



Morphology development in thermoplastic vulcanizates (TPV): Dispersion mechanisms of a pre-crosslinked EPDM phase

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ABSTRACT

The fragmentation and dispersion in molten polypropylene (PP) of several pre-crosslinked and plasticized ethylene–propylene–diene terpolymer (EPDM) networks was studied. Thus, the morphologies and mechanical properties of PP/EPDM blends having similar compositions but made from either un-crosslinked, pre-crosslinked or dynamic-crosslinked EPDMs were compared. The results first highlight the importance of the gel fraction of the pre-crosslinked EPDMs, as well as the impact of the thermoplastic matrix proportion on the quality of the dispersion of such networks. As a result, pre-crosslinked EPDM having a gel fraction below $g_{EPDM} = 0.7$ can be finely and homogeneously fragmented and dispersed in presence of PP. It can be then admitted a collision–coalescence–separation type erosion mechanism of the EPDM domains. Nevertheless, contrarily to some theoretical model expectations, a partial fragmentation of the chemical networks was always observed even at very high crosslink density ($g_{EPDM} > 0.7$). Finally, the blends crosslinked under shearing (dynamic-crosslinked) showed a clear mechanical property synergy due to their fine and homogeneous morphology coupled with the full crosslinking of the elastomer. In the end, these results brought significant information on TPV morphology stabilization and their related mechanical properties.

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1. Introduction

Ethylene–propylene–diene (EPDM)/polypropylene (PP) blends are surely one of the most currently used elastomer/thermoplastic blends on the market. The study of the inner source of their impressive processing and mechanical properties is a subject of great interest having many relevant consequences on the industrial thermoplastic vulcanizates (TPVs) production [1–4]. Actually, such

thermoplastic/elastomer blends present some specific and very interesting properties depending on their morphology, as they can combine the elasticity of the cross-linked elastomeric phase with the processability of the thermoplastic. Over the years, many studies have brought very useful information regarding the highly important correlation between such polymer blend morphology and their final mechanical properties [5–8]. Thus the key to adjusting and optimising their properties is to exhaustively control their morphology development, which can be quite complex especially regarding the quality of the dispersion of the elastomer in presence of the thermoplastic phase.

Obviously, the final morphology of such blends directly depends on the composition and compounding route

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which clearly play a primary role on the final properties of TPVs [9–14]. The initial morphology of such blends prior to the crosslinking step is also a subject of great interest. It has to be set to endure the forthcoming modifications through the crosslinking step which irremediably leads to a drastic increase of viscosity of the elastomeric phase during crosslinking, inducing a complex morphology evolution and stabilization. Additionally, the nature of the crosslinker and the extent of crosslinking of the elastomeric phase are very important as it modifies the structure, the viscosity and the elasticity of the elastomeric phase, thus the final morphology and properties of such blends [15–26]. Such dynamic crosslinking (crosslinking under processing conditions) can also induce a phase inversion which must be taken into consideration during the processing of such blends [27,28].

Just as well, the interface ruled by the interfacial tension of the polymers [29], also plays an active role on the final morphology stabilization [30,31]: as generally observed, a phase compatibilization can drastically modify the morphology and improve the final properties of the blends [32–38]. Furthermore, the addition of nano-particles such as silica or carbon black can strongly modify the interactions balance at the blend interfaces [39–46]. Additionally, the effect of the proportion of plasticizer and its diffusion within each phases are just as important [47–51].

Thus, the main objective of this paper is to study the dispersion of crosslinked and plasticized EPDM networks in presence of a thermoplastic matrix at the most relevant compositions. Also, due to the complexity of the involved mechanisms which are, indeed, tightly linked to the elaboration of any TPV, we intend to separate the effect of blending from the actual chemical crosslinking aspect. We thus focus on the impact of the shearing on both the thermoplastic and the pre-crosslinked EPDM phases. Actually, virtually no study of this type has been reported in the literature, this paper therefore aims at addressing new information on that matter. Henceforth, we will first describe the main morphologies of blends elaborated with PP and pre-crosslinked EPDMs having various crosslink densities, as well as with un-crosslinked and dynamic-crosslinked EPDM. We will then examine their morphology stabilization in function of the time of mixing to investigate the mechanisms of morphology development in TPVs. We will finally bring forwards new results concerning the morphology – mechanical properties correlation, to further discuss on the impact of a dynamic crosslinking step during such blend elaboration.

2. Experimental part

2.1. Materials

PP was supplied by Arkema (PPH 3060) with a melt flow index MFI = 12 g/10 min. The molecular weights are: $\overline{M}_n = 67,300 \text{ g mol}^{-1}$ and $\overline{M}_w = 273,000 \text{ g mol}^{-1}$.

Experiments were carried out with an EPDM from ExxonMobil Chemical (Vistalon 8800), an ethylene terpolymer that comprises 53.5 wt.% of ethylene and 10 wt.% of

ethylidene norbornene. The following values of molecular weight were measured: $\overline{M}_n = 160,000 \text{ g mol}^{-1}$ and $\overline{M}_w = 310,000 \text{ g mol}^{-1}$. This terpolymer has a specific gravity of 0.86 g cm^{-3} , and is oil-extended with 13% in weight of paraffinic oil, which yields to a total specific gravity of 0.87 g cm^{-3} and a Mooney viscosity $ML_{(1+4)}$ of 73 at $125 \text{ }^\circ\text{C}$. Additionally, paraffinic oil (Torilis 7200, TotalFina-Elf, France) was incorporated as oil extender into the Vistalon 8800 to mimic industrial compositions. The specific gravity of this oil is 0.90 g cm^{-3} at $20 \text{ }^\circ\text{C}$. Its proportion in the PP/EPDM/plasticizer blend was set, according to the industrial standard, to 60 phr (grams per hundred grams of Vistalon 8800) for all blends. The corresponding volume fraction of oil (initially present in EPDM + added) is 0.445. Furthermore, radical crosslinking of EPDM was carried out by means of an octylphenol-formaldehyde resin (SP1045, Schenectady International, USA) called resol in the following. The polymers and chemicals were kindly supplied by Hutchinson (Chalette-sur-Loing, France) and were used as received from the supplier.

2.2. Compounding routes

2.2.1. Dispersion of pre-crosslinked EPDM networks in PP

First of all, concerning the elaboration of randomly crosslinked and plasticized EPDM networks, such samples were made of the elastomer, the processing oil extender and the curing system were prepared in an internal batch mixer (Haake Rheomix 600, Thermo Electron) at $100 \text{ }^\circ\text{C}$. As shown in Fig. 1, the following protocol was used: first, the polymer was introduced (at time $t = 0$) into the batch chamber and sheared for 2 min at 120 rpm in order to ensure the thermal homogenization of the elastomer. The plasticizer was then poured in and the two components were mixed until torque stabilization. Prior to introducing the curing system, the temperature and rotation speed were decreased ($80 \text{ }^\circ\text{C}$ and 50 rpm, respectively). As soon as the torque had stabilized, the curing system (resol and catalyst) was introduced and the mixing was allowed to go on until torque started to increase. The blends were then quickly quenched in order to prevent the crosslinking reaction from occurring inside the mixer, then compression molded at $100 \text{ }^\circ\text{C}$ for 2 min into 1 mm thick samples, then stored away from light and heat until further testing.

The standard reference amount of resol was 4% w/w (or phr) on the EPDM basis, and 0.6 phr SnCl_2 was used as catalyst for all sample preparations i.e. 0.37% weight fraction for all these blends. In order to vary the degree of crosslinking from the standard formulation, the materials were prepared with various amounts of curing resin: 1, 1/4, 1/7, 1/10 and 1/30 of the reference quantity of curing crosslinker (resol resin) as described in our previous paper [52]. In the following, the EPDM preparation crosslinked with the regular amount of curing additives will be named the “reference” sample (REF), whereas the others will be referred to via the corresponding ratios of crosslinking agent used in their formulation (REF1/4 to REF1/30) as presented in Table 1. The fraction of plasticizer includes both the 60 phr of paraffinic oil and the fraction of processing plasticizer originally included in the Vistalon 8800.

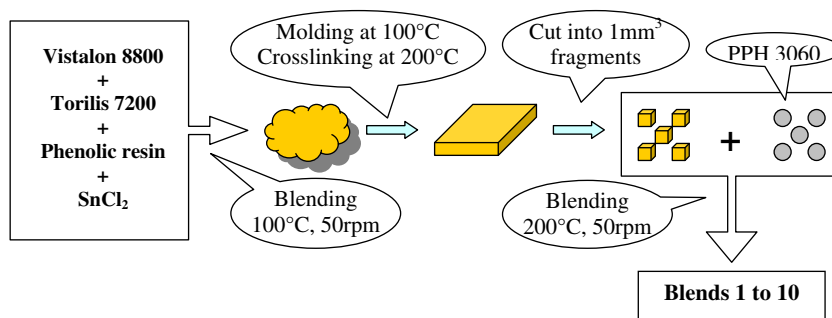


Fig. 1. Schematic representation of the blend preparation.

The molded sheets were then crosslinked during subsequent molding in a press at 200 °C for adjustable times according to our previous work [52]. As shown in Table 1, different properties of these plasticized and crosslinked EPDM samples have been determined. The gel fraction of the EPDM phase as well as the linear viscoelastic parameters were determined according to our previous work [52]. To determine the gel fraction of the cross-linked samples, soluble chains were extracted with tetrahydrofuran using standard procedure over 96 h with renewals of the solvent.

Furthermore, by applying the Cox-Merz rule between absolute complex viscosity and steady shear flow viscosities we determined the viscosity ratios between these pre-crosslinked EPDM preparations and the isotactic PP at 200 °C and 50 s⁻¹ for further discussions. Finally, the tensile properties (Young modulus, stress and deformation at break) of these EPDM samples have been determined at a constant speed of displacement (25 mm/min, *T* = 25 °C).

These samples, showing a large panel of crosslink densities, were then manually cut into 1 mm³, dimension very similar to the size of the PP granules used for the following blending. Such blends were prepared using isotactic PPH3060 and each of the previous EPDM samples at 200 °C without any additional plasticizer. Blends were dumped after stabilization of the torque and left to cool at room temperature. The first series (Blends 1–5) was made using 80% of PPH3060 and 20% of each of the five crosslinked and plasticized EPDM samples. The second series (Blends 6–10) was prepared using 30% of the same isotactic polypropylene and 70% of each of the five EPDM preparations.

On the other hand, sampling of the material has been done within the mixing chamber at various times in order to assess the variation of the morphology of the blend with the time of mixing. Two representative kinetics have been selected: Blend 5 (PP/EPDM (80/20), pre-crosslinked EPDM: REF, $\eta_{EPDM}^* = 0.998$) and Blend 7 (PP/EPDM (30/70), pre-crosslinked EPDM: REF1/10, $\eta_{EPDM}^* = 0.896$). Such a study has been achieved by taking samples at the exact same location within the internal mixer at various times of blending, thus allowing us to follow the blend morphology evolution with the time of mixing.

2.2.2. Dynamic-crosslinked PP/EPDM samples

Additionally to these Blends 1–10 made of pre-crosslinked EPDMs, we prepared two blends with the reference quantities of reactants (i.e. 4 phr of resol + 0.6 phr of SnCl₂) but by dynamic crosslinking the EPDM in presence of either 80% or 30% of PP. These formulations will be referred as DynCross1 and DynCross2, respectively. These blends were thought to highlight the importance of the dynamic crosslinking route on the final morphology and mechanical properties. Furthermore, two corresponding blends (Uncross1: 80% PP and Uncross2: 30% PP) were also prepared without any curing agent for comparison purposes.

To prepare these samples, the EPDM phase was first introduced into the blender and sheared for 2 min at 120 rpm and 200 °C. The plasticizer was then poured in and the blend was mixed at 50 rpm until torque stabilization. As soon as the torque had stabilized, the polypropylene was introduced and the torque was left to stabilize. For reactive blends DynCross1 and DynCross2, the curing system (resol and catalyst) was added and the mixing was

Table 1

Linear viscoelastic and tensile strength properties of plasticized EPDM crosslinked at different density. With $\tan \delta = C''/G'$ the loss tangent at the equilibrium, μ the density of chemical crosslinking bridges, G_e the equilibrium elastic modulus, swelling ratio in THF solvent at room temperature, η_{EPDM}^* the absolute complex viscosity of the EPDM crosslinked at 50 rad s⁻¹ samples ($\eta_{PP}^* = 2000$ Pa s at 200 °C and 50 rad/s [49]), *E* Young's modulus, σ_b and ϵ_b the stress and strain at break, respectively.

Samples	% w/w of resol	% w/w of plasticizer	Gel fraction	$\tan \delta$	Swelling ratio	μ (mol m ⁻³)	G_e (Pa)	η_{EPDM}^* (Pa s)	$\eta_{EPDM}^*/\eta_{PP}^*$	<i>E</i> (kPa)	σ_b (kPa)	ϵ_b (%)
REF	2.43	37	0.998	0.01	4.3	64	3.3×10^5	3.4×10^4	17	620	920	140
REF1/4	0.62	37	0.989	0.07	8.0	21	9.8×10^4	1.6×10^4	8	390	680	490
REF1/7	0.35	37	0.962	0.12	11.0	9.6	5.8×10^4	8.5×10^3	4.25	380	620	810
REF1/10	0.25	37	0.896	0.18	14.7	3.90	3.4×10^4	5.5×10^3	2.75	170	440	870
REF1/30	0.08	37	0.700	0.40	26.7	0.80	2.0×10^3	2.2×10^3	1.1	180	210	950

allowed to go on for 10 min to ensure the complete crosslinking of the EPDM. Finally the blends were compression molded at 200 °C for 2 min into 1 mm thick samples which were stored away from light and heat until testing. Insoluble fraction measurements led to the conclusion that both the samples crosslinked under shearing show a gel fraction of 1, whereas the un-crosslinked samples were confirmed not to have sustained any crosslinking during their elaboration (gel fraction ~ 0).

2.3. Morphology characterization

The morphology of these blends was first observed using a Scanning Electron Microscope (SEM) Hitachi S800 instrument. The samples were cryo-fractured in liquid nitrogen to avoid any morphology alteration. The EPDM phase was selectively extracted as previously described [45]. The fractured surfaces were sputter-coated with gold in order to deposit a 50 nm homogeneous conductive layer. Additionally, Transmission Electron Microscopy (TEM) was another helpful and complementary means of characterization. All blends were observed using a Philips CM120 microscope after preparing the sample surface via an ultra cryo-microtomy process. Samples were ultra-microtomed into 50 nm thin films at -110 °C using a crystal blade to ensure that no phase deformation occurred (as these sample preparations were realised below both the PP and EPDM glass transition temperatures). Samples were then marked using a Ruthenium oxide solution which induced an oxidation and fixation of the metal on the diene functions of the EPDM thus showing dark on MET micrographs due to the diffusion of the electrons by the fixed metal [53]. All micrographs and sample preparations were done at the Technological Centre of Microstructures of the University of Lyon 1.

3. Results

3.1. PP/EPDM (80/20) blends

As it can be seen in Fig. 2, all blends (Blends 1–5) show a continuous PP matrix with a dispersed EPDM phase as expected for such concentration of the EPDM phase (20%wt.). As any would expect, Blend 1 ($g_{EPDM} = 0.7$) shows a homogeneous morphology made of a continuous PP matrix with micrometric and sub-micronic EPDM nodules whose size varies from 100 nm to 2 μm . Only rare nodules with a size above 2 μm can be observed. Surprisingly enough, the morphology of Blend 1 (Fig. 2b) is thus nearly identical to the blend 'UnCross1' (Fig. 2a) made of un-crosslinked EPDM which shows perfectly dispersed EPDM nodules all smaller than 1 μm . Thus, an insoluble fraction of 0.7 of the EPDM dispersed phase does not induce any major influence on the dispersion of the EPDM. Thus, even above the gel point such a chemical network can be as finely dispersed as un-crosslinked EPDM whereas their rheological behaviours are significantly different.

Blend 2, ($g_{EPDM} = 0.896$, Fig. 2c) compared with Blend 1, shows clearly thicker dispersed nodules of EPDM with a size varying from 1 μm up to 100 μm . Concerning Blends

3–5 ($g_{EPDM} = 0.962$, 0.982 and 0.998, respectively) their morphology is rough and very heterogeneous as the characteristic size of the pre-crosslinked phase is close to 500 μm . Furthermore, it can be pointed out that these samples could not be molded properly because of the presence of EPDM fragments with a size increasing with the crosslink density of the EPDM. Thus, the more the EPDM is crosslinked prior to blending the less it gets fragmented and dispersed homogeneously within the PP phase. For EPDM samples having an insoluble fraction under 0.9 the EPDM may get fragmented into micrometric and sub-micronic nodules whereas only big nodules and fragments of several hundreds of micrometers remain for blends made of pre-crosslinked EPDM having a higher insoluble fraction. Thus, there is a critical concentration ($g_{EPDM} = 0.7$) beyond which the crosslinked EPDM cannot be fragmented and finely dispersed within the PP and will remain into rough fragments under these processing conditions. Nevertheless reminding that the initial size of pre-crosslinked EPDM is 1 mm³, we can appreciate that in every cases the EPDM networks still get fragmented somehow in a fairly nodular shape. The size and size polydispersity of these nodules increase with the increase of the crosslinking density of the pre-crosslinked EPDM from sub-micron size ($g_{EPDM} = 0.7$) to few hundred micron ($g_{EPDM} = 0.998$).

Finally, comparing Blend 5 ($g_{EPDM} = 0.998$) with the dynamic crosslinking one (DynCross1, $g_{EPDM} = 1$) it can be pointed out a drastic difference of the morphologies: As previously explained, the pre-crosslinked EPDM phase of Blend 5 could not be dispersed at the micro-scale, whereas the dynamic-crosslinked blend presents a sub-micronic morphology (Fig. 2g) nearly as fine as the un-crosslinked blend (Fig. 1a). This observation emphasizes the importance of the processing on the TPV final morphology and more particularly the competition between crosslinking kinetics and mixing efficiency.

The mechanical properties from tensile-strength experiments are generally relevant parameters for a comprehensive purpose of the blend morphology development. In Table 2 are reported these mechanical properties of the PP/EPDM (80/20). As expected, Table 2 shows that the properties of the blends made of pre-crosslinked EPDMs are drastically affected by their compounding route. Whatever the pre-crosslink density of the EPDM, the final properties are extremely poor especially regarding their elongation at break ϵ_r and yield stress σ_y . On the other hand, the heterogeneity of the morphology of Blends 3–5 is such that it is extremely difficult to mold them into testing specimens under a press. The EPDM nodules, roughly broken down and dispersed within the PP phase, represent non-cohesive defects which literally ruin the material macroscopic properties.

Interestingly, it can be pointed out that the elongation at break of Blend 1 ($g_{EPDM} = 0.7$) is approximately 30 times lower than that of the UnCross1 blend ($g_{EPDM} = 0$) whereas these two blends have very similar morphologies in size. On the other hand, very satisfactory tensile properties of dynamic-crosslinked PP/EPDM blend (DynCross1, $g = 1$) blend can be observed similarly to those of the blend made of un-crosslinked EPDM, or only PP. As a result, the crosslinking under shearing do not induce any significant weak-

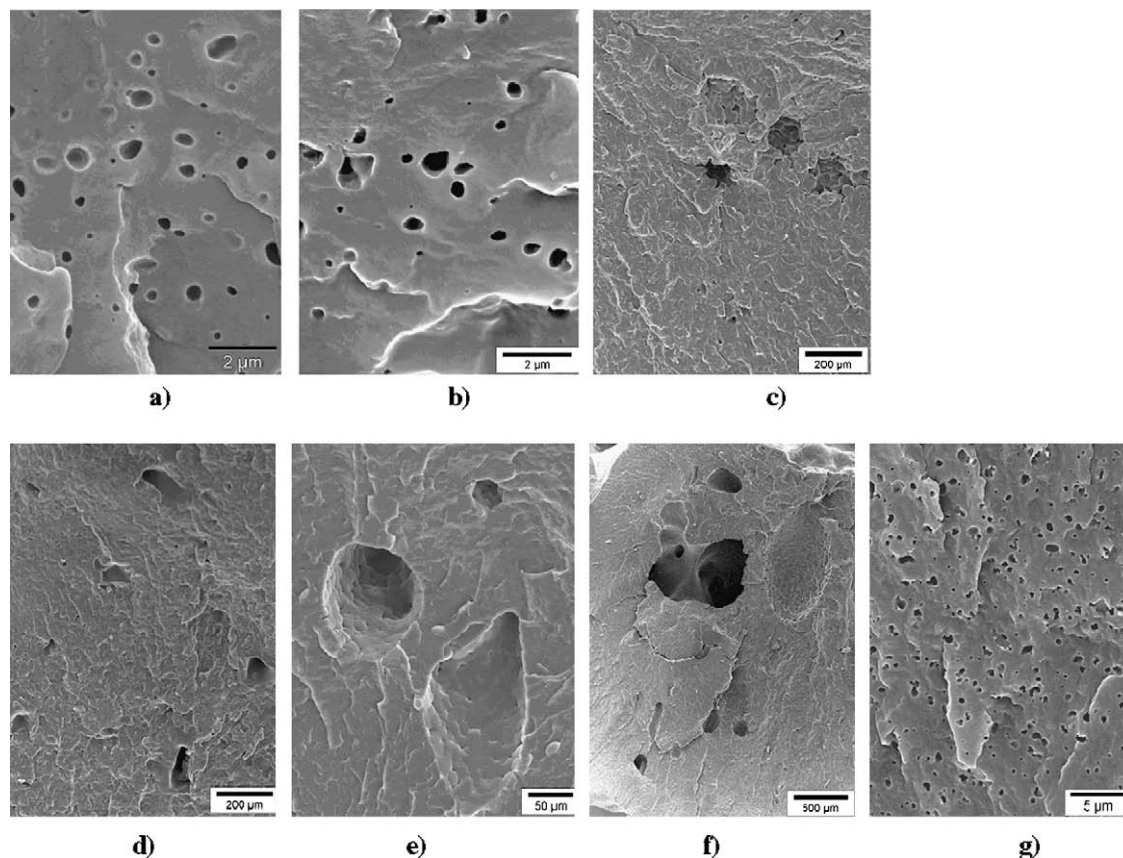


Fig. 2. SEM micrographs (a–g pictures) of PP/EPDM (80/20) blends. In the following caption, g_{EPDM} is the gel fraction of the EPDM phase. (a) Un-crosslinked blend (UnCross), $g_{EPDM} = 0$. (b) Blend 1 (EPDM: REF1/30, $g_{EPDM} = 0.7$). (c) Blend 2 (EPDM:REF1/10, $g_{EPDM} = 0.896$). (d) Blend 3 (EPDM: REF1/7, $g_{EPDM} = 0.962$). (e) Blend 4 (EPDM:REF1/4, $g_{EPDM} = 0.989$). (f) Blend 5 (EPDM:REF, $g_{EPDM} = 0.998$). (g) Dynamically crosslinked blend (DynCross1, $g_{EPDM} = 1$).

Table 2

Mechanical properties of PP/EPDM (80/20) blends. E Young's modulus, σ_y the yield stress and ε_b the strain at break.

Blends	E (MPa)	σ_y (MPa)	ε_b (%)
PP neat	660	29	640
UnCross1	470	21	520
1	380	18	20
2	310	115	12
3–5	<280	<13	<10
DynCross1	510	20	530

ening contrarily to all blends made of pre-crosslinked EPDMs. Therefore, such a dynamic crosslinking of the EPDM under shearing in presence of the thermoplastic phase leads to an improved cohesion of the blend phases which cannot be achieved by simply blending pre-crosslinked EPDM into PP. Nevertheless, the explanation of such drastic differences of the tensile behaviours of these blends having a nearly identical morphology is not trivial and will be discussed in the next section. Anyway, such results actually confirm the usefulness of the dynamic crosslinking step on the tight combination of the phase properties.

The morphology development of Blend 5 (pre-crosslinked EPDM: REF, $g_{EPDM} = 0.998$) versus time of mixing

has been studied. Hence, Fig. 3 shows the evolution of the morphology of the Blend 5 which has then been characterized over 45 min of blending. After 3 min of blending, the fragments of the pre-crosslinked EPDM preparation are virtually intact as shown in Fig. 3a. Their average size is above 400 μm and some of them are actually still present at their original size and shape. This high crosslink density network may not be broken over such a short period of time with such a shearing and process. After 8 min of blending, Fig. 3b shows that the EPDM is now present as large fragments of around 300 μm wide, thus several times smaller than their original size. At this stage of mixing, the breaking up mechanism induced by the shearing of the phases provokes a modification of the shape of the EPDM fragments as they start to look like huge nodules a few hundreds of micrometers large. Thus, even in presence of a continuous molten thermoplastic phase, such shearing can allow some significant erosion and deformation of such a dense chemical network.

As the time of blending increases, the size of the EPDM nodules slowly and progressively decreases, and their shape tend to be more fibrillar, highlighting a progressive and ongoing deformation and dispersion of the elastomeric phase as we can observe in Fig. 3c and d. This finally leads, after 45 min of blending, to long EPDM ellipsoids and

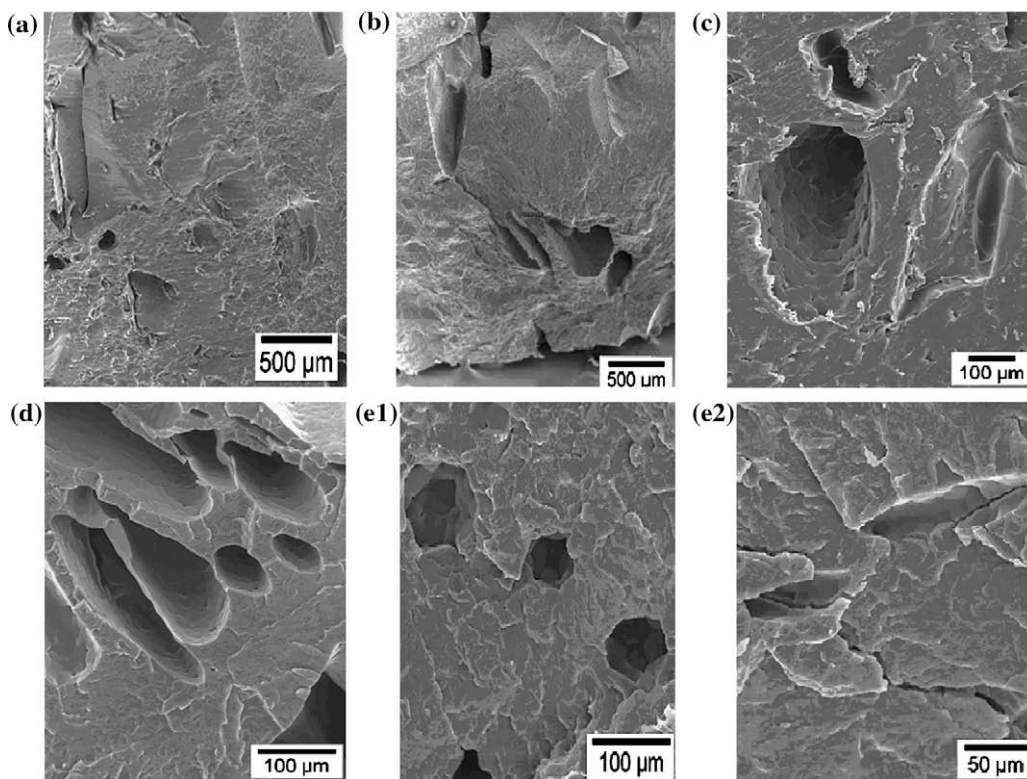


Fig. 3. SEM micrographs of Blend 5 after different times of mixing: PP/EPDM (80/20, pre-crosslinked EPDM: REF, $g_{EPDM} = 0.998$). Sampling at: (a) 3 min; (b) 8 min; (c) 18 min; (d) 28, and (e1 and e2) 45 min.

nodules of around 50 and up to 200 μm as shown in Fig. 3e1 and e2. Furthermore, it could not notice any EPDM nodule of a size below 50 μm at any stage of the blending. The large EPDM nodules get stretched and deformed by the shearing and broken down into smaller nodules and ellipsoids, but the quality of the dispersion is still quite rough and leads to a heterogeneous material due to the size ($\sim 50 \mu\text{m}$) of the EPDM phase.

3.2. PP/EPDM (30/70) blends

This blend is surely the most interesting one as PP/EPDM (30/70) blend can lead to co-continuous morphologies as in TPV systems. As exhaustively discussed in our previous paper [45], the blend made of un-crosslinked EPDM shows a perfectly homogeneous and co-continuous morphology where the size of the two continuous phases ranges from around 1 to 2 μm with nodules of one phase included into the other of dimensions varying from 50 to 500 nm (Fig. 4a1 and a2). Upon these results we studied the morphologies of the blends made of pre-crosslinked EPDM at this precise blend composition to assess the impact of the crosslink density of the EPDM on the final blend morphology.

Hence, Fig. 4b1 and b2 show that Blend 6 (pre-crosslinked EPDM: REF1/30, $g_{EPDM} = 0.7$) is partially made of a clearly continuous PP phase with numerous EPDM nodules of a few micrometers wide perfectly included into it. How-

ever, some large co-continuous regions are still presents. As a matter of fact, as this EPDM has a very low but yet significant pre-crosslink density its viscosity is obviously higher than an un-crosslinked EPDM. Nevertheless, this pre-crosslinked EPDM has actually been quite well dispersed in the matrix and the morphological changes are not so important since, apart from some residual nodules, Blend 6 is co-continuous in its majority. Some nodules are still present and the morphology is not as thin and homogeneous as the un-crosslinked blend, but the chemical network has actually been efficiently fragmented and dispersed in the thermoplastic leading to a partially co-continuous blend.

On the contrary, all other blends (7–10 i.e. for $g_{EPDM} > 0.896$) do not present a co-continuous morphology. Blend 7 (pre-crosslinked EPDM, $g_{EPDM} = 0.896$) shows numerous large EPDM fragments and its dispersion within the continuous PP matrix has not been very effective. Furthermore, micrographs of Blends 8–10 (pre-crosslinked EPDM, $g_{EPDM} = 0.896$, 0.989 and 0.998, respectively) show that the higher the original EPDM crosslink density, the less it gets fragmented and dispersed.

More particularly, the PP phase can be clearly distinguished from the removed clusters and fragments of EPDM by a selective solvent. Nevertheless, the extraction of such big EPDM fragments was not fully achieved due to their impressive size and rough shape as we can see for Blends 8–10. At this stage of the blending some huge aggregates

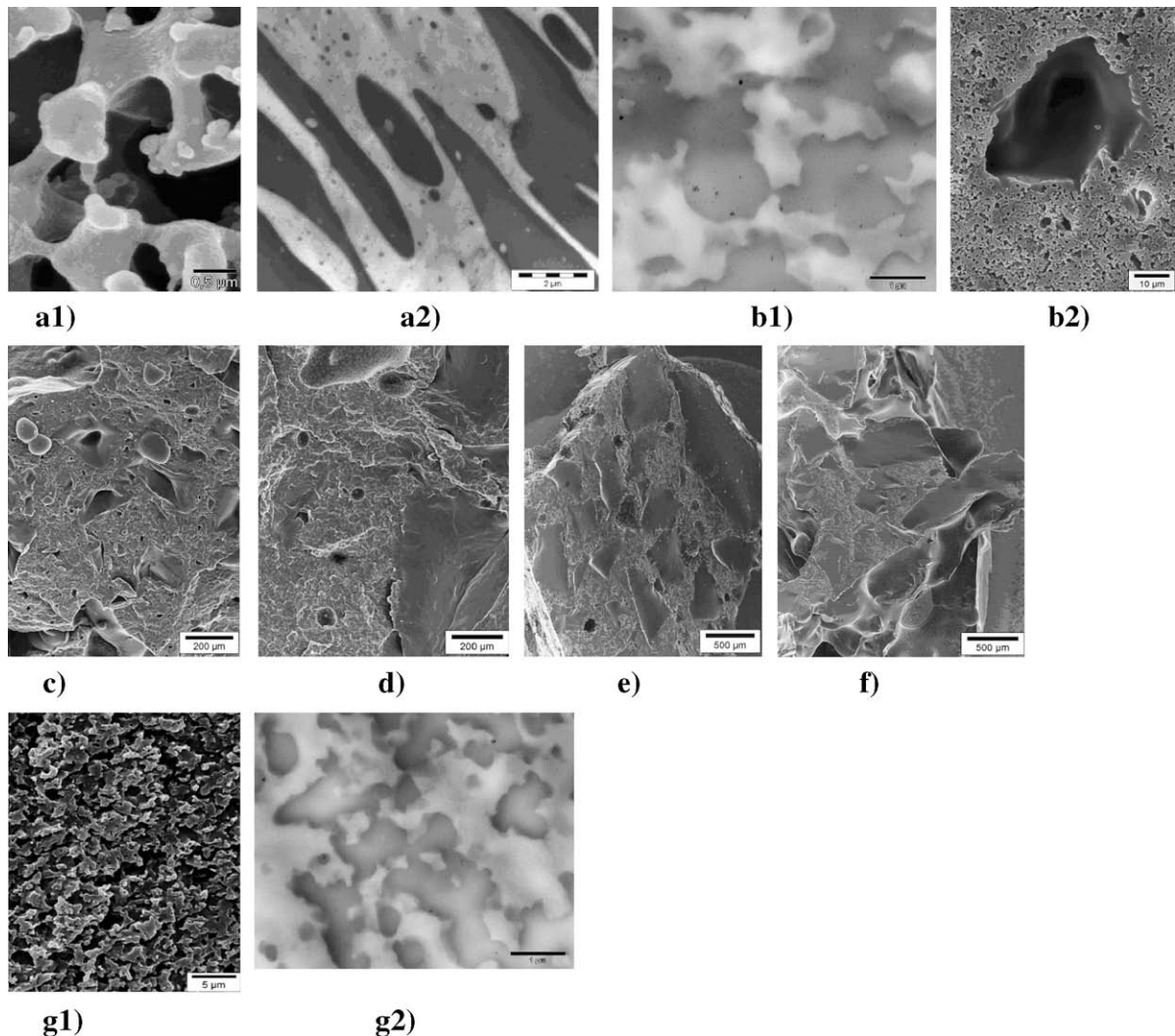


Fig. 4. SEM and TEM micrographs of PP/EPDM blends (30/70) after 10 min of mixing. In the following caption, g_{EPDM} is the gel fraction of the EPDM phase. (a1 and a2) Un-crosslinked blend (UnCross2) at different scales. (b1 and b2) Blend 6 (EPDM: REF1/30 – $g_{EPDM} = 0.7$). (c) Blend 7 (EPDM: REF1/10, $g_{EPDM} = 0.896$). (d) Blend 8 (EPDM: REF1/7, $g_{EPDM} = 0.962$). (e) Blend 9 (EPDM:REF1/4, $g_{EPDM} = 0.989$). (f) Blend 10 (EPDM:REF, $g_{EPDM} = 0.998$). (g1 and g2) Dynamically crosslinked blend (DynCross2, $g_{EPDM} \sim 1$).

are fully included in the continuous PP matrix and very few micron-size nodules of EPDM are present in the PP phase. As a matter of fact, Blends 8–10 could not be molded properly under a press and turned into powders due to the presence of too numerous and huge heterogeneities.

Therefore, increasing the gel fraction above 0.7 prevents any proper dispersion of the EPDM and homogeneous morphology under these processing conditions. The pre-crosslinked EPDM fragments did not sustain a sufficient continuous shearing and then could not be deformed, broken and dispersed properly. Furthermore, as it can be seen in Fig. 4g1 and g2 the dynamic-crosslinked blend (DynCross2, $g_{EPDM} = 1$) exhibits a co-continuous structure which is very similar to the one generally observed for TPVs based PP/EPDM. We can thus assess the morphological differences induced by the dynamic crosslinking of the EPDM phase in presence of PP in opposition to the simple blend-

ing of the pre-crosslinked EPDMs with PP. Indeed, the dispersion of a pre-crosslinked EPDM phase having a very high insoluble fraction ($g_{EPDM} \geq 0.896$) is very rough and lead to a very coarse morphology as seen for Blend 10 while the dynamic crosslinking of the EPDM under shearing leads to a fine and regular co-continuous morphology under the processing protocol. Actually, above a gel fraction of 0.7 the EPDM phase cannot be properly dispersed under these experimental conditions. The impact of the crosslinking route is thus straightforward. As a conclusion from a practical point of view, it is necessary to disperse the EPDM phase before its gel fraction reaches 0.7 in order to obtain a co-continuous morphology.

Regarding tensile mechanical properties, Blends 8–10, similarly to Blends 3–5 (pre-crosslinked EPDMs, $g_{EPDM} \geq 0.896$) show extremely poor tensile behaviours (Table 3). These three blends do not present any co-continuity and

Table 3

Mechanical properties of PP/EPDM (30/70) blends. E : Young's modulus, σ_y the yield stress and ϵ_b the strain at break.

Blend	E (MPa)	σ_y (MPa)	ϵ_b (%)
UnCross2	44	3.9	210
6	30	3.4	200
7	24	0.5	120
8–10	<20	<0.5	<20
DynCross2	27	4.7	260

clearly show large EPDM fragments of over 100 μm roughly dispersed in the PP matrix. These blends are not cohesive at all and their poor mechanical properties are due to their very coarse morphology.

However, Blend 6 ($g_{\text{EPDM}} = 0.7$) shows tensile properties very similar to the one relative to the blend made of un-crosslinked EPDM. Among all blends prepared from pre-crosslinked EPDM, only Blend 6 has shown a partial co-continuity which has a significant impact on its tensile properties. Although this blend presents some domains with a continuous PP phase with dispersed 20 μm large EPDM fragments and nodules, this morphology represents only minor imperfections at a macroscopic scale for tensile properties.

In comparison with blends based on pre-crosslinked EPDM phase, the tensile properties of the dynamic-crosslinked blend (DynCross2, $g_{\text{EPDM}} = 1$) are much better and consistent with TPV properties generally observed. This re-

sult proves once again the strong impact of the dynamic crosslinking route on the final properties of TPV materials.

To complete this study on PP/EPDM (30/70) blends, the morphology development of a blend based on the pre-crosslinked EPDM phase (REF1/10, $g_{\text{EPDM}} = 0.896$) was investigated. Note as discussed previously, blends made of pre-crosslinked EPDM preparations having an insoluble fraction above 0.9 lead to un-cohesive materials after 10 min of blending. Fig. 5 shows the SEM micrographs of the blend morphology development with the time of mixing.

As a result, Fig. 5a1 and a2 show that, after only 3 min of blending, the pre-crosslinked EPDM is present as fragments of around 500 μm but also as sharp nodules of 2 μm dispersed in the PP continuous phase. The size polydispersity is very broad and the shape of the EPDM fragments is always sharp. The large majority of the pre-crosslinked EPDM preparation (REF1/10, $g_{\text{EPDM}} = 0.896$) has been fragmented into 100 μm -large fragments dispersed into the PP matrix. The EPDM network is clearly under fragmentation and the morphology has not stabilised yet. After 8 min of blending (Fig. 5b), the PP phase is still continuous but gets richer in EPDM nodules and the size of the EPDM fragments is clearly decreasing. The fragmentation thus affects the entire fraction of the EPDM which can potentially, under these conditions, be partially broken down and dispersed within such a thermoplastic phase. Ten minutes later of blending, we can notice in Fig. 5c very few fragments more than 100 μm wide, some

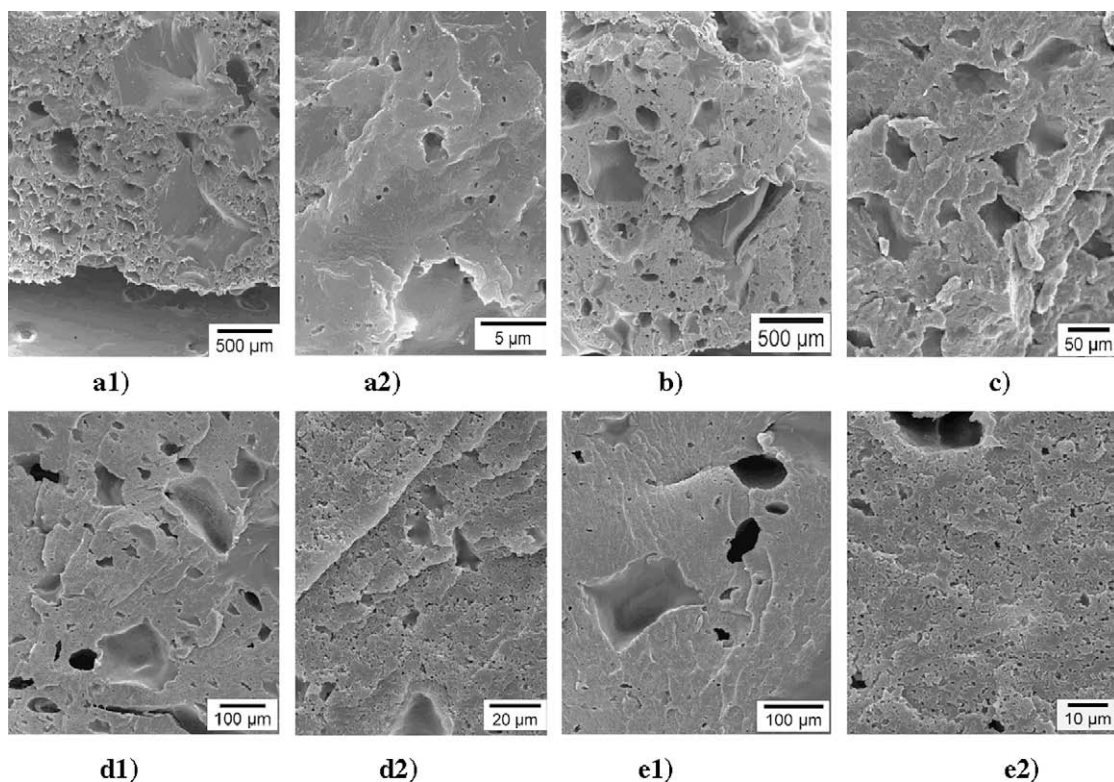


Fig. 5. SEM micrographs of Blend 7 at different times of mixing, PP/EPDM (30/70, pre-crosslinked EPDM: REF1/10, $g_{\text{EPDM}} = 0.896$). Sampling at: (a1 and a2) 3 min; (b) 8 min; (c) 18 min; (d1 and d2) 28 min and (e1 and e2) 45 min.

of them having a nodular shape which confirms the role of the shearing on their deformation and stabilization. With the increase of the time of blending, micron-size EPDM nodules get more and more numerous, the PP continuous phase gets richer in EPDM nodules and the number of huge fragments of a few hundreds micrometers decreases. Finally, the pre-crosslinked EPDM fragments get finely and homogeneously dispersed as small nodules with the time of mixing. Nevertheless there are still important sharp fragments which have not been properly broken down even after 45 min of shearing. Anyhow the PP phase is always clearly continuous and only very rare regions present a slight co-continuity, indicating that such processing does not lead to the expected morphology. Furthermore, the fragmentation of the EPDM after 45 min of blending is still ongoing. Even though most of the EPDM gets fragmented into nodules, the morphology has not stabilized yet and the blend still appears very lumpy due to some remaining sharp EPDM fragments having a broad size polydispersity.

4. Discussion

First of all and from a qualitative point of view, it can be concluded from the blend morphologies (PP/EPDM: 80/20 or 30/70) that the dispersion of pre-crosslinked EPDM strongly depends on its crosslinking density. Furthermore, a gel extent close to 0.7 appears to be a critical crosslinking density for morphology development. Indeed, only pre-crosslinked EPDMs having a gel fraction below 0.7 have been significantly fragmented and dispersed homogeneously in presence of PP.

Regarding blend with a continuous PP phase (PP/EPDM: 80/20, $g_{EPDM} = 0.7$), the morphologies (Fig. 2b) are quite similar compared with the morphologies of un-crosslinked (Fig. 2a) and dynamic-crosslinked (Fig. 2g) blends. At higher crosslinking density ($g_{EPDM} \geq 0.896$), a coarse morphology with a characteristic size of few hundred micrometers is observed. A longer time of mixing over 45 min, only reduced the morphology size to around 50 μm . However, compared with the initial macroscopic-size of pre-crosslinked EPDM (1 mm^3) the size of the pre-crosslinked EPDM has been reduced by a factor 20. On the other words, the cubic-shape initial pellets of EPDM have been divided in ellipsoid-shape smallest particles 8000 times as numerous. Such mechanism of size reduction of elastic particles can be only achieved by an erosion process due to the stress applied by the viscous matrix (PP continuous phase). Actually, in the hypothesis of a homogeneous blend having a continuous PP matrix and submitted to a shear rate $\dot{\gamma}$ the applied stress can be simply expressed by: $\tau = \eta\dot{\gamma}$. According to the mixing condition, $\dot{\gamma}$ can be approximated by: $\dot{\gamma} \approx 0.8 \times N$ with N the number of rotations per minute. Consequently with: $\eta_{PP}^* \approx 2000$ Pa s, the imposed shearing stress is approximately 80 kPa. This value can be qualitatively compared to the tensile properties at break of the EPDM preparations ($\sigma_T = 440$ kPa, as presented in Table 1).

Regarding blends with a rich EPDM phase (PP/EPDM: 30/70), the morphology of Blend 6 ($g_{EPDM} = 0.7$, Fig. 4b1 and b2) are totally different of the morphology of un-crosslinked blend (UnCross2, $g_{EPDM} = 0$, Fig. 4a1 and a2).

Actually the blend morphology of Blend 6 is similar to the morphology of the dynamic-crosslinked blend ($g_{EPDM} = 1$, Fig. 4g1 and g2). At higher crosslinking density ($g_{EPDM} \geq 0.896$, Blends 7–10), a coarse morphology of few hundred microns can be observed. Note that Blends 8–10 ($g_{EPDM} \geq 0.962, 0.989$ and 0.998) turned into powder during mixing. Such phenomenon is due to the mechanical grinding action (shearing in the gap between the rotor and chamber surface of the mixer) of the pre-crosslinked EPDM phase. However, a spectacular reduction of the morphology size with a co-continuous morphology of Blend 7 ($g_{EPDM} \geq 0.896$, Fig. 5e1 and e2) can be achieved by mixing longer (45 min) even some EPDM domains of few micron are still present.

From mechanical point of view, quite different results can be derived depending on EPDM phase concentration and crosslinking density. The mechanical properties of Blends 1–5 (PP/EPDM 80/20) are totally ruined ($\varepsilon_b < 20\%$) compared with un-crosslinked and dynamic-crosslinked samples ($\varepsilon_b > 500\%$) although all these blends have apparently the same type in size of morphology. On the contrary, compared with Blend 1 (PP/EPDM (80/20, $g_{EPDM} = 0.7$), blend 6 (PP/EPDM (30/70, $g_{EPDM} = 0.7$) presents mechanical properties ($\varepsilon_b = 200\%$) similar with un-crosslinked (UnCross2, $\varepsilon_b = 210\%$) and dynamic-crosslinked samples (DynCross2, $\varepsilon_b = 260\%$). For such blends and from a mechanical point of view, the critical concentration is in the range between $0.7 < g_{EPDM} < 0.896$.

To understand the interrelation between morphology and mechanical properties of PP/EPDM (pre-crosslinked, or dynamic-crosslinked) blends, the morphology development of un-crosslinked system must be discussed. Actually, the phase continuity and co-continuous morphologies of PP and un-crosslinked EPDM have been recently investigated by Bhadane et al. [54,55]. First of all, blends of EPDM and PP are characterized by a very low interfacial tension of about 0.3 mN/m. As a result, the miscibility-immiscibility issue in this blend system is an important feature. This issue is complex and still controversial in the literature as the morphology are observed at room temperature and are not then a faithful image of the morphology in molten conditions. However, Bhadane et al. [54] demonstrated that PP/EPDM blends are partially miscible in the melt and that the crystalline nature of PP forces the blend to completely phase separate upon cooling. Furthermore, they showed [55] for low concentrations EPDM in the blend that EPDM phase coexists in a variety of unexpected morphologies such as stable isolated nanometer diameter fibers, very large particles, partially coalesced particles and numerous particles interconnected by nanofillers. This unusual morphology development leads to a novel co-continuous structure. Such a structure was not reveal in the present work since only the EPDM phase was selectively removed and the sample was analysed by SEM. However, image analysis (Fig. 4a1 and a2) at higher concentration of EPDM shows this unusual morphology at the co-continuity. SEM image (Fig. 4a1) shows a usual morphology at the co-continuity while TEM image (Fig. 4a2) shows an unusual morphology as described by Bhadane et al. [54,55]. This novel co-continuity structure is made of interpenetrated phases at the micro-scale, each

phase including at a nanoscale droplets or filament of the other phase.

Regarding pre-crosslinked PP/EPDM blend, it can be then assumed that the permanent elasticity of the EPDM phase totally changes the mechanisms of morphology developments in such blends. However, the apparent viscosity ratio $p = \eta_{EPDM}^*/\eta_{PP}$ at $\dot{\gamma} = 50 \text{ s}^{-1}$ is close to 1 for Blend 1 ($g_{EPDM} = 0.7$). According to our previous work [56] on blends of high viscosity ratio, the Taylor model [57] can be successfully used even this model does not take into account elastic effects. Actually, the shear viscosity ratio is the dominant parameter in droplet deformation whereas the Taylor–Rayleigh instabilities could be the relevant mechanism of droplet break-up under shear ($p < 4$). Nevertheless the surface erosion of the EPDM particles is a priori the dominant parameter as already pointed out by Mighri and Huneault [58]. These authors undoubtedly showed that in viscoelastic materials at high shear stress the actual deformation of dispersed droplets cannot follow any type of Taylor–Rayleigh mechanism.

Furthermore, for droplet systems having a permanent elasticity we observed [59] a severe decrease of droplet deformation for elastomer droplets having gel fraction higher than 0.7. This critical gel fraction was also reported in other works. For example, Fenouillot and Perrier-Camby [60] observed that, for a thermoplastic/thermoset with a gel fraction between 0.4 and 0.7, it was possible to make long and thin elastomeric fibers, which can potentially break-up into droplets, within a thermoplastic matrix. Few years later DeLoor et al. [61,62] showed the equilibrium between break-up and coalescence of a in situ crosslinked dispersed phase was shifted toward coalescence, whereas at high extent (gel fraction of the dispersed phase higher than 0.6), the classical mechanisms were largely modified and replaced by a “coagulation” mechanism. Furthermore, it was shown that, for the fully crosslinked dispersed phase, the final morphology remained remarkably stable during successive extrusion steps. To sum up, all the results of the literature agree with the same order of magnitude of the gel fraction of the dispersed phase ($g \sim 0.7$) as the critical value for drastic modification of break-up and coalescence mechanisms.

Finally, regarding the morphology of PP/EPDM, Bhadane et al. [55] showed that un-crosslinked EPDM tends to form an interconnected dispersed phase made of nodules linked by nanofibers. Such type of morphology was also observed for another low interfacial tension systems [63] such as high mass molar PP dispersed in low molar mass PP. The main mechanism of this morphology development is the collision-coalescence-separation type erosion mechanism for high viscosity ratio. But a blend made of pre-crosslinked EPDM with a perfectly homogeneous chemical network cannot lead to such a complex structure. This explains the extremely poor mechanical properties of all blends made of pre-crosslinked EPDMs. Nevertheless, the blend with a majority of pre-crosslinked EPDM phase presents good mechanical properties (compared with un-crosslinked and dynamic-crosslinked samples). This phenomenon can be explained by possible coalescence mechanism near the co-continuity of the pre-crosslinked EPDM domains even at a gel fraction around 0.7. This

discussion leads to the following question: Why dynamic-crosslinked PP/EPDM blends (TPV) have so good and specific mechanical properties? As generally admitted and observed, the crosslinking reaction of the EPDM phase must be longer than the characteristic time of mixing. According to the present results, the time of crosslinking is the time necessary to reach a gel fraction of the EPDM phase close to 0.7 and the time of mixing is the time needed to obtain the morphology observed in un-crosslinked blends. Consequently, the best route from a processing point of view should be to add the crosslinker system just after the blending stage of both thermoplastic and elastomeric phases. However, this conclusion is a simply view of the complexity of the morphology development in TPVs elaboration. Furthermore, Litvinov [51] from Proton NMR relaxation experiments suggested that the polypropylene rich chain fragments of EPDM and the amorphous PP phase form a thin interfacial layer which is the source of physical junctions (or entanglements) at the EPDM/PP interface. It is then clear that such interface cannot be reached for pre-crosslinked EPDM phase as they behave as elastic domain without any mobility of the EPDM chains. However, such behaviour can be expected for low density crosslinking ($g_{EPDM} < 0.7$) of the EPDM phase as some chains and more precisely the shortest one are free to reptate to the interface.

From a chemistry point of view, the homogeneity conditions of the crosslinking reaction are also questioning. Regarding dynamic-crosslinked blend, EPDM domains can present a gradient of crosslink density due to the specific processing condition during which the crosslinker diffusion is in direct competition with the dispersion of the EPDM domains. Then, some EPDM domains, domains with a low crosslinking density, can sustain an erosion mechanism thanks to a partial inter-diffusion/agglomeration before to be reach the critical crosslinked density ($g_{EPDM} = 0.7$). Note that this mechanism of erosion is quite different of the mechanism observed for pre-crosslinked EPDM domain at higher crosslinking density ($g_{EPDM} \geq 0.896$).

5. Conclusion

The main objective of this work was to study the dispersion mechanisms under mixing of pre-crosslinked and plasticized EPDM networks in presence of polypropylene in various proportions. Furthermore, the morphologies and mechanical properties of such samples were compared with un-crosslinked and dynamic-crosslinked blends made in the same proportions. Consequently, this paper aimed at better understanding the various mechanisms of fragmentation and dispersion involved in the morphology stabilization of thermoplastic vulcanizates. As far as we know, no such work has been quantitatively reported in the literature yet.

First of all and under our experimental conditions of shearing, it appeared possible to fragment and homogeneously disperse EPDM networks having a gel fraction as high as 0.7 into a thermoplastic matrix, whatever the proportion of the PP/EPDM phases (80/20 or 30/70). Above this critical value, the pre-crosslinked EPDM networks

are not dispersed efficiently into fine particles, leading to coarse morphologies with quite large remaining fragments (size of 200 μm of order of magnitude with a broad distribution) which act as strong imperfections literally ruining the macroscopic properties of the blends.

Although the Rayleigh–Taylor instabilities can be involved in such immiscible blend morphology development, another dominant mechanism such as erosion has to be taken into account depending on the EPDM crosslink density and concentration in PP/EPDM blends.

Actually, two mechanisms of erosion are mainly observed for EPDM depending on gel fraction. For crosslinking density, such as $g_{\text{EPDM}} < 0.7$, a particle collision-coalescence-separation type of erosion proposed by Bhadane et al. can be assumed. However, we suppose from mechanical properties that morphology at the nanoscale cannot be achieved from pre-crosslinked EPDM even at low crosslinking density. At higher crosslinking density ($g_{\text{EPDM}} > 0.7$) another mechanism of erosion, observed to be time dependent, can be suggest. This mechanism is only pure mechanical erosion by stress break-up of EPDM domains. At low concentration of the EPDM phase (20%), the stress is applied through the viscosity of the molten PP while at higher concentration of EPDM (70%) pure mechanical breaking (grinding process) induces a rough but effective breaking up of the EPDM fragments.

Finally, the crosslinking under mixing of the EPDM phase in molten PP (i.e. dynamic crosslinking) leads to a very fine and homogeneous morphology with a complex and cohesive EPDM structure. Such samples lead to improved mechanical properties. The advantage of the crosslinking under shearing, compared to the fragmentation and dispersion of pre-crosslinked EPDM in presence of a thermoplastic phase, appears clearly vital to elaborate cohesive TPVs. From our results it can be concluded that the crosslinking time (time needed to reach $g_{\text{EPDM}} = 0.7$) must be longer than the time of mixing (time necessary to get the morphology by a type of erosion). Furthermore, it appears from this study and conclusions that a gradient a crosslinking density is required to have the best mechanical properties. However further works are needed to check this hypothesis.

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References

- [1] Bhadane PA, Virgilio N, Favis BD, Champagne M, Huneault MA, Tofan F. *Am Inst Chem Eng J* 2006;52(10):3411–20.
- [2] Van Duin M. *Macromol Symp* 2006;233(1):11–6.
- [3] Coran AY, Patel RP. Thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends. In: *Thermoplastic elastomers*. Munich, Vienna, New York: Hanser-Garner Publications; 1996.
- [4] Da Silva AL, Tavares M, Politano D, Coutinho F, Marisa CG, Rocha M. *J Appl Polym Sci* 1997;66:2005–14.
- [5] Hoppner D, Wendorff JH. *Colloid Polym Sci* 1990;268(6):500–12.
- [6] Naderi G, Lafleur PG, Dubois C. *Polym Eng Sci* 2007;47(3):207–17.
- [7] Ha CS, Kim SC. *J Appl Polym Sci* 1989;37(2):317–34.
- [8] Lee KY, Goettler LA. *Polym Eng Sci* 2004;44(6):1103–11.
- [9] Joubert C, Cassagnau P, Michel A, Choplin L. *Polym Eng Sci* 2002;42(11):2222–33.
- [10] Wang X, Sun J, Huang R. *J Appl Polym Sci* 2006;99:2268–72.
- [11] Shafei Sararudi S, Nazockdast H, Katbab AA. *Rubber Chem Technol* 2004;77(5):847–55.
- [12] Prut E, Erina NA, Karger-Kocsis J, Medintseva TI. *J Appl Polym Sci* 2008;109(2):1212–20.
- [13] Van Duin M, Machado AV. *Polym Degr Stab* 2005;90:340–5.
- [14] Machado AV, Van Duin M, Covas JA. *Mater Sci Forum* 2006;514–516:838–42.
- [15] Ellul MD, Tsou AH, Hu W. *Polymer* 2004;45:3351–8.
- [16] Prut E, Medintseva T, Dreval V. *Macromol Symp* 2006;233:78–85.
- [17] Jain AK, Nagpal AK, Singhal R, Gupta NK. *J Appl Polym Sci* 2000;78:2089–103.
- [18] Mousa A. *Int J Polym Mater* 2005;54:619–31.
- [19] Hernandez M, Gonzalez J, Albano C, Ichazo M, Lovera D. *Polym Bull* 2003;50(3):205–12.
- [20] Ohm B, Annicelli R, Jablonowski T, Mazzeo R. *Rubber World* 2002;226(5):33–7.
- [21] Li Z, Kontopoulou M. *Polym Eng Sci* 2009;49(1):34–43.
- [22] Wang W, Wu Q, Gu B. *Polym Eng Sci* 2003;43(11):1798–805.
- [23] Xiao HW, Huang SQ, Jiang T. *J Appl Polym Sci* 2004;92:357–62.
- [24] Zaharescu T, Setnescu R, Jipa S, Setnescu T. *J Appl Polym Sci* 2000;77:982–7.
- [25] Marinovic T, Susteric Z, Dimitrievski I, Veksliz Z. *Kaut Gummi Kunstst* 1998;51(3):189–93.
- [26] Verbois A, Cassagnau P, Michel A, Guillet J, Raveyre C. *Polym Int* 2004;53:523–35.
- [27] Mekhilef N, Verhoogt H. *Polymer* 1996;37(18):4069–77.
- [28] Machado AV, Van Duin M. *Polymer* 2005;46(19):6575–86.
- [29] Willemse RC, Posthuma de Boer A, Van Dam J, Gotsis AD. *Polymer* 1999;40:827–34.
- [30] Wang W, Wang SJ, Qi ZN. *J Polym Sci* 1996;34:193–9.
- [31] Lacasse C, Favis BD. *Adv Polym Technol* 1999;18(3):255–65.
- [32] Kim BC, Hwang SS, Lim KY, Yoon KJ. *J Appl Polym Sci* 2000;78:1267–74.
- [33] Koning C, Van Duin M, Pagnoulle C, Jerome R. *Prog Polym Sci* 1998;23:707–57.
- [34] Li J, Ma PL, Favis BD. *Macromolecules* 2002;35(6):2005–16.
- [35] Zhang D, Liu Y, Yang Q, Hecheng Xiangjiao Gongye 1986;9(6):415–9.
- [36] Hong BK, Jo WH. *Polymer* 2000;41:2069–79.
- [37] Cimmino S, D'Orazio L, Greco R, Maglio G, Malinconico M, Mancarella C, et al. *Polym Eng Sci* 1984;24(1):48–56.
- [38] John B, Varughese KT, Oommen Z, Pötschke P, Thomas S. *J Appl Polym Sci* 2003;87(13):2083–99.
- [39] Bazgir S, Katbab AA, Nazockdast H. *J Appl Polym Sci* 2004;92:2000–7.
- [40] Elias L, Fenouillot F, Majesté JC, Cassagnau P. *Polymer* 2007;48(20):6029–40.
- [41] Yang H, Li B, Wang K, Sun T, Wang X, Zhang Q, et al. *Eur Polym J* 2008;44(1):113–23.
- [42] Yang H, Zhang Q, Guo M, Wang C, Du R, Fu Q. *Polymer* 2006;47(6):2106–15.
- [43] Yang H, Zhang X, Qu C, Li B, Zhang L, Zhang Q, et al. *Polymer* 2007;48(3):860–9.
- [44] Katbab AA, Nazockdast H, Bazgir S. *J Appl Polym Sci* 2000;75:1127–37.
- [45] Martin G, Barres C, Sonntag P, Garois N, Cassagnau P. *Mater Chem Phys* 2009;113:889–98.
- [46] Elias L, Fenouillot F, Majesté JC, Martin G, Cassagnau P. *J Polym Sci B Polym Phys* 2008;46:1976–83.
- [47] Jayaraman K, Kolli VG, Kang SY, Kumar S, Ellul MD. *J Appl Polym Sci* 2004;93:1–9.
- [48] Joubert C, Cassagnau P, Choplin L, Michel A. *J Rheol* 2002;46(3):629–50.
- [49] Ponsard-Fillette M, Barres C, Cassagnau P. *Polymer* 2005;46(23):10256–68.
- [50] Medintseva T, Erina N, Prut E. *Macromol Symp* 2001;175(1):49–54.
- [51] Litvinov VM. *Macromolecules* 2006;39(25):8727–41.
- [52] Martin G, Barres C, Cassagnau P, Sonntag P, Garois N. *Polymer* 2008;49:1892–901.
- [53] Trent JS, Scheinbeim JI, Couchman PR. *Macromolecules* 1983;16:589–98.
- [54] Bhadane PA, Champagne M, Huneault MA. *Polymer* 2006;47:2760–71.

- [55] Bhadane PA, Champagne M, Huneault MA, Tofan F, Favis BD. *J Polym Sci B Polym Phys* 2006;44:1919–29.
- [56] Deyrail Y, Michel A, Cassagnau P. *Can J Chem Eng* 2002;80(6):1017–27.
- [57] Taylor GI. *Proc R Soc Lond A* 1950;201:192–6.
- [58] Mighri F, Huneault MA. *J Appl Polym Sci* 2006;100(4):2582–91.
- [59] Deyrail Y, Cassagnau P. *J Rheol* 2004;48(3):505–24.
- [60] Fenouillot F, Perier-Camby H. *Polym Eng Sci* 2004;44(4):625–37.
- [61] Deloor A, Cassagnau P, Michel A, Vergnes B. *Int Polym Process* 1994;9(3):211–8.
- [62] DeLoor A, Cassagnau P, Michel A, Vergnes B. *J Appl Polym Sci* 1994;3(12):1675–86.
- [63] Huneault MA, Mighri F, Ko GH, Watanabe F. *Polym Eng Sci* 2001;41(4):672–83.