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Curing agent-dependent localization of carbon black in thermoplastic vulcanizates

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Abstract

PP/EPDM Thermoplastic Vulcanizate (TPV) filled with carbon black (CB) has been prepared and the localization of the filler in the blend was depending on the crosslinking chemistry: in the rubber phase when the EPDM was crosslinked with phenolic resin (resol) and at the interface when the EPDM was crosslinked with dicumyl peroxide (DCP). It was proved, based on model reactions that mimicked what could happen during the process at high temperature, that DCP led to polymer chains grafting at the surface of the CB. This phenomenon was additional to the classical EPDM crosslinking and PP β -scission reactions. These reactions involved a modification of the interfacial tensions within this ternary blend, and explained preferentially the carbon black localization at the interface between the PP and the EPDM.

Key words: TPV, Carbon Black, grafting reactions, DCP, resol

1. Introduction

Thermoplastics vulcanizate (TPVs) are polymer blends of interest as they combine the properties of a crosslinked elastomer with the processability of a thermoplastic [1]. The elastomer is crosslinked during the mixing process leading to a polymer phase inversion because of the rapid and significant change in viscoelastic behavior of the elastomer, from viscoelastic liquid to viscoelastic solid. The most famous system is based on Polypropylene (PP) and Ethylene-Propylene-Diene-Monomer copolymer (EPDM) [2]–[8] as also from an industrial point of view, this blend is attractive because of its competitive price and its ability to be recycled.

The final properties of the material depend on many factors, in particular the relative proportions of each component and the morphology induced within the material as shown in our previous study [9]. Additionally, the presence of fillers, its localization and affinities with the polymers in presence can, as illustrated in the following paragraph, greatly influence the final properties in particular the mechanical ones.

Khodabandelou et al. [10] studied the impact of the localization of multi-walled carbon nanotubes (MWCNTs) in a PP/EPDM/MWCNTs (80/20/0.5 wt%) ternary system. They showed that it is beneficial to disperse the filler in the PP matrix to increase the Izod impact strength of the blend by reducing the spherulite size of the PP matrix. However, they noted that filler aggregates acted as fracture initiator. Zhu et al. [11] showed that the ideal localization of the CNT in PP/NBR (Acrylonitrile butadiene rubber)/CNT (30/70/1 wt%) TPVs is at the interface as it allows a better conductivity. Dubey et al. [12] showed that the addition of CB fillers in PE/PP/EPDM/CB blends with different compositions lead to a lack of compatibilization between the rubber and the immiscible thermoplastic blend. While the addition of EPDM to the blend resulted in a 200% improvement in elongation at break, the addition of CB filled EPDM improved this property by only 10%. They explained this phenomenon because of the accumulation of CB in EPDM that restricted the segmental mobility of EPDM. In our previous study [9], the addition of CB in a PP/EPDM based TPV

crosslinked with DCP allowed the elongation at break to be significantly improved (from 60 % to 220%) at a low PP concentration (25 phr).

Thus, many studies, as for example reviewed by Fenouillot et al. [13] and Taguet et al. [14], showed that the filler can be located in different phases of polymer blends and that different aspects must be considered to explain this preferential localization. Sumita et al. [15] in 1991 explained the wetting behavior of powder at the interface of two liquid phases and extended this approach to the localization of CB in a polymer blend. They used the wetting coefficient ω_a :

$$\omega_a = \frac{\gamma_{CB/B} - \gamma_{CB/A}}{\gamma_{A/B}} \quad \#(1)$$

Where $\gamma_{i/j}$ is the surface tension of i/j interface.

If:

- $\omega_a > 1$ CB particles distribute within the A phase
- $\omega_a < -1$ CB particles distribute within the B phase
- $-1 < \omega_a < 1$ CB particles distribute at the interface

The polymer blending process has also its influence on blend morphology. Zhang et al. [16] reported that the final filler localization in a polymer blend can be influenced by the sequence of addition of the components. For example, Elias et al. [17] have selected different sequences of addition for a PP/EVA(Ethylene-Vinyl Acetate copolymer)/hydrophilic silica (80/17/3 w/w/w) system. When the three components were loaded simultaneously in the mixing chamber, the silica was essentially dispersed in the EVA droplets. However, if the silica was pre-compounded with the PP and then blended with EVA, the silica particles appeared to be in the EVA phase too but closer to the interface. In 1998, Gubbels et al. [18] showed that the compounding time may also influence the localization of CB in PE(Polyethylene)/PS(Polystyrene) (45/55 w/w) immiscible blend. Gödel et al. [19], Baudouin et al. [20], Elias et al. [17] or Ma et al. [21] also reported the importance of the viscosity ratio onto the differences of the location of fillers in polymer blends.

All these studies showed that the prediction of the fillers localization in polymer blends is not straightforward and that a lot of parameters can influence it. Especially in the case of carbon black,

which is a filler with many polar sites, its surface modification can lead to intrinsic interactions with other components.

The main objective of this paper is to understand why carbon black filler is distributed in the EPDM phase in the case of a TPV crosslinked with phenolic resin (resol), whereas when the EDPM is crosslinked with dicumyl peroxide (DCP), the filler is rather at the interface as seen in our previous study [9]. This preferential localization at the interface in the presence of a radical initiator will be explained by simulating a model alkane chain grafting reaction on the surface of carbon black and by interfacial tension measurements.

2. Materials and methods

2.1. Materials

An ethylidene norbornene (ENB) based EPDM was selected. Vistalon 8600 (ExxonMobil Chemical, Houston, TX, USA) presents the following average molar masses values: $M_n = 69\,000\text{ g mol}^{-1}$ and $M_w = 203\,000\text{ g mol}^{-1}$ (Measured by size exclusion chromatography at 150°C with a conventional calibration in trichlorobenzene) The ^1H NMR analysis allowed to determine the molar composition of each monomer: 71.6 mol% ethylene, 26.4 mol% propylene and 2.0 mol% ENB respectively. The density and the Mooney viscosity ML(1+8) at 125°C of this EPDM are respectively 0.86 g cm^{-3} and 81 . PPH 3060 (Total Petrochemicals, Courbevoie, France) is an isotactic PP with the following characteristics given by the supplier: $M_n = 72\,000\text{ g mol}^{-1}$ and $M_w = 380\,000\text{ g mol}^{-1}$ melt flow index MFI = 1.8 g/10 min at 230°C/2.16 kg. Nypar 330 (Nynas, Stockholm, Sweden) paraffinic oil with a density of 0.87 g cm^{-3} at 15 °C was incorporated with the following proportion in the binary EPDM/plasticizer mixture: 122 phr (grams per hundred grams of Vistalon 8600). The crosslinking agents were dicumyl peroxide [(DCP) 99% purity, Sigma Aldrich, Saint-Louis, MO, USA] or resol (Nures 2055 octylphenol-formaldehyde resin from Newport Industries, ShanXi, China). The N550 carbon black (CB) (Lehvoss, Cherisy, France) with a density of $1.7\text{-}1.9\text{ g cm}^{-3}$ at 20 °C and specific surface area of $40\text{ m}^2\text{ g}^{-1}$ was selected.

The grafting reactions have been carried out in the 1,4-dioxane (Sigma-Aldrich France; 99% pure) with squalane (PP-like structure) (Sigma-Aldrich France; 96% pure) and ethylenecyclohexane (norbornene-like structure) (Sigma-Aldrich France; 99% pure). Their chemical structures are presented in **Fig 1**.

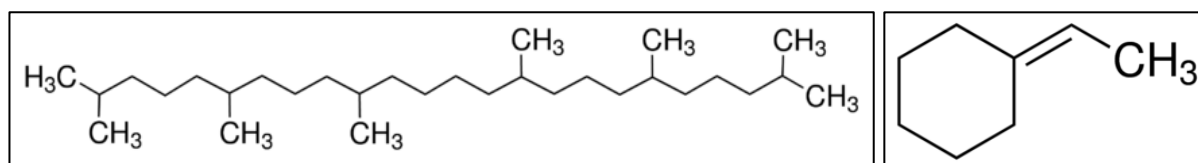


Fig 1: Chemical structure of squalane ($C_{30}H_{62}$) (left) and ethylenecyclohexane (C_8H_{14}) (right).

2.2. Samples preparation

2.2.1. Thermoplastic vulcanizates

The sample preparation is the same as employed in our previous study [9]. First the EPDM, the crosslinking agent, the carbon black and the plasticizer were introduced at 50 rpm at 60 °C in an internal batch mixer (Haake Rheomix 600, Thermo Fisher Scientific) and mixed until the torque stabilized. In a second step, the PP pellets were introduced and mixed for around 5 minutes. After that, the temperature was increased up to 180 °C while keeping the rotation speed at 50 rpm. For further characterization, the samples were finally processed with a compression mold into 2 mm-thick sheets. The specific procedures were 10 min at 180 °C for the samples cured by peroxide and 20 min at 200 °C for those cured by resol.

The carbon black concentration was kept at 12 wt%. The amount of crosslinking agent was selected to have one sample of each system with low crosslinking agent concentration (1 phr) and two others with an equivalent molar concentration of crosslinking agent, which corresponded respectively to 4 phr of DCP and 7 phr of resol (around 80 mol m⁻³). The four samples are thus composed by 100 phr of EPDM, 122 phr of paraffinic oil, 75 phr of PP, 41 phr of CB (equivalent of 12 wt%) and with 1 and 7 phr of resol or with 1 and 4 phr of DCP respectively. This composition corresponds to a weight ratio

of 57/43 EPDM/PP. They are presented in **Table 1**, with the expected crosslinking density determined from swelling measurements made on EPDM systems in our previous study [22]. In fact, thanks to the Flory-Rehner expression and by performing swelling experiment at equilibrium, the density of elastically active chains has been calculated on EPDM crosslinked samples. Since this measurement cannot be performed on TPV due to the plasticity of PP, the values determined on EPDM systems are assumed to be those expected for EPDM in TPV system.

Table 1: Samples prepared in the batch mixer, composed by 100 phr of EPDM, 122 phr of paraffinic oil, 75 phr of PP, 41 phr of CB (equivalent of 12 wt%) and crosslinking agent with their expected crosslinking density ν .

TPV 1 resol – 12 wt% CB		TPV 7 resol – 12 wt% CB		TPV 1 DCP – 12 wt% CB		TPV 4 DCP – 12 wt% CB	
Resol (phr)	ν (mol m ⁻³)	Resol (phr)	ν (mol m ⁻³)	DCP (phr)	ν (mol m ⁻³)	DCP (phr)	ν (mol m ⁻³)
1	12	7	71	1	14	4	87

2.2.2. Grafting model reaction onto CB in presence of DCP

Based on the works of Papirer et al. in 1996 [23] and more recently of Guimont et al. [24], model grafting reactions on the CB structure in presence of DCP have been performed.

For this purpose, carbon black N550 (500 mg) and anhydrous 1,4-dioxane (17.5 mL) in a round-bottom flask was sonicated for 1.5 h using an ultrasonic bath. Then, 60 mL (114 mmol) of squalane or 15 mL (114 mmol) of ethylenecyclohexane, and 0.68 g (2.52 mmol) of dicumyl peroxide were added. Grafting reactions were carried out under constant stirring and heating under reflux at 180 °C for 6 h. At the end of the reaction, grafted CB were centrifuged and further purified 6 times by centrifugation with THF as solvent. The solid material was collected, dried at 80 °C for 48 h and pressed into a thin pellet before being characterized.

The expected scheme of the grafting reaction is presented in **Fig 2**.

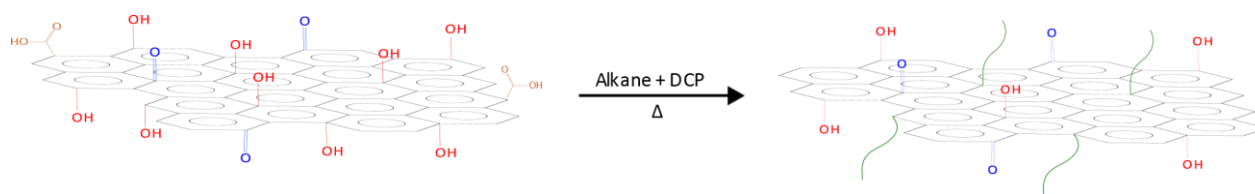


Fig 2: Scheme of the grafting reaction of alkane chains (green) onto CB surface in presence of DCP.

Different CB samples have been prepared and are described in **Table 2**.

Table 2: Description of the grafting model reactions recipe.

	CB	1,4-dioxane	squalane	ethylidene-cyclohexane	DCP
CB	✓	✓	-	-	-
CB / squalane	✓	✓	✓	-	-
CB / squalane / DCP	✓	✓	✓	-	✓
CB / ethylidencyclohexane	✓	✓	-	✓	-
CB / ethylidencyclohexane / DCP	✓	✓	-	✓	✓

2.3.Characterizations

2.3.1. Scanning and Transmission Electron Microscopy (SEM and TEM)

For SEM analysis, ultramicrotomy was used to obtain cryogenically surfaced samples. The equipment was a QUANTA 250 SEM with the following specificities used for the observations: Vacuum at 1 torr and a voltage of 10 kV.

For the TEM analysis, a Leica UC 7 working under liquid nitrogen atmosphere at - 160 °C was used to reach thin samples of about 70 nm in thickness. The observation of these samples deposited on copper grids (Mesh 300) was carried out with a Philips CM 120 TEM transmission electron microscope at 120 kV.

2.3.2. Soxhlet extraction and Size Exclusion Chromatography analysis

The different phases of TPV samples were separated by Soxhlet extraction. The sample (1 g) is placed in small pieces in a thimble and subjected to Soxhlet extraction during 48 h with 250 mL of p-xylene to solubilize the PP. The system is placed at 180 °C. The extracted PP is then analyzed by size exclusion chromatography. It has been done in 1,2,4 trichlorobenzene at 150 °C on a Viskotek HT-GPC with a differential refractometer detector.

2.3.3. Grafted carbon black characterizations

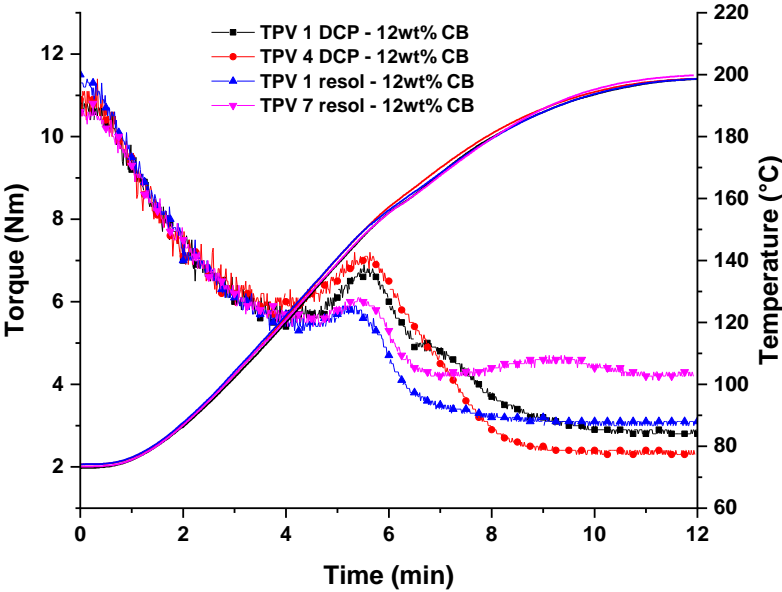
TGA analyses were carried out with a Mettler Toledo Thermal Analysis TGA/DSC. Samples were heated at 10 °C min⁻¹ from 25 to 900 °C under helium flow (25 ml min⁻¹).

Contact angle measurements with water and diiodomethane on pressed carbon black pellets were performed at room temperature with an optical tensiometer (KRÜSS Scientific) equipped with a camera to visualize the drop on the surface of powder-pressed tablet. The volume of the drop deposited during the measurements is 1 µL and for reasons of drop stability, contact angle were measured 2 sec after the drop was deposited. Each time, four measurements are performed at different locations on the surface to ensure the reproducibility.

3. Results and discussion

When the TPV is processed under the temperature increase from 60 to 180 °C, the dynamic crosslinking takes place and consequently modify the viscosity ratio between the two phases that induces the phase inversion within the blend as described in literature [25][26][27]. The **Fig 3** shows the torque evolution for each prepared TPV during the second step of the process in the internal mixer: the increase in temperature from 60 to 190 °C. At time = 0, all the components have already been introduced in the mixer. The first increase in torque at about 5 – 6 min corresponds to the melting of the PP [9]. A second increase in torque can also be observed in the case of the TPV crosslinked with 7 phr resol and the one with 1 phr DCP. This second increase in torque is actually the

signature of the phase inversion of the blend. This phenomenon is not observed at 1 phr resol as the crosslinking reaction advancement may be low and so the phase inversion in the material cannot be observed. In fact, based on our previous study, the crosslinking density of the EPDM phase



crosslinked with 1 phr of resol in the TPV should be low around 12 mol m^{-3} [22].

Fig 3: Variation of the torque versus mixing time during TPVs processing crosslinked with DCP or resol in presence of 12 wt% of CB.

Actually, from the electron microscopy images in **Fig 4** it can be confirmed that in this blend the phase inversion has not yet taken place. Note that for 4 phr DCP the phase inversion phenomenon is not observable on the torque evolution but certainly masked under the signal corresponding to the PP melting. Concerning the value of the torque at the end of the process, it can be noted that in the case of the TPV crosslinked with resol, the torque is higher the more crosslinking agent is in the mixture. This reflects a higher viscosity of the material and therefore a higher crosslinking of the elastomer. In the case of TPV crosslinked with DCP, the more crosslinking agent there is, the lower the torque. This decrease in viscosity cannot be not due to a lower crosslinking density as we showed in our previous study [22] crosslinking densities of 14 mol m^{-3} and 87 mol m^{-3} for EPDM crosslinked with 1 and 4 phr of DCP respectively. Thus, this result indicated that free radicals initiated by the DCP

decomposition may causes β -scission reactions of the PP chains in the blends as well described in literature [28]–[31].

To highlight the β -scission reactions of PP chains, TPV were submitted to a Soxhlet extraction in p-xylene for 48 h and soluble PP chains were analyzed by size exclusion chromatography. The results are reported in **Table 3**.

Table 3: Average molar mass of PP determined by size exclusion chromatography.

	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w / M_w PPH3060
PPH3060	70 000	380 000	1
PP (TPV 7 resol – 12 wt% CB)	30 000	200 000	0.5
PP (TPV 4 DCP – 12wt% CB)	20 000	75 000	0.2

It can be observed a drastic decrease in the average molar masses of the PP chains (divided by 5) from the TPV crosslinked with DCP. This confirms the PP β -scission reactions is in accordance the torque decrease of the blend. A slight decrease in the average molar mass can also be observed for the PP from the TPV crosslinked with resol and could be explained by thermo-mechanical degradation during the melt shear process. This phenomenon was for example observed by Oliveira et al. [32] studying the role of shear in the degradation process of polylactic acid (PLA). They observed that thermo-mechanical degradation induced a larger decrease in PLA molar mass than thermo-oxidative degradation. The intrinsic viscosity has decreased from 83 mL g⁻¹ to 43 mL g⁻¹ after 25 min in an internal mixer at 100 rpm, while it only decreased to 60 mL g⁻¹ after 120 h in an oven at 140 °C.

Concerning now the morphology evolution of these systems (**Fig 4**), it can be observed that the morphology of the TPV crosslinked with 7 phr of resol has drastically changed in comparison to the blend crosslinked with only 1 phr of resol because phase inversion occurred. In this blend, CB fillers appear to be located in the EPDM phase, which is in the foreground of the image. In contrast, in the blends crosslinked with DCP, the CB fillers appear to be more located at the interface between EPDM

and PP. This difference in the localization of the filler in the material is highlighted in **Fig 5**, which shows the filled TPVs crosslinked with 4 phr of DCP and 7 phr of resol, whose different phases have been contoured. This figure comes from our previous study [9].

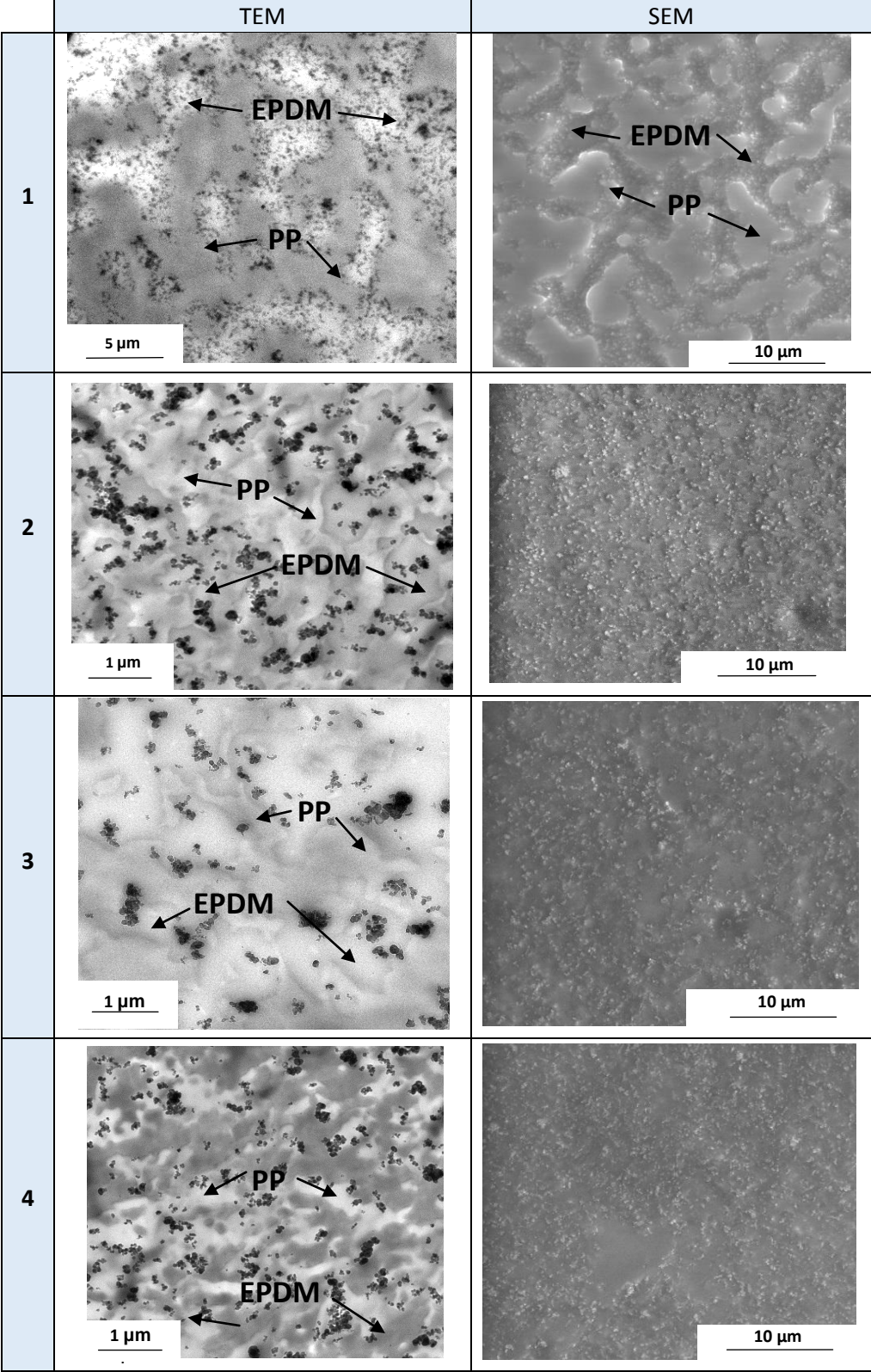


Fig 4: TEM and SEM images of the TPVs (1: TPV 1 resol – 12 wt% CB, 2: TPV 7 resol – 12 wt% CB, 3: TPV 1 DCP – 12 wt% CB, 4: TPV 4 DCP – 12 wt% CB).

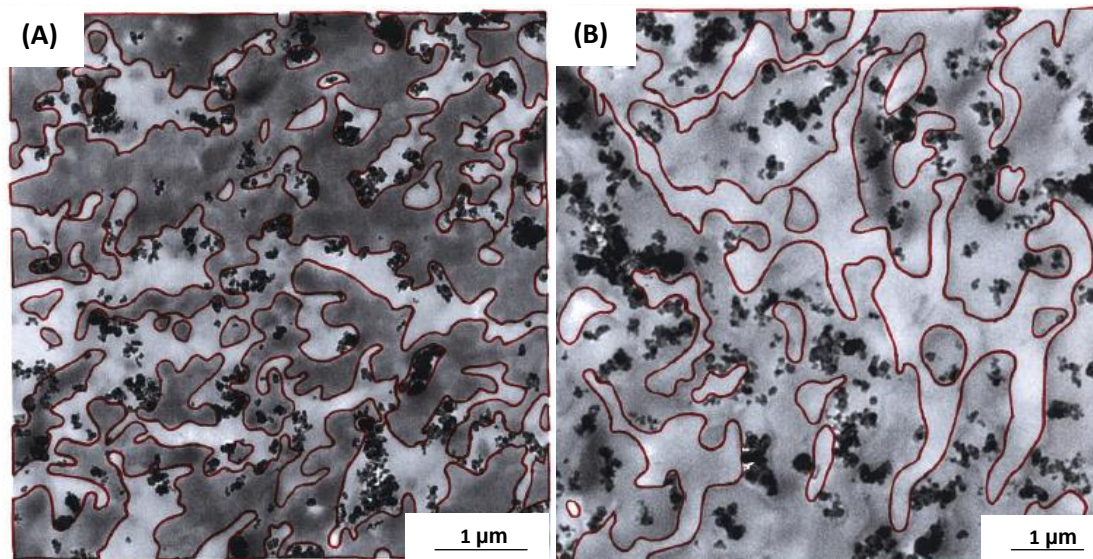


Fig 5: Location of the CB filler into TPV observed by TEM: **(A)** TPV 4 DCP – 12 wt% CB with filler located at the interface, **(B)** TPV 7 resol – 12 wt% CB with the filler located in the EPDM phase [9].

To explain this difference in the location of the CB when using DCP model grafting reactions between squalane or ethylenecyclohexane, whose structure are close to that of PP or the norbornene unit of the EPDM respectively (**Fig 1**), and carbon black in presence of DCP were carried out to simulate what could happen during the TPV processing. Moreover, contact angle measurements and wettability coefficients calculations have been done to evaluate if a modification of the surface energy occurred.

On the TGA thermogram shown in **Fig 6**, neat CB particles show good thermal stability while modified CB particles present mass losses due the presence of grafted organic compounds. In the case of fillers modified in the presence of DCP with ethylenecyclohexane, a mass loss of 2.6 %, and one of 4.5 % with squalane can be observed respectively. Note that without the action of DCP, alkane grafting reactions were observed (respective masses loss of 2.3 % and 3.3 % with ethylenecyclohexane and squalane) which may be due to free radicals initiated at high temperature during the reaction times (6 h at 180 °C). However higher values of masses loss obtained in presence of DCP evidenced the contribution of the peroxide in the alkane grafting reaction. The data calculated from TGA curves of all the samples are listed in **Table 4**. To calculate the grafting density, a specific area of 40 m² g⁻¹ for

the CB has been used. We can notice a higher grafting density in the case of the use of ethylenecyclohexane in comparison to the use of squalane and this grafting density is also higher than that reported previously by Guimont and co-workers [24] (0.09 mmol of pentadecane groups per gram of graphite oxide sheets) while their grafting density is close to the one for CB grafted with squalane.

This can be explained by the fact that the ethylenecyclohexane molecule is smaller than squalane or pentadecane thus limiting the steric hindrance. In addition, the allylic proton of the ethylenecyclohexane may be more prone to grafting reaction in the presence of free radicals. As said previously, the grafting occurred even without the presence of DCP due to the high temperature but the role of DCP is evidenced in the case of squalane grafting as the grafting density is increased respectively from 1.6 to 5.3 $\mu\text{mol m}^{-2}$ without and with DCP.

It can be concluded that the grafting reaction took place on the carbon black surface and is enhanced by the addition of DCP.

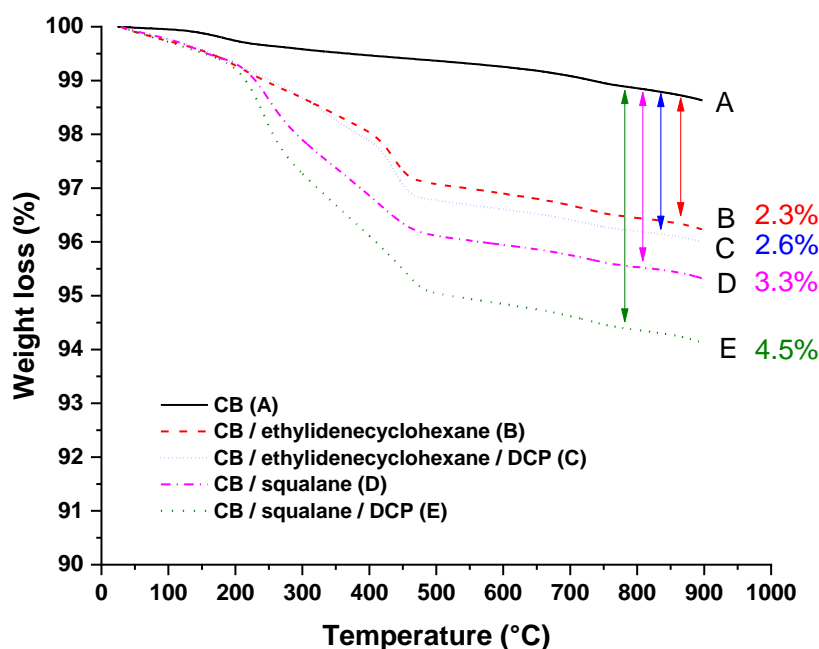


Fig 6: Thermogravimetric data for CB (A), CB / ethylenecyclohexane (B), CB / ethylenecyclohexane / DCP (C), CB / squalane (D), and CB / squalane / DCP (E) treated at 10 °C/min.

For comparison, a grafting reaction with ethylenecyclohexane was also performed using resol instead of DCP. However, no mass loss was observed, the thermogram is shown as supporting information in **Fig S1**. Thus, no further attention is paid to the resol action in the following discussion.

These observations when transposed to the TPV classical elaboration explained the grafting of polymer at the CB surface when DCP is used and in particular PP chains whereas the resol does not

have any action. **Table 4:** Data calculated from TGA curves of grafted CB.

Samples	TGA weight loss (%)	Concentration (mmol g ⁻¹)	Grafting density (μmol m ⁻²)
CB / ethylenecyclohexane (B)	2.3	0.34	8.5
CB / ethylenecyclohexane / DCP (C)	2.6	0.36	9.0
CB / squalane (D)	3.3	0.06	1.6
CB / squalane / DCP (E)	4.5	0.21	5.3

Moreover, from the contact angle measurements of these carbon blacks in **Fig 7**, it can be pointed out that initially the CB has a hydrophilic surface behavior ($\theta_{\text{water}} = 18 \pm 6^\circ$) while the wettability of grafted carbon blacks are largely modified (CB / squalane: $\theta_{\text{water}} = 118.5 \pm 2.5^\circ$; CB / ethylenecyclohexane: $\theta_{\text{water}} = 123 \pm 0^\circ$). The powder has a hydrophobic behavior which is even more pronounced when the grafting has been carried out in the presence of DCP for the squalane grafted CB ($\theta_{\text{water}} = 131 \pm 2^\circ$). This hydrophobic behavior evidenced the alkane chains grafting on the surface of CB and the modification of its surface tension [33]. Again, the highest value obtained when the reaction is carried in presence of DCP confirmed the highest squalane grafting yield. Moreover, a significant decrease in the polar component γ_s^D can be noted from $73 \pm 2 \text{ mN.m}^{-1}$ for the CB to less than 11 mN.m^{-1} for the grafted-CB. This decrease can be explained by the increase of non-polar groups in the CB surface evidencing again the grafting of the alkane chains.

	Θ_{water} (°)	$\Theta_{\text{diiodomethane}}$ (°)	γ_s^d (mN/m)	γ_s^p (mN/m)	γ_s (mN/m)	Picture with water
CB (A)	18 ± 6	0 ± 0	53 ± 1	73 ± 2	80 ± 2	
CB / ethylidenecyclohexane (B)	123 ± 1	16 ± 2	52 ± 1	6 ± 1	58 ± 1	
CB / ethylidenecyclohexane / DCP (C)	124 ± 5	12 ± 1	51 ± 1	6 ± 1	58 ± 1	
CB / squalane (D)	118 ± 2	5 ± 3	53 ± 1	11 ± 1	57 ± 1	
CB/ squalane / DCP (E)	131 ± 2	16 ± 2	51 ± 1	8 ± 1	59 ± 1	

Fig 7: Contact angle measurements and pictures associated of CB tablets.

The wettability coefficient ω (equation (1)) used by Sumita et al. [15] can be determined by the calculation of the surface tensions $\gamma_{i/j}$ of i/j interfaces as follows:

$$\gamma_{i/j} = \gamma_i + \gamma_j - 4 \left(\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \right) \quad \#(3)$$

With γ_j^d the dispersive component of j, and γ_j^p its polar component.

Table 5: Wettability coefficients calculated with equations (1) and (3) for filled TPVs crosslinked by resol or DCP.

	PP	EPDM / resol	EPDM / DCP	CB	ω
System	✓	✓	-	✓	-3,7
	✓	-	✓	✓	-0,8

Thus, these coefficients, reported in **Table 5**, evidenced that in TPV system crosslinked with resol, the carbon black will be preferentially located in the EPDM phase ($\omega = - 3.7 < 1$). In the case of TPV crosslinked with DCP, the surface tension is modified, and the resulting wettability coefficient is $-1 < \omega < 1$. The carbon black filler is well located at the interface between the PP phase and the crosslinked EPDM one which is in accordance with the electronic microscopy observations.

4. Conclusion

In this study, different localizations of the CB fillers depending on the crosslinking chemistry used to cure the EPDM phase of the PP/EPDM TPV have been discussed. The carbon black is in the EPDM phase when resol is used, which is in accordance with the wettability coefficient calculation. However, the filler is at the interface when DCP is used and due to several reactions. Firstly, it allows the dynamic crosslinking of the elastomer but also generates chain breaks by β -scission reactions either on the PP or on the EPDM. Moreover, this reactivity induced grafting reactions on the carbon black surface as demonstrated with model reactions that mimicked what could happen in the polymer medium during the process. In addition, the interfacial tension is also modified in

comparison with the one of the TPV crosslinked with resol. These phenomena explained the different location of the carbon black on the system.

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Supporting information

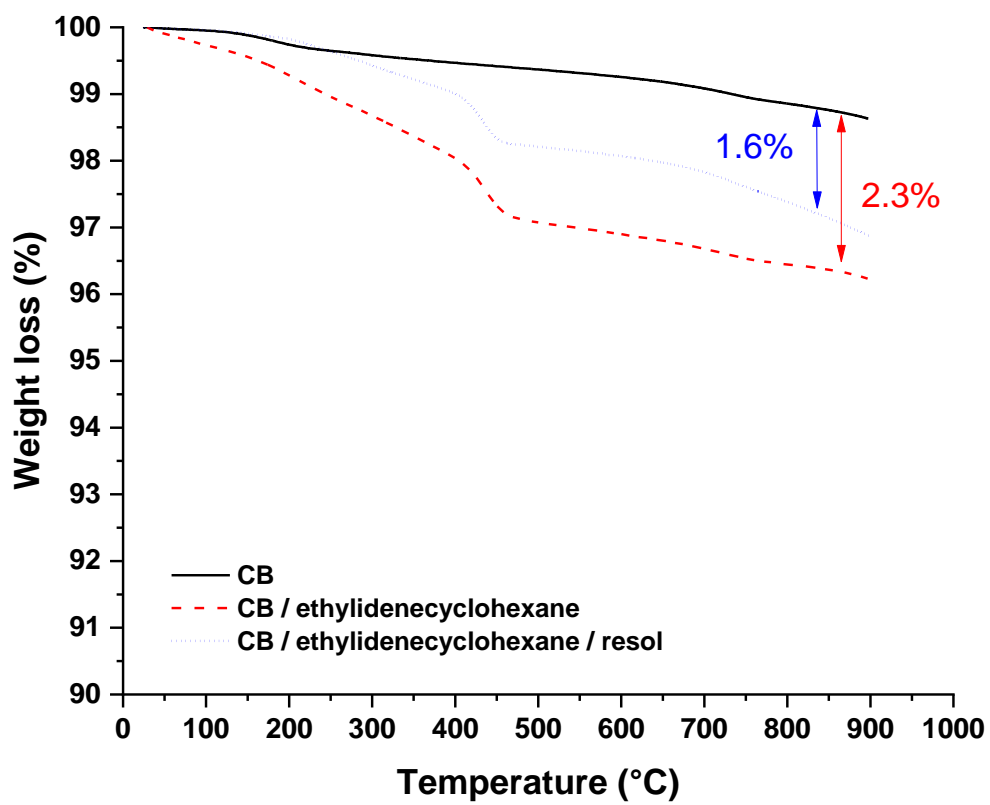


Fig S1: Thermogravimetric data for CB (line), CB / ethylenecyclohexane (dash), CB / ethylenecyclohexane / resol (dot).