol/m ³)	v^* (mol/m ³)	Cs (%)
TPV R1	7/2.30			40	71	56 ± 2
TPV R1CB	7/2.03		41	40	71	55 ± 1
TPV D1		4/1.33		40	83	56 ± 2
TPV D1CB		4/1.17	41	40	83	50 ± 1

Rheological measurements

The experiments were carried out using an ARES (TA instrument) rheometer under inert atmosphere (nitrogen). A plate-plate geometry (diameter = 8 mm, sample thickness = 2 mm) was used.

Elongation measurements were performed on an ARES-G2 rheometer (TA instrument) using the extensional viscosity fixture (TA instrument). The experiments were conducted at 180°C for 3 different strain rates: 0.01 s⁻¹, 0.1 s⁻¹, 1 s⁻¹.

Foaming process

The foaming of the TPV samples was carried out on discs of 2 mm thick and 25 mm in diameter. The foaming process was performed on a Paar Instrument system (reference: mini bench reactor 4567) and divided in two phases. The first one consists in a pressure saturation of the PP phase at 180 °C (above its $T_m \approx 165^\circ\text{C}$). Then, the temperature is set at 130 °C. Once the equilibrium temperature and pressure are reached, the samples are left in place for 45 minutes. The global time of the saturation process is about 2 hours. Under these conditions, the solubility of CO₂ in PP and EPDM phase is respectively 7.9 wt% and 4.4 wt% of CO₂ [10][24][25]. The depressurisation is made at a rate of 1.5 MPa/s.

SEM and TEM observations

Two sample preparations are made: i) for the lower density foams ($\rho < 300 \text{ kg/m}^3$), a high sharp blade is used at ambient temperature to avoid the destruction of the foam morphology under ultra-microtome at low temperature (- 90 °C), ii) for higher density foams ($\rho > 300 \text{ kg/m}^3$), ultra-microtomy is used at - 90 °C using liquid nitrogen. SEM observations are made using a Hirox SH4000M SEM.

TEM observations are made on a Philips CM 120 TEM (transmission electron microscope) at 120 kV after being ultra-microtomed with a Leica UC-7 at $-160\text{ }^{\circ}\text{C}$ using liquid nitrogen. Samples are about 70 nm thick.

Density measurement

First, the thickness of the sample is measured and a square of $10 \times 10\text{ mm}^2$ is cut of the foam. Then the extracted part of the foam is weighted using a laboratory scale (sensibility of 0.1 mg).

Results and discussions

The influences of the chemistry nature and the crosslinking density on the morphology and mechanical properties of the EPDM network have been deeply studied in our previous work [22]. The morphology of PP/EPDM blend is shown in Fig 1 depending on the crosslinking agent. Except for the location of the carbon black (into the PP phase for DCP crosslinking and in the EPDM phase for Resol crosslinking), no PP/EPDM morphological difference is observed. From these observations we can assume that the morphology does not depend on the crosslinking chemistry (as long as the crosslinking level are close) or at least it is difficult from these images to observe any significant influence. Regarding the crosslinking density of each formulation, and/or the elastic equilibrium modulus ($\approx 3.10^5\text{ Pa}$ [22]), the rubber phase is too crosslinked to be able to foam [12][24]. Foaming of pure crosslinked EPDM samples with each content and type of crosslinker was performed to verify the literature conclusion that a high level of crosslinking prevents physical foaming. As expected, none of the crosslinked EPDM samples has demonstrated ability to foam under the foaming conditions. Furthermore in literature, it is assumed that TPV foaming is only induced by the PP phase foaming [26,27] which is confirmed by these preliminary results.

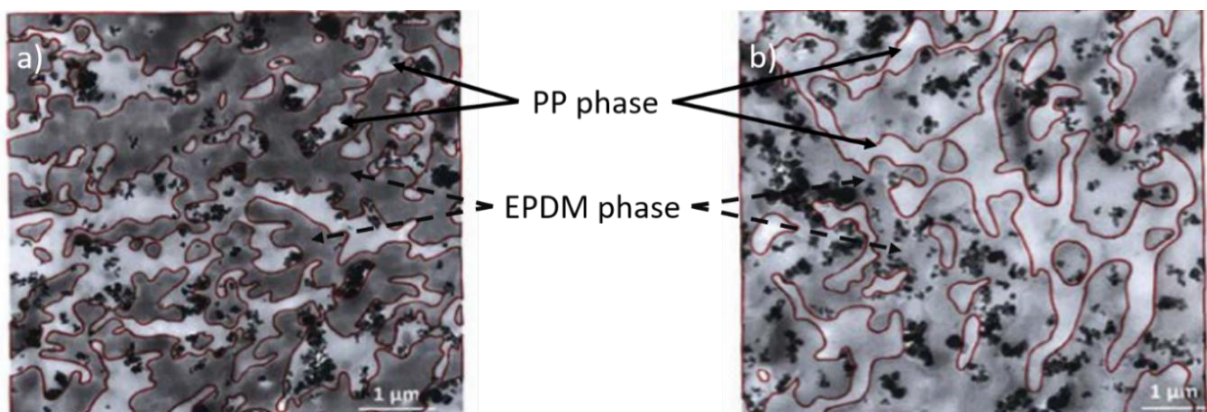


Fig 1:TEM morphology of TPV filled with 12% carbon black. a) TPV/DCP and b) TPV/Resol.

The rheological behaviour of TPV has been studied in the literature [3,7,14,19] and these studies have lightened the influence of the crosslinking density, the viscosity of both PP and EPDM on the rheology

of the TPV. The viscoelastic behaviour (apparition of strain hardening) of the polypropylene and/or EPDM does not necessarily induce the same extensional properties [7] of the resulting TPV. So, the viscoelastic behaviour of the TPV depends on the interaction of both polymers and not only on the rheology of the matrix and/or the rubber phase. However, it has been shown that the rheological behaviour of the polypropylene phase modifies the foamability of the TPV [28]. Furthermore, Li et al [29] worked on the TPV rheology with different fractions of EPDM, and concluded that the rheological behaviour of the blend tends to be closer to the rheology of pure crosslinked EPDM.

From the literature, the non-linear rheology of TPV does not come from the only rheological behaviour of the polypropylene phase. Thus, the addition of branched PP, that has demonstrated strain hardening, will not necessary induce the same rheology on the TPV [7]. So, the rheological behaviour of complex blend such as TPV is multifactorial, and not only due to the thermoplastic phase. In Fig 2, the extensional viscosity has been compared, depending on the crosslinking system containing filler (12 w% of carbon black), highlights two drastically different behaviours.

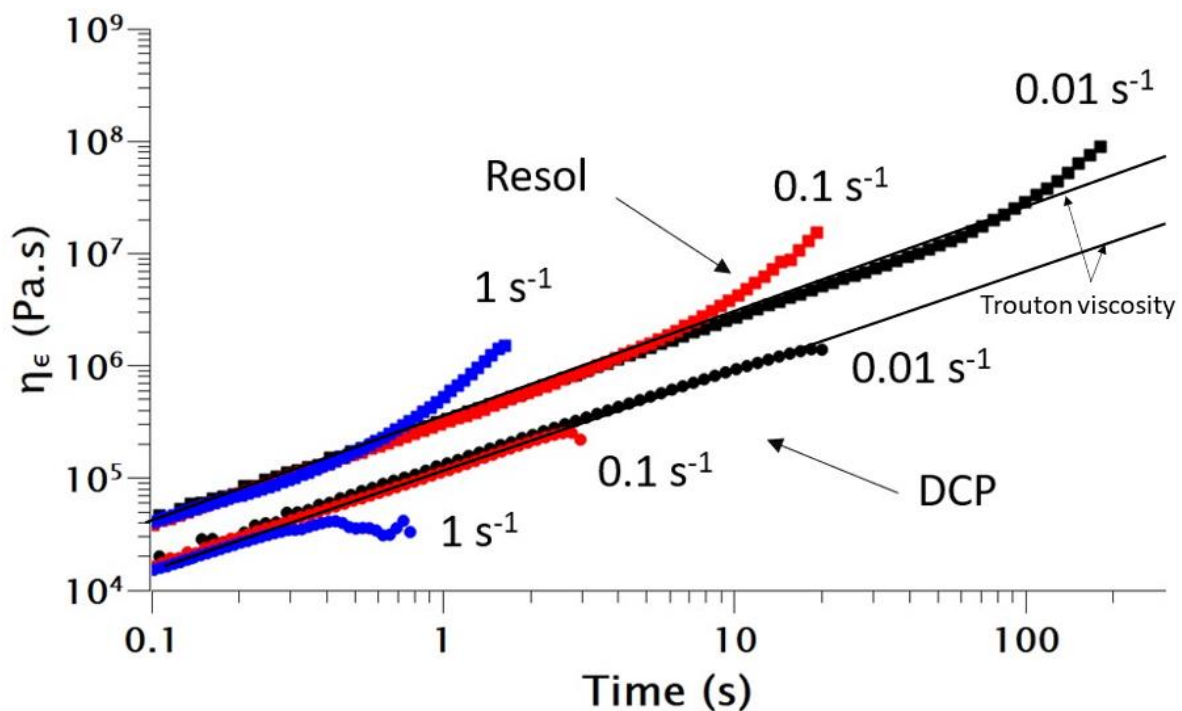


Fig 2: Extensional viscosity under three different strain rates for TPV crosslinked using Resol (square dot: $v^* = 71 \text{ mol/m}^3$) and DCP (round dot: $v^* = 83 \text{ mol/m}^3$)

The extensional viscosity of TPV/Resol samples exhibits strain hardening behaviour unlike the TPV/DCP samples. In addition, the linear viscosity of both TPV are different, indeed a difference on the value of the linear viscosity behaviour at low deformation (0.1 s^{-1}) is observed (Resol = $4 \cdot 10^4 \text{ Pa.s}$; DCP = $1.5 \cdot 10^4 \text{ Pa.s}$). This difference between these two systems is probably due to the degradation of the PP by

β -scission induced by the DCP as the elasticity of the EPDM phase are the same for both systems (table 1).

To go further, the extensional viscosity of the TPV/Resol, shown in Fig 3, proves that carbon black has little or no influence on the extensional rheology of these samples. Actually, it was proved that the carbon black has no influence on the foaming for TPV/Resol system. This could be explained by the location of carbon black, in the crosslinked EPDM phase which is a non-foaming phase [as stated before](#).

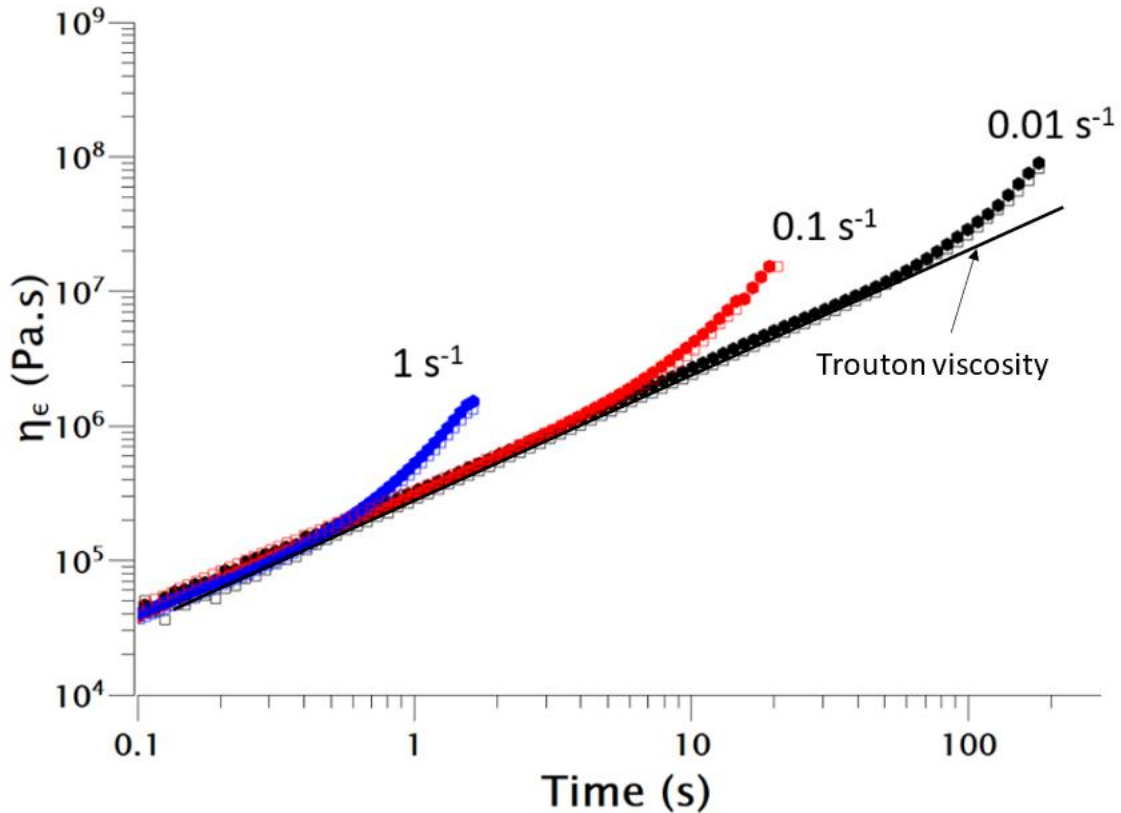


Fig 3: Extensional viscosity for TPV crosslinked with Resol, full symbols correspond to TPV filled with carbon black, open symbol corresponds to unfilled TPV

Furthermore, CB particles which are located in the EPDM phase do not influence the extensional viscosity of the TPV as the EPDM phase can be viewed as solid domains dispersed in the PP matrix.

Regarding TPV/DCP, it can be observed that the presence of carbon black fillers at the PP/EPDM interface (Fig 1) does not impact the extensional viscosity (Fig 4). However, and compared with Fig 1, the use of DCP as crosslinking agent drastically changes the extensional rheological behaviour. [Then, compared to TPV Resol samples, there is a clear decrease of the maximal Hencky deformation at break \(< 0.5\) and a non-strain hardening behaviour is observed.](#)

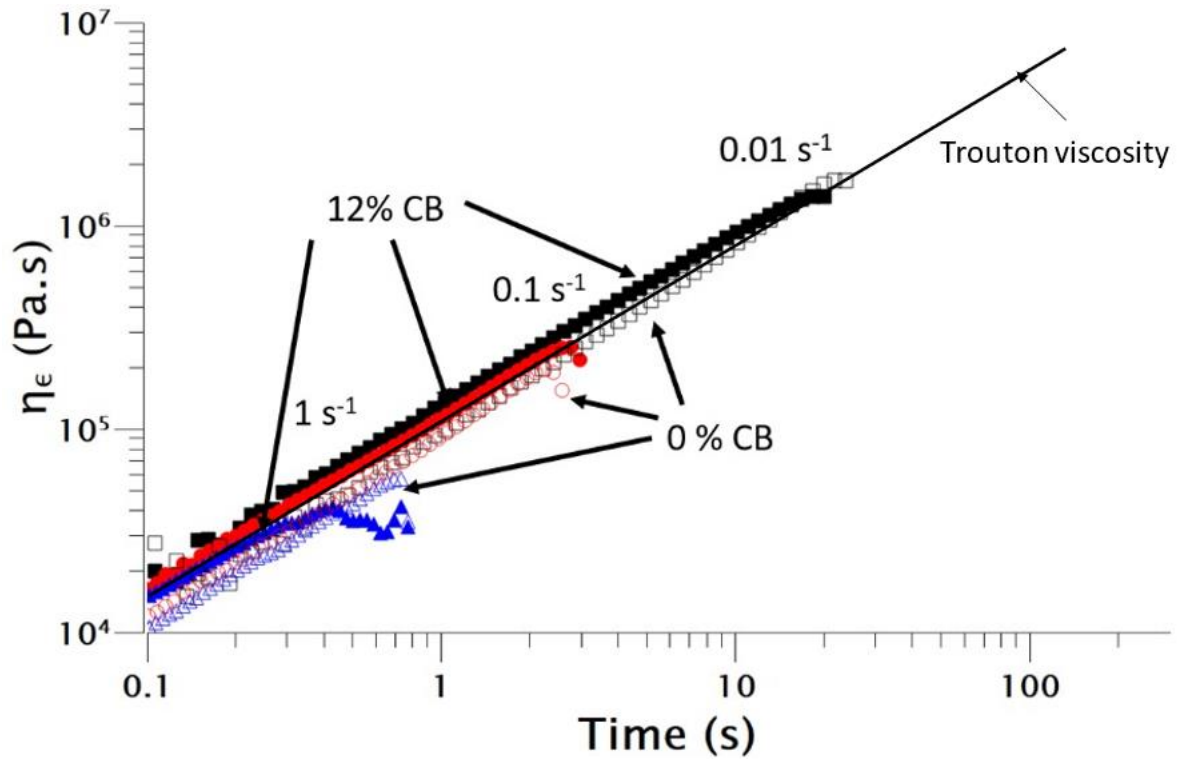


Fig 4: Extensional viscosity of TPV/DCP samples unfilled (open symbols) and filled (full symbols) with carbon black

As assumed before, the degradation of the polypropylene by β -scission reaction, due to the use of radical crosslinking chemistry, would explain the difference observed between our two system. This phenomena is well known and described in the literature [30,31]. In another work, we were able to selectively separate the PP chains by the Soxhlet extraction method. As result, the corresponding values of PP molar mass (Table 2) demonstrates the importance of DCP on the degradation of PP chain compared to Resol. However, it can be noted that the polypropylene molar mass has been decreased in the case of TPV/Resol. In this case the chain scission comes from the thermal oxidative degradation under processing.

Table 2: molar mass of the PP phase extracted by soxhlet from TPV samples

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n (PPH3060)
PP (PPH3060)	70000	380000	1
PP (TPV/Resol-12wt% CB)	30000	200000	0.5
PP (TPV/DCP-12wt% CB)	20000	75000	0.2

This result indicates that the viscosity/molar mass of the polypropylene is the first order parameter that determines the extensional viscosity of the TPV.

Furthermore, it must be pointed out that neat PP [used in this work](#) does not show any strain hardening properties as it is constituted of linear chains. In addition, it is well known that filled polymers above filler percolation exhibit strain softening even if the pure polymer matrix has a strain hardening behaviour. So, the TPVs should exhibit strain softening behaviour or at least no strain hardening. In TPV, the EPDM domains form a 3D network and due to the high volumetric fraction of EPDM (EPDM represent ~60% in volume of the TPV) the PP macromolecular chains are constrained by the elastomeric nodules. [As a result, the physical interactions in the EPDM interphase volume create a high degree of connectivity of the PP chains leading to a broadening of relaxation modes. In other words, temporary physical entanglements become permanent entanglements due to the confinement that actually defines the chain interconnectivity. This interconnectivity by the chain confinement depends on the volume fraction and diameter of the dispersed phase \[32\] as schematically shown in Fig 5.](#) Finally, the 3D network of EPDM domains resulting in the confinement of PP chains lead to a phenomena that is analogous to the grafting chain or part of PP chains just as silane (Bis[3-(triethoxysilyl)propyl]) tetrasulfide) grafting on silica blend with butane rubber leads to strain hardening [33].

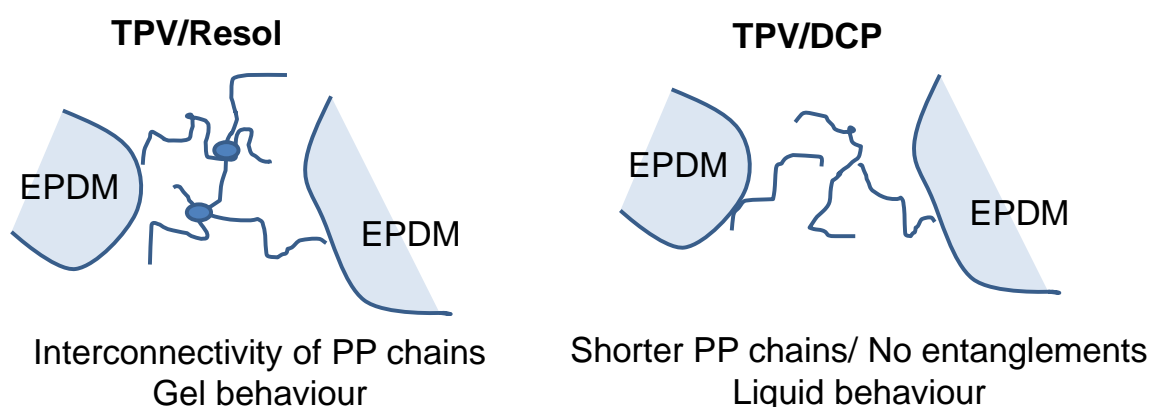


Fig 5: Scheme of the chain interconnectivity by interphase confinement between crosslinked EPDM domains. In the case of TPV/Resol the confinement leads to chain interconnectivity (permanent entanglements) whereas in the case of TPV/DCP, the β -scission leads to shorter polymer chains and therefore untangled chains

So, the PP entanglement with EPDM at the interface and confinement [induced](#) by EPDM domains can explain the strain hardening apparition in TPV/Resol samples. On the other hand, this phenomenon disappears for TPV/DCP samples because the PP chains have been degraded and are too short to induce this specific rheological behaviour. Finally, the relationship between extensional viscosity and foamability for neat polymers can be extended to complex and heterogenous system like TPV.

The strain hardening phenomenon and the maximal Hencky strain at break have been proven to be a relevant criterion to predict the ability to foam for neat polymer[13][15-18]]. Based on these extensional rheological results, the TPV/Resol samples (strain hardening) are expected to have a great ability to foam, in contrast to TPV/DCP samples which are expected to exhibit low foaming ability. Foam morphology of TPV/DCP (Fig 6) and TPV/Resol samples (Fig 7) demonstrate the relationship between foaming and extensional rheology even for complex and non-homogenous system in agreement with our extensional result. The importance of strain hardening is confirmed by the foam morphologies and the density of TPV/Resol samples (with or without carbon black) compared with the TPV/DCP sample as shown in Fig 8.

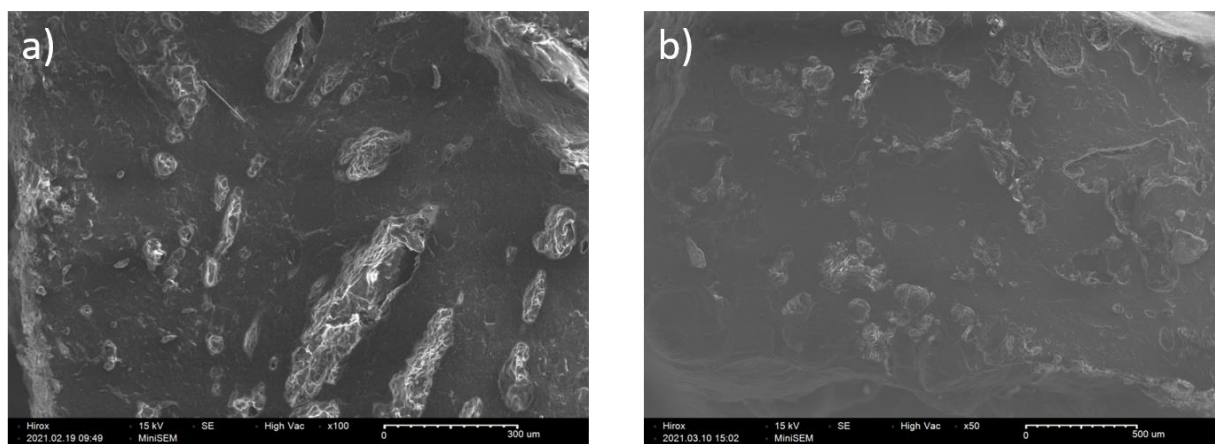


Fig 6: SEM observations of TPV/DCP foams. a): unfilled (0% CB) and b): filled with 12 wt%CB.

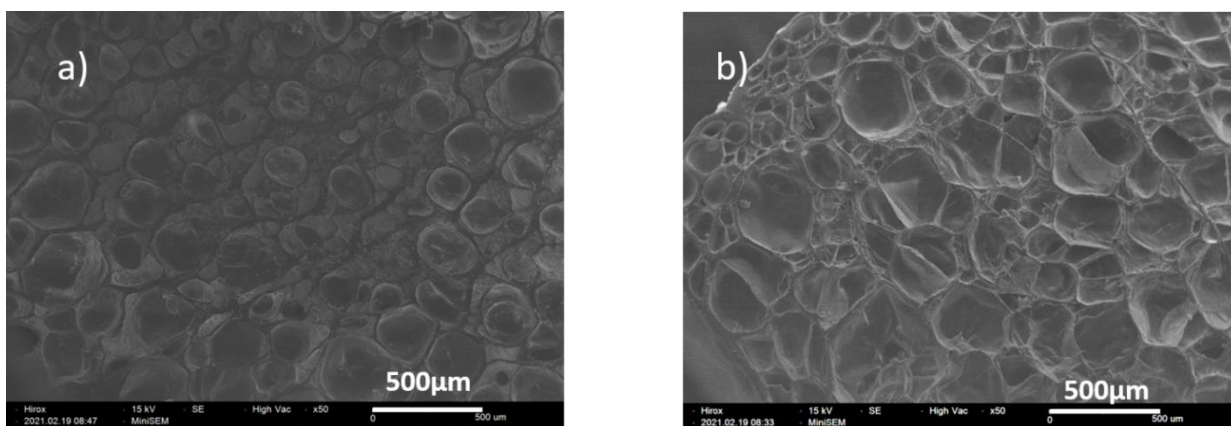


Fig 7: SEM observations of TPV/Resol foams. a): unfilled (0% CB) and b): filled with 12 wt%CB.

As expected for TPV/Resol samples, the foams obtained demonstrates a closed cell morphology with low-density ($\rho \approx 300 \text{ kg/m}^3$) whereas the density of the DCP system is around 600 kg/m^3 .

On the other hand, it could be expected that the presence of nucleating agent (carbon black in our case) enhances the foamability as the filler increases nucleation [34]. However, the addition of carbon

black on TPV does not improve the foamability of the TPVs (Fig 8). This indicates the major influence of rheological behaviour (strain hardening) on the foam expansion.

To conclude, the nature of the crosslinking chemistry of the EPDM has an influence on the foaming behaviour of the TPV even though the PP is the foaming polymer since EPDM is not able to foam at this level of crosslinking density.

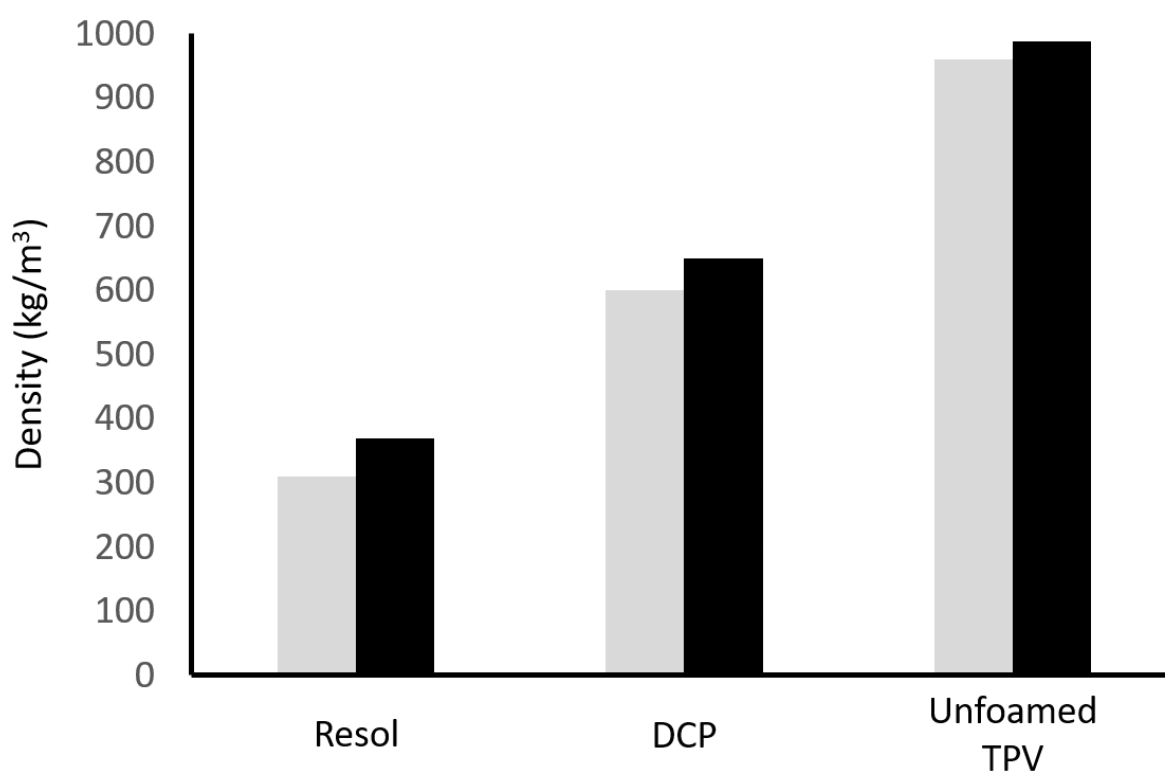


Fig 8: Density of both TPV/Resol and TPV/DCP foamed with and without carbon black (grey column: no filler, black full column: filled with 12wt% carbon black) compared with unfoamed TPV system.

Conclusions:

In this work, we have studied how the chemical nature of the crosslinking agent used during the dynamic crosslinking of EPDM influences the extensional viscosity and consequently how it affects the foaming ability of TPV samples. Due to the very high level of crosslinking density of the EPDM phase, only the polypropylene phase can foam under CO₂ batch conditions. The two TPV systems (TPV/Resol and TPV/DCP) with close crosslinking densities show distinct extensional viscosity due to the crosslinker-induced modification of the polypropylene chains. In fact, the results show the limitation of DCP as a crosslinking agent due to the β -scission degradation reaction of the polypropylene chains. On the contrary, strain hardening appears for TPV/Resol whose physic origin can be explained by the confinement of the polypropylene chains between the EPDM domains.

Thus, this work demonstrates the relationship between extensional viscosity, strain hardening precisely, and foaming ability of TPV. This type of behaviour is observed only for TPV/Resol. Indeed, a high strain hardening behaviour and a Hencky deformation show a high foaming ability even for these inhomogeneous two-phase systems. The addition of carbon black does not modify this behaviour.

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