

# Morphology development and phase inversion during dynamic vulcanisation of EPDM/PP blends

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## Abstract

Morphology development and phase inversion were investigated during dynamic vulcanisation of ethylene-propylene-diene terpolymer (EPDM)/polypropylene (PP) blends. The effects of viscosity ratio and cross-linking reactions were also addressed. EPDM/PP blends were dynamically vulcanised in a Haake batch mixer using resole and SnCl<sub>2</sub> as cross-linking agents. The morphology development and cross-linking degree with reaction time were followed by morphology analysis (SEM and TEM) and measurement of EPDM gel content, respectively. For the same reaction time, it was found that the EPDM gel content decreased when the low-molecular-weight EPDM was used. As a result, the morphological development was delayed and the phase-inversion point was shifted to higher reaction times, allowing us to monitor morphological development during a thermoplastic vulcanisate (TPV) preparation. Using the low-molecular-weight EPDM and increasing the PP viscosity accelerated the morphological development, shifting phase-inversion to lower reaction times. While blend composition influenced final TPV morphology, it had a minor effect on the mechanism of morphological development. A correlation between cross-linking degree and morphology development was established. The results obtained allowed to propose a

mechanism of morphology development during dynamic vulcanisation of the EPDM/PP blends, including phase inversion.

## Introduction

Thermoplastic vulcanisates (TPVs) are a particular group of thermoplastic elastomers (TPEs). These materials combine the melt processability of the thermoplastics and the elastic and mechanical properties of the thermoset cross-linked rubbers [1-3]. Thus, they can be processed by conventional techniques such as extrusion, blow moulding, injection moulding, vacuum forming and calendaring. The combination of their properties, recyclability and relatively low price explain the abundant and still growing application of these materials, especially in the automotive sector [4]. TPVs are produced via dynamic

vulcanisation of immiscible blends of a thermoplastic and an elastomer. Dynamic vulcanisation consists of the selective cross-linking of the elastomer and its fine dispersion throughout the thermoplastic phase under intensive mixing [3]. Therefore, the final TPV morphology consists of cross-linked rubber particles finely dispersed in a thermoplastic matrix. Typical TPVs are formulated with high elastomer/thermoplastic ratios. Because the initial blend morphology consists of a thermoplastic phase dispersed in an elastomeric matrix, or co-continuous phases, phase inversion must occur during TPVs production.

TPVs morphology results from complex interrelationship among composition, viscosity and elasticity ratios of individual components, processing conditions and crosslinking reaction. Several authors have previously investigated the morphology development during dynamic vulcanisation [5-11]. It has been shown that if the rubber is partially cross-linked a co-continuous morphology is established, even if the initial non-cross-linked blend consists of a thermoplastic phase dispersed in the rubber phase [6,11]. Abdou-Sabet [12] suggested that phase inversion during dynamic vulcanisation occurs through co-continuous morphology, i.e., a co-continuous structure is formed in the initial stages of cross-linking and as the cross-linking degree increases the continuous rubber phase becomes more elongated and then breaks up into microgel particles. According to Radush et al. [8], at high rubber contents, the formation of fine rubber particles dispersed in the thermoplastic phase is only achieved if an initial co-continuous blend morphology exists before the addition of the cross-linking system. A scheme for morphology development was suggested based on these observations [9]. According to this scheme, the co-continuous structure is deformed by shear and elongation stresses but it remains the same until the addition of the cross-linking system. As the cross-linking degree increases, shear and elongation stresses increase and the rubber phase is stretched out until it reaches a critical stress then breaks up into small particles. Machado et al. studied the morphology development of EPDM/HDPE/oil-based TPVs with different compositions along the screw axis in a co-rotating twin-screw extruder [13]. They reported that the melt temperature increased very quickly in the first kneading zone (mainly for high EPDM levels) and that the rubber gel content was close to 100% before HDPE melting was completed. For a 33/33/33 (w/w/w) EPDM/HDPE/oil TPV, phase inversion of the EPDM was found to be driven by a combination of the completed melting of the HDPE phase and the continued cross-linking of the EPDM phase. Verbois et al. [14] showed that phase inversion in an EVA/PP system during dynamic vulcanisation occurred via a cocontinuous morphology at an EVA gel content of approximately 60wt. %.

Despite of the studies to date, following the morpho-logical-development mechanism during EPDM(ethylene-propylene-diene terpolymer)/ PP (polypropylene)-based TPVs production remains a difficult task, mainly due to the speed of the cross-linking reaction. Final TPV morphology can be achieved in less than one minute [7,8,13,15]. Therefore, the collection of samples to follow the morphological development and correlate it with the evolution of the physical and chemical phenomena taking place is rather complex. In the present work, a strategy was adopted to overcome these problems, namely, the use of two low-molecular-weight (low-Mw) EPDMs. This formulation was expected to retard the cross-linking of the EPDM phase, resulting in a slower morphological development during dynamic vulcanisation. Thus, this work aimed to obtain a better understanding of the mechanisms of morphology developed and phase inversion during the production of EPDM/PP TPVs. To achieve this goal, EPDM/PP blends with different weight ratios and EPDM and PP polymers with different Mws were dynamically vulcanised using resole/ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as the crosslinking agent. TPVs were prepared in a Haake Batch mixer and samples were collected over time for subsequent characterization.

## Experimental

### Materials

All polymers used in this work are designed by a code, which is EPDMX or PPX (where X is the polymer complex viscosity at  $65 \text{ s}^{-1}$  ).

EPDM1648 is a commercial product (K2340A: 53wt. % ethylene and 6wt. % ethylidene norbornene (ENB); with a weight-average molecular weight of 160 kg/mol ) supplied by DSM Elastomers B.V. and EPDM3.4 is a liquid EPDM (Trilene <sup>(8)</sup> 67: 54% ethylene and 9.5% ENB, with a weightaverage molecular weight of 7.2 kg/mol ) provided by Chemtura. EPDM53 (56 wt.% ethylene and 4wt. % ENB, with a weight-average molecular weight of 47 kg/mol ) was prepared in our laboratory by controlled degradation of EPDM1648 using 0.05 phr of cumyl hydroperoxide. The EPDM1648 was premixed with the peroxide and processed in a Leistritz LSM 30.34 intermeshing co-rotating twin extruder at a throughput of 0.33 kg/h, a screw speed of 10 rpm and a barrel set temperature of 380°C. The changes of copolymer composition are due to chain scission and reaction of the ENB groups during degradation.

The PP homopolymers, PP2116, PP950, PP443 and PP184, are commercial products supplied by Sabic Europe; 531P: MFI = 0.3; 524P: MFI = 2; 575P: MFI = 10.5; and 579 S: MFI = 47 g/10 min, all at 230°C/2.16 kg.

The cross-linking system was composed of an octylphenol-formaldehyde resin (SP1045, Schenectady International, USA) called a "resole" ( 5 phr ), and a combination of stannous chloride (  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  ) ( 1.5 phr ) and zinc oxide (  $\text{ZnO}$  ) ( 1.8 phr ) as activators (both from Aldrich). The designation phr is used in the rubber industry, it means parts per hundred rubber. Irganox 1076 from Aldrich was used as a stabilizer ( 0.25wt. % relative to the total amount of polymer (EPDM and PP)).

### Rheological characterization

Dynamic rheological measurements were performed at 200°C over the range of 0.1 – 100rad/s using a stress-controlled rotational rheometer (TA Instruments AR-G2) equipped with parallel-plate geometry. Samples with a diameter of 25 mm and a thickness of 1 mm were compressed molded from the pure polymers (EPDM and PP) at 200°C under a pressure of 30 tons. EPDM53 and 3.4, which are liquids at room temperature, were placed

Table 1  
Melt-complex viscosities and the storage modulus of the EPDMs and PPs used.

Material code	$\eta^{* a}$ (Pa s)	$G' a$ (Pa)
PP2116	2116	$1.2 \times 10^5$
PP950	950	$5.0 \times 10^4$
PP443	443	$1.9 \times 10^4$
PP184	184	$5.4 \times 10^3$
EPDM1648	1648	$8.1 \times 10^4$
EPDM53	53	$9.0 \times 10^2$
EPDM3.4	3.4	$1.3 \times 10^1$

Table 2  
Compositions of the EPDM/PP blends without (PBs) and with cross-linking (TPVs).

Coding	EPDM (wt.%)	PP (wt.%)	Irganox (wt.%)	ZnO (wt.%)	Resole (wt.%)	SnCl <sub>2</sub> (wt.%)
PBs						
30/70	29.93	69.83	0.25	-	-	-
50/50	49.88	49.88	0.25	-	-	-
70/30	69.83	29.93	0.25	-	-	-
TPVs						
30/70	29.20	68.13	0.24	0.53	1.46	0.44
50/50	47.89	47.89	0.24	0.86	2.39	0.72
70/30	66.00	28.29	0.24	1.19	3.30	0.99

directly in the rheometer. For each polymer, a stress sweep was carried out from 0.5 to 5000 Pa at frequencies of one and 10 Hz to determine the linear viscoelastic domain.

The rheological characterization of the raw polymers has been reported elsewhere [16]. Thus, only the meltcomplex viscosities and the storage moduli of the EPDMs and PPs at a

shear rate of  $65 \text{ s}^{-1}$  (estimated for the batch mixer used at 80 rpm using the model developed by Bousmina et al. [17]) are shown in Table 1.

## Compositions

Blends and TPVs (without and with cross-linking, respectively) were prepared using different EPDM/PP weight ratios. Three EPDMs (EPDM1648, EPDM53 and EPDM3.4) were combined with each PP (PP) at 30/70, 50 / 50 and 70/30 (EPDM/PP, w/w) compositions. The compositions in terms of the weight percentage of components for blends and TPVs are presented in Table 2. The amount of stabilizer, Irganox 1076, was maintained constant relative to the total amount of polymers (EPDM plus PP). The weight percentage of cross-linking agents was varied for each composition to maintain a constant concentration relative to the amount of EPDM.

## Blend and TPV preparation

Blends and TPVs were prepared in a Haake batch mixer (HAAKE Rheomix 600 OS ; volume 69 mL ) at  $200^\circ\text{C}$  and a rotor speed of 80 rpm . The PP pellets were introduced into the hot mixer first; after the PP was melted, the stabilizer was added and then the EPDM rubber. After about three minutes the torque reached a constant value, indicating the formation of a homogenous melt; a sample was then collected (i.e., at time zero). Then the mixing was continued and ZnO , resole and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were added in this order (which took about 5 s ). Time zero (beginning of the reaction) was defined as the instant when  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added. After that, samples were collected at different reaction times ( 45, 120 and 300 s and/or at 30, 60, 90, 120 and 300 s). For sampling, the rotors were stopped and samples weighing approximately 1.5 g were quickly taken from the mixer using a spatula, which took about 5 s . Then mixing was continued and this process was repeated several times up to 300 s . At this time ( 300 s ), the total amount of material was removed.

The blends were prepared and collected using the same procedure as for the TPVs, with the exception of the addition of the cross-linking system. All of the samples collected from the mixer were cooled between two metal plates to stop the cross-linking reaction and to avoid morphological changes.

## Sample characterization

The EPDM gel content was determined as a measure of the cross-linking degree by extraction in cyclohexane at room temperature. For extractions, approximately 200 mg of TPV sample was weighed and then immersed for 48 h under gentle stirring; the solvent was refreshed after 24 h . The residual weight was determined after drying the sample in a vacuum oven at  $100^\circ\text{C}$  for 12 h with nitrogen purging. The EPDM gel content was calculated assuming that the residue consisted of insoluble PP, ZnO, resole,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and cross-linked EPDM.

The degree of equilibrium swelling was measured because it can be used to confirm the trends in cross-linking and also gives a qualitative indication of the occurrence of phase inversion. The procedure was the same as described previously for the determination of EPDM gel content. However, in this case the swollen sample was weighed in a sealed glass bottle after carefully removing the excess cyclohexane with a tissue before drying. The swelling degree was calculated as the ratio of the weights of the swollen and dried sample.

The morphology was studied by scanning electron microscopy in back-scattering mode (SEM-BSE) using a Leica Cambridge S360 scanning electron microscope. Samples were fractured in liquid nitrogen and vapor stained with ruthenium tetroxide for 120 min. In the case of TPVs produced with the high-viscosity EPDM (EPDM1648), the morphology was also characterized by TEM using a Philips CM120 transmission electron microscope (TEM); samples were cryomicrotomed into 100 -nm-thick sections at  $-130^{\circ}\text{C}$  and then vapor stained with ruthenium tetroxide for 20 min. Disintegration tests were performed on samples collected before adding the cross-linking system (at time zero) to provide complementary information on phase morphology. Tests in cyclohexane were carried out at room temperature and done according to a procedure described elsewhere [16].

## Results and discussion

Even though it has been reported in the literature that the morphology of EPDM/PP blends is established quite rapidly and a (significant) reduction of domain size occurs during melting (or softening in case of an elastomer) [1823], the morphology development of these blends during mixing was further investigated here. The morphology of the physical blend, corresponding to each TPV prepared in the present work, were also analyzed after 300 s of mixing [16]. Comparing the morphologies of the physical blends samples collected along the time with the samples collected at time 0 s (before the addition of the crosslinking system), no significant changes in morphology were generally observed. The exceptions to this behavior were the blends made with the lowest-Mw EPDM. In the case of the EPDM3.4/PP2116 blend with 50wt.%PP, it was verified that the initial blend morphology, consisting of PP dispersed in the EPDM matrix, became co-continuous after five minutes of mixing. Phase inversion during mixing occurred for the EPDM3.4/PP2116 blend with 70wt.% EPDM; the initial blend morphology (0 s), consisting of PP dispersed in an EPDM matrix, changed to EPDM, partially dispersed and partially continuous, within a PP matrix (at 300 s). Thus, to guarantee that these changes in TPV morphology were only induced by cross-linking, blend morphology development over time was first investigated.

### Blend morphology development

Fig. 1 shows the morphology development during melt mixing of the EPDM3.4/PP950 blend with a 50/50 composition together with a plot of the torque as a function of mixing time. The first peak in the torque curve corresponds to the loading of PP; after PP melting, EPDM3.4 was added and a decrease of the torque, to close to 0 Nm, was observed. The torque then remained fairly stable until the end of mixing; however, a slight increase in the torque at around four minutes of mixing was noticed. The SEM-BSE micrograph of a sample collected at 0 s (the formation of a homogenous melt) shows a coarse dispersion of PP phase, very small and large PP domains co-exist in the EPDM matrix. After 30 s, a better dispersion of PP was achieved. Although the torque slightly increased just before a sample was collected at 60 s, no significant difference in morphology between the 30-s and 60-s samples was detected. At 90 and 120 s, the EPDM matrix seemed to become thinner at some locations and began to break up while PP became more continuous, this being more evident at 120 s. At longer mixing times, e.g., 600 s, it seems that the shear induced some phase coarsening. This behavior was also reported by Thomas et al. [24] in the case of blends with a pronounced tendency to coalesce. These results show that the blend morphology changed slightly during mixing and was most likely not stable

up to 600 s ; additionally, after 300 s a considerable degradation of the PP can occur, which also contributes to morphological changes.

Taking these results into consideration, the mechanism of morphology development during dynamic vulcanisation of this blend was investigated at two times (0 and 90 s ) with the addition of the cross-linking system. Because no significant differences on either cross-linking degree or morphology development were observed, the cross-linking system was subsequently added at 0 s for all of the TPVs prepared.

## Dynamic vulcanisation

### Torque and temperature

Fig. 2 shows the torque and temperature evolution as a function of time recorded during the dynamic vulcanisation of 50/50 (w/w) EPDMs/PP950 blends. The marked points correspond to sample collections ( 0,45,120 and 300 s ). For all torque curves, the first peak corresponds to the introduction of PP into the mixer. The second peaks in the cases of EPDM1648 and EPDM53 correspond to EPDM loading. For the EPDM/PP TPV with EPDM3.4, a decrease of torque was observed when the EPDM was added, which is associated with the low viscosity of this rubber. Afterward, the torque reached a relatively constant value, indicating that PP melting was complete and the EPDM/ PP mixture was fully homogenized. The addition of the phenolic resin caused a sudden decrease in the torque due to a lubricating effect. This effect was not noted in the case of EPDM3.4 due to the very low torque values before its addition. The torque then increased sharply, which

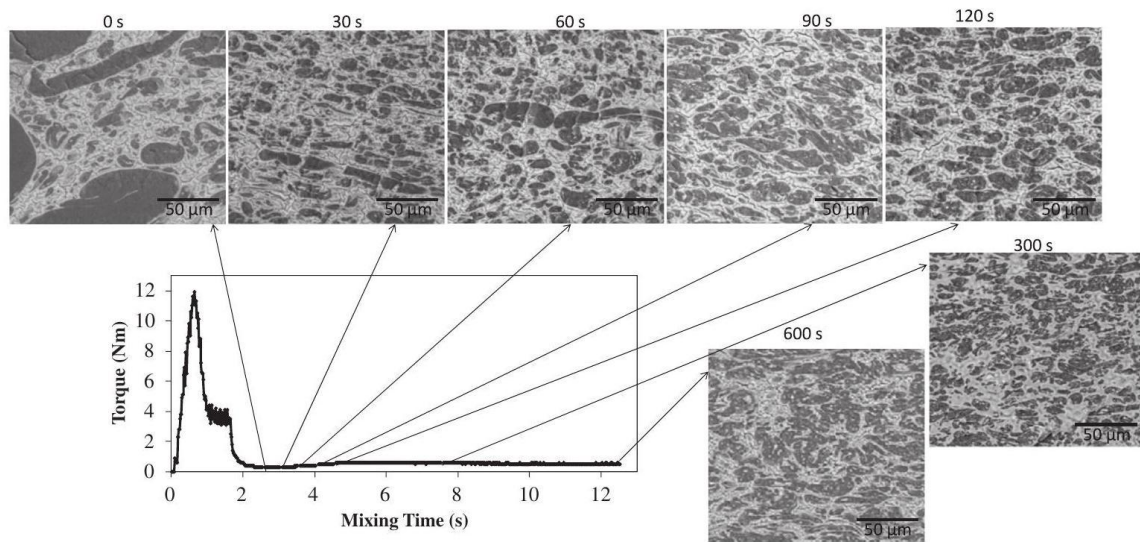


Fig. 1. Torque and SEM-BSE micrographs of EPDM3.4/PP950 blend with 50wt%PP versus mixing time.

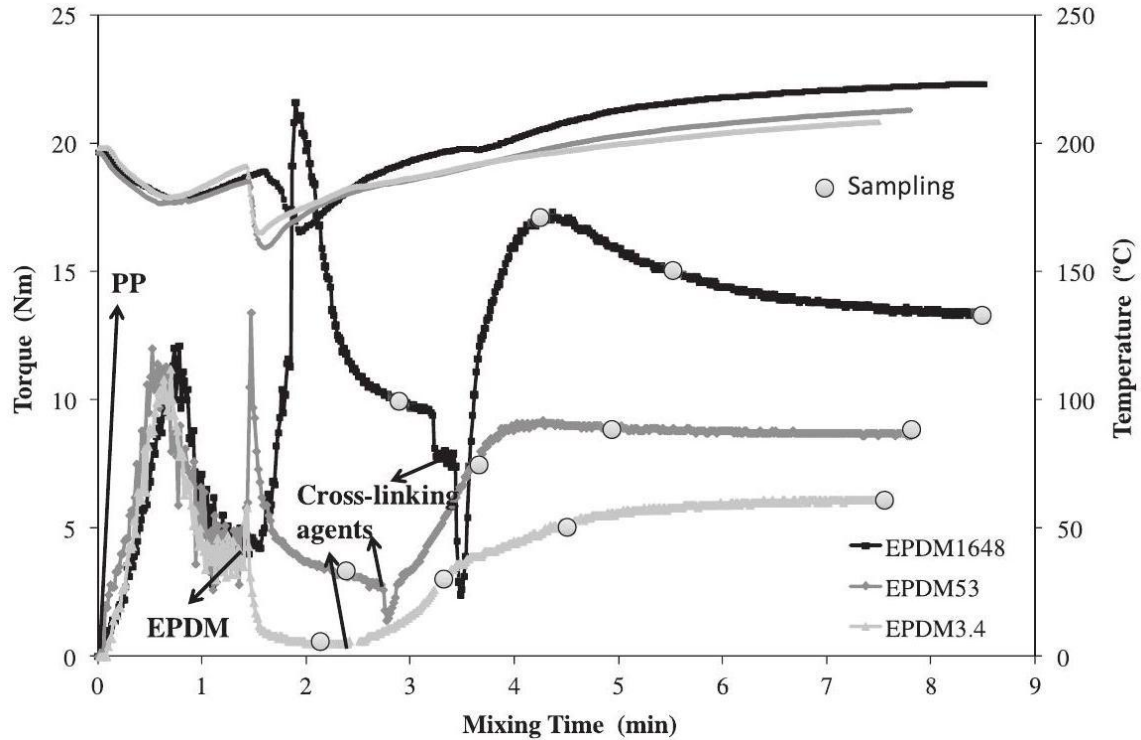


Fig. 2. Torque and temperature of EPDM/PP TPVs made with the various EPDMs and PP950 at 50wt%PP during mixing time. is related to the drastic changes in the viscosity and elasticity of the EPDM phase due to cross-linking. As expected, at the end of mixing, the torque value was correlated with the molecular weight of the non-cross-linked EPDM, i.e., the final torque value increased as the EPDM Mw increased.

The temperature curves show a decrease when the polymers were fed due to the introduction of a cold mass into the hot mixer and the melting of PP. Upon EPDM addition, a continuous increase in the melt temperature was observed, surpassing the set temperature after the addition of the cross-linking system due to viscous energy dissipation enhanced by the cross-linking reaction. The melt temperature increased as the EPDM molecular weight increased, as expected. Both the torque and temperature curves are similar to those reported in other studies of the dynamic vulcanisation of EPDM/PP blends [15,25-27].

## Disintegration tests

The results of the disintegration tests performed in cyclohexane at room temperature on samples collected

Table  
Disintegration tests of the EPDM/PP blends.

Blend at 0 s	EPDM/PP composition		
EPDM/PP	70/30	50/50	30/70
1648/2116	ND	ND	ND

1648/950	ND	ND	ND
1648/443	ND	ND	ND
1648/184	ND	ND	ND
53/2116	D	ND	ND
53/950	D	ND	ND
53/443	D	ND	ND
53/184	D	ND	ND
3.4/2116	D	D	D
3.4/950	D	D	ND
3.4/443	D	ND	ND
3.4/184	D	ND	ND

before adding the cross-linking system are shown in Table 3. Extractions give complementary information on phase morphology. As only EPDM dissolves in cyclohexane at room temperature, the following can be concluded from these tests: (i) if the sample disintegrates (D), it means that EPDM phase is the matrix; (ii) if the sample does not disintegrate (ND), it means that PP is the continuous phase.

Disintegration was not observed for blends made with EPDM1648, even in EPDM-rich compositions ( 30wt. % PP ), suggesting that PP was continuous for all of the blend compositions at time zero, as shown in Table 3. In the case of the EPDM53/PP blends, disintegration was observed for all EPDM-rich compositions ( 30wt. %PP ), indicating that the EPDM phase was the matrix. For EPDM/PP blends with 50 and 70wt. %PP, the samples remained intact, suggesting that PP was already fully continuous. In the case of blends made with EPDM3.4, disintegration was observed for blends with 30wt. %PP, with 50wt. %PP with high viscosity (PP2116 and PP950) and with 70 wt. % PP2116. Blends prepared with EPDM53 and EPDM3.4 containing high EPDM amount were too sticky and soft and their samples could not be characterized by microscopy.

## Cross-linking degree

The EPDM gel content and the degree of equilibrium swelling were determined as a measure of the cross-linking degree of the EPDM phase. In a previous study [27], it was shown that the EPDM gel content determined by extraction in cyclohexane at room temperature is affected by the EPDM/PP weight ratio and morphology. Because the residue after extraction consists of PP, cross-linked EPDM and cross-linking agents, if the PP phase is the matrix and the EPDM phase is the dispersed phase, the solvent will not be able to efficiently remove all of the non-crosslinked EPDM. As PP dissolves in boiling xylene, extraction in boiling xylene would be more suitable for determining

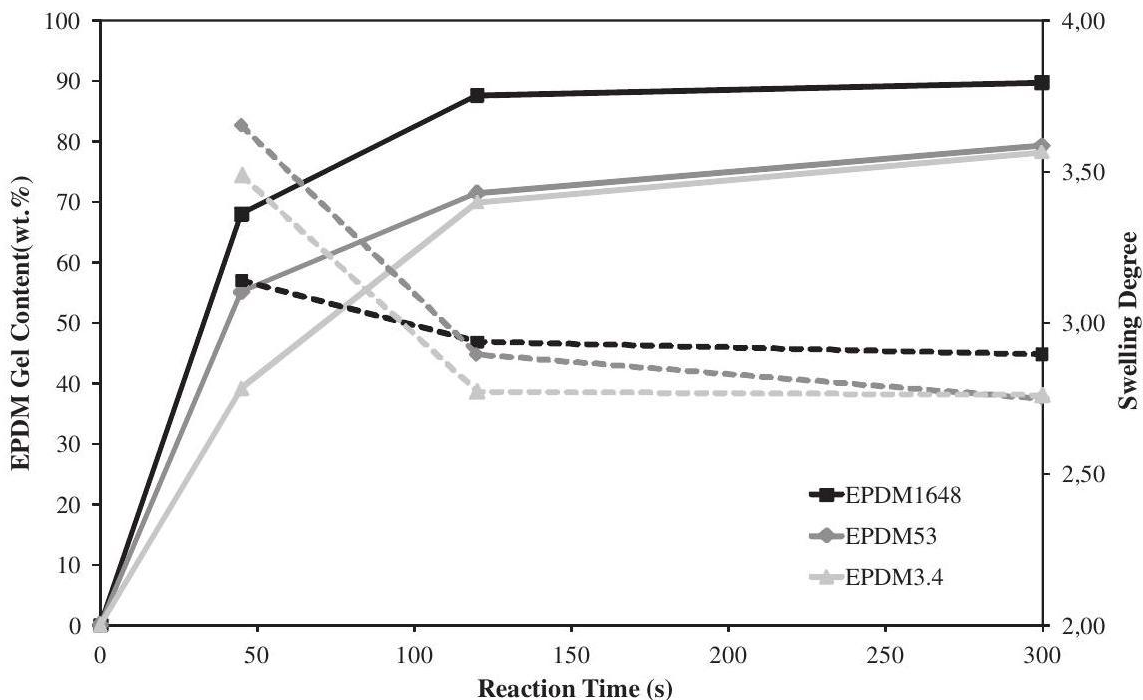


Fig. 3. Evolution of EPDM gel content and swelling degree of EPDM/PP950 TPVs with 50wt. %PP with reaction time. the cross-linking degree [27]. However, due to the high boiling temperature of xylene, samples collected at the early reaction times might contain unreacted resol and cross-linking might proceed during extraction. Consequently, to follow the evolution of the cross-linking degree as a function of time, EPDM gel content was determined by extractions in cyclohexane at room temperature instead.

Because the rigid PP becomes the matrix when phase inversion occurs, a significant decrease in the swelling degree is expected after the phase-inversion point. Thus, swelling degree was also used as a qualitative measure of phase inversion.

The values determined for the gel content and swelling degree will be presented later, during the morphology discussion, to make it easier to correlate the evolution of cross-linking degree and swelling with morphology development. Nevertheless, to compare the cross-linking kinetics of the different EPDMs used (i.e., of varying Mw), the EPDM gel content and the equilibrium swelling degree versus reaction time are shown in Fig. 3 for EPDM/PP950 TPVs with 50wt. %PP as an example. The absolute error of the EPDM gel content values for the TPV samples was approximately 5%. Generally, the EPDM gel content increased and the swelling degree decreased with reaction time, indicating that the degree of cross-linking increases, as expected. A more detailed analysis shows that at 45 s after adding the cross-linking system, the EPDM gel contents were 68%, 55% and 39% for the EPDM1648, EPDM53 and EPDM3.4, respectively. Then at 120 s, the EPDM gel content increased to 87% for EPDM1648 and to around 70% for the others. After that, the EPDM gel content slightly increased, reaching 90% for the high-Mw EPDM and close to 80% for the low-Mw EPDMs. These results suggest, as expected, that the cross-linking reaction slowed down as the Mw EPDM decreased, mainly in the early mixing stages ( 45 s ). The final cross-linking degree of the TPVs was higher for the highest-Mw EPDM and no significant differences were found between the other two blends prepared with lower Mw EPDMs.

The swelling degree of EPDM1648/PP950 TPV remained almost unchanged after 45 s , ( 3.1 at 45 s and 2.9 at 300 s ) suggesting that PP was already the matrix at 45 s . TPVs made with low-Mw EPDMs exhibited a different behavior; here, a significant decrease of the degree of equilibrium swelling was detected between 45 and 120 s, from 3.7 to 2.8 and 3.5 to 2.8 for TPVs made with EPDM53 and EPDM3.4, respectively. This decrease suggests that phase inversion occurred or was fully completed during this time period.

## **Influence of EPDM Mw on morphology development**

Micrographs of the samples collected before (at 0 s ) and after adding the cross-linking system (at 45, 120 and 300 s ) are depicted in Fig. 4 for the EPDM/PP950 TPVs with 50 wt. % PP. Here EPDM appears as the darker phase and PP as the lighter one. On the contrary, in SEM-BSE micrographs EPDM is white and PP is the dark phase. Generally, the morphologies shown in the micrographs are representative of the whole sample. The exceptions are the samples collected at 45 s , which had rather heterogeneous morphologies.

The initial morphology of the EPDM1648/PP950 TPV before adding the cross-linking system (at 0 s ) was co-continuous, i.e., both EPDM and PP were continuous. At 45 s, the EPDM (dark phase) appear to be dispersed, but several elongated EPDM domains, sometimes connected by a thin EPDM thread, were also observed. At 120 and 300 s, similar morphologies were obtained, consisting of EPDM domains dispersed within the PP matrix.

Even though the PP phase (dark phase) seems to be mainly dispersed in the EPDM matrix in the EPDM53/ PP950 TPV at 0 s , the sample did not disintegrate in cyclohexane (Table 3), suggesting that PP is a continuous structure here. At 45 s, EPDM and PP were stretched, resulting

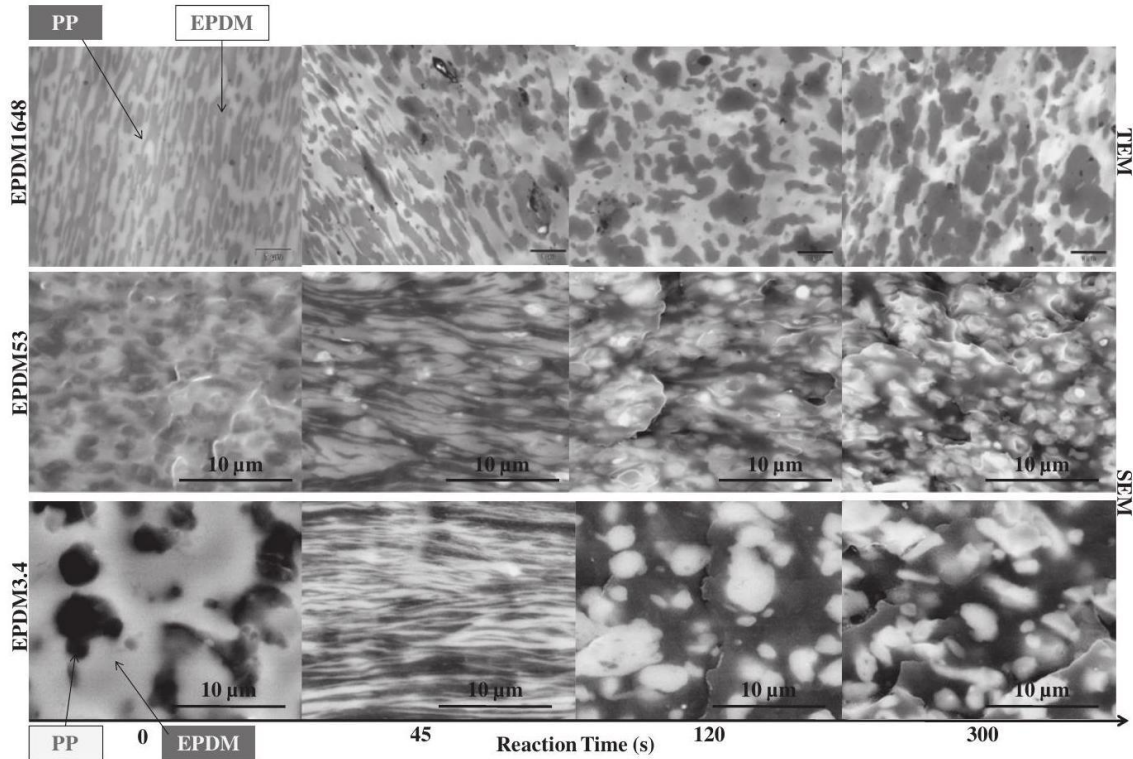


Fig. 4. Micrographs of samples of EPDM1648/PP950 (TEM) and EPDM53/PP950 and EPDM3.4/PP950 (SEM-BSE) TPVs with 50 wt. % of PP, collected at 0,45 , 120 and 300 s

in elongated structures. Although both phases appear continuous, PP seems to be more the matrix. Micrographs of the samples collected at 120 and 300 s exhibited EPDM dispersed in the PP the matrix without significant differences between the morphologies.

At 0 s in the EPDM3.4/PP950 TPV, PP was dispersed in the EPDM matrix before the addition of the cross-linking system. It can be seen that the PP domain size was rather heterogeneous, which was probably related to the large difference between the PP and EPDM viscosities. This morphology is in agreement with the disintegration tests (Table 3); the sample disintegrated, meaning that EPDM was the matrix. In the early stage of cross-linking, 45 s , both EPDM and PP were continuous and exhibited elongated structures. It seems that the EPDM phase was connected by thin layer that started to break up, leading to the formation of EPDM threads dispersed in the PP phase. At later reaction times (120 and 300 s), EPDM was already the dispersed phase and PP was the matrix.

Comparing the TPV morphologies at 45 s , the EPDM phase became less continuous as the EPDM Mw increased. This is related to the differences in the cross-linking degree and probably to the initial blend morphology. As stated above, the EPDM gel contents were 68%, 55% and 39% for EPDM1648, EPDM53 and EPDM3.4, respectively (Fig. 3). Thus, the cross-linking reaction was slower for the lowMw EPDM and, consequently, the morphology development was also slower. At 120 s, the morphology of all TPVs was already established, with EPDM dispersed in the PP matrix independently of the EPDM gel-content value, meaning that phase inversion occurred before the formation of an EPDM gel content of 70wt. %.

Comparing the morphological development with the data for the degree of equilibrium swelling, a pronounced decrease in swelling values for EPDM53 and EPDM3.4 between 45 and 120 s can be observed in Fig. 3. This change was not only related to the increase of cross-linking degree but also to the morphological changes (phase inversion). In the case of EPDM1648, at 45 s, PP was already the matrix and, thus, no pronounced decrease in the swelling degree was observed.

## Influence of EPDM/PP weight ratio on morphology development

To investigate the effect of composition on morphology development during dynamic vulcanisation, SEM-BSE micrographs, EPDM gel contents and the degrees of equilibrium swelling for the EPDM53/PP950 TPVs with 30 and 70wt. %PP were determined and are depicted in Fig. 5.

For the EPDM-rich TPV ( 30wt. %PP ), PP was dispersed in the EPDM matrix before the addition of the cross-linking system ( 0 s ). This was also confirmed by the disintegration tests. At 45 s , the initial structure was strongly deformed and EPDM started to break up, leading to the formation of elongated EPDM domains and, simultaneously, the deformed PP phase started to coalesce. The morphologies obtained at 120 and 300 s were quite similar, suggesting that morphology was already stable at 120 s . It was observed that the EPDM phase had a greater tendency to be dispersed; however, it appears rather continuous here, suggesting that the cross-linking reaction was insufficient to achieve complete phase inversion in this case.

For the PP-rich compositions ( 70wt. %PP ) before crosslinking began, PP was the matrix and EPDM was dispersed

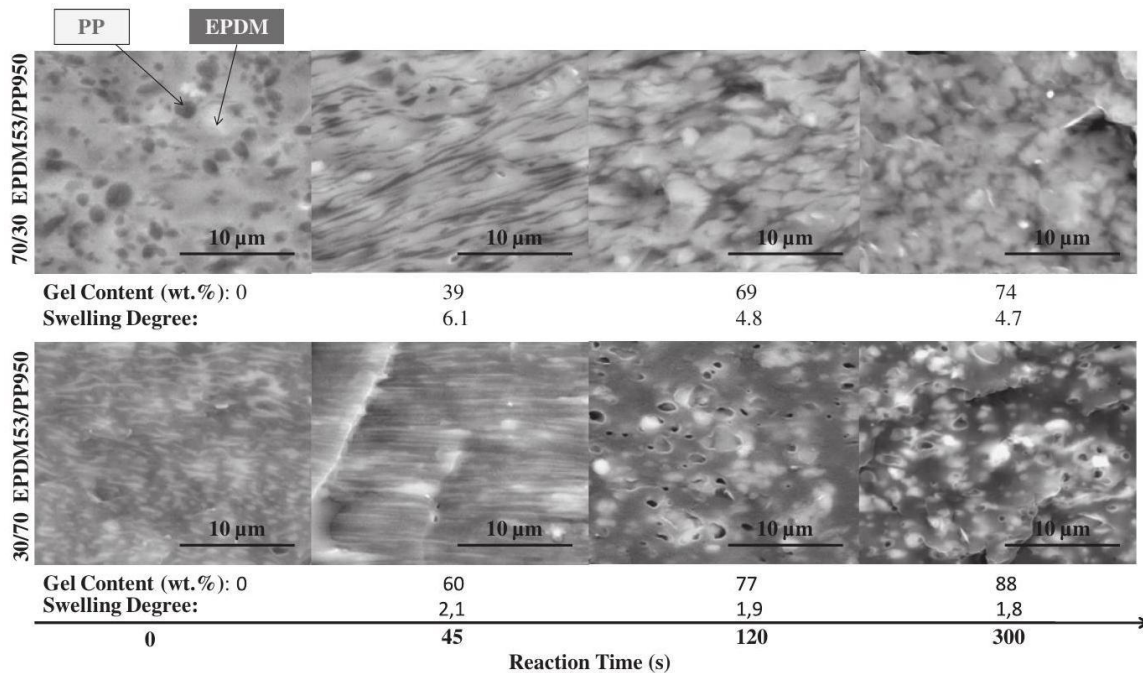


Fig. 5. SEM-BSE micrographs of samples of EPDM<sub>53</sub>/PP<sub>950</sub> TPVs with 30 and 70wt%PP collected at 0,45,120 and 300 s . Below the micrographs are the corresponding EPDM gel contents and swelling degrees. with a heterogeneous domain size. After 45 s , thin EPDM threads were detected in the PP matrix, which broke up and led to the formation of homogeneous EPDM particles dispersed in the PP matrix at 120 s . As no significant differences were detected between the morphologies at 120 and 300 s here, it seems that the morphology was fully developed at 120 s , consisting of EPDM particles dispersed in a PP matrix.

Despite the composition difference (30 and 70wt. % ), the mechanisms of morphology development in the two blends seem to be quite similar and also similar to that observed with 50wt. % (Fig. 4). Taking into account the EPDM gel contents, i.e., 39%, 55% and 60% for compositions of 30 , 50 and 70wt.%PP, respectively, the stage of morphological development seems to be more related to the cross-linking degree than to composition. Although composition influenced the final TPV morphology, the general stages of the morphology development mechanism seem to be independent of the composition. At early reaction stages, 45 s , the structure was highly deformed; here, it seems that the cross-linking reaction induces the formation of a lamellar/fibrillar structure which then breaks up, resulting in small particles. Then at 120 s , the morphology is fully developed and stabilized.

## **Influence of PP viscosity on morphology development**

It is known that the viscosity ratio affects the initial blend morphology and the EPDM particle size of the TPV final morphology [9,15]. However, there have been no reports on the influence of the viscosity ratio on morphology development during dynamic vulcanisation. Fig. 6 depicts SEM-BSE micrographs of TPVs prepared with EPDM<sub>3.4</sub> and PPs of different viscosities. The micrographs of the samples collected at different reaction times are displayed in relation to EPDM gel content. The morphology of the EPDM<sub>3.4</sub>/PP<sub>2116</sub> at 0 s was not available, but extraction experiments confirmed that EPDM was the matrix and PP seemed to be dispersed. For the EPDM<sub>3.4</sub>/PP<sub>950</sub>, the morphology at 0 s consisted of PP dispersed in an EPDM matrix, whereas for the EPDM<sub>3.4</sub>/PP<sub>443</sub> a co-continuous morphology was observed. As before, in TPVs made with PP<sub>950</sub>, cross-linking induced the formation of elongated EPDM structures at 45 s , appearing as lamellar structures. The elongated EPDM structures seen at 45 s were also observed for PP<sub>443</sub>, even when the initial morphology (at 0 s ) was co-continuous rather than PP dispersed in the EPDM matrix. The formation of these elongated structures occurred in the range of EPDM gel contents between 20% and 60%. In contrast, for EPDM gel contents around 20% the morphology remained co-continuous; for EPDM gel contents around 60%, dispersed and somewhat continuous elongated EPDM structures were observed. At 120 s, the EPDM was fully dispersed in the PP matrix. In Fig. 6, a plot of swelling degree versus reaction time is also shown. The TPVs made with PP<sub>950</sub> and PP<sub>443</sub> exhibited significant decreases in swelling degree between 45 and 120 s, corroborating the morphological changes from co-continuous to dispersed-matrix morphologies.

The EPDM<sub>3.4</sub>/PP<sub>2116</sub> TPV presented a different behavior. The initial blend morphology consisted of PP dispersed in an EPDM matrix and, 45 s after adding the cross-linking system, EPDM was already dispersed in the PP matrix. The swelling degree (Fig. 6) was practically unchanged, also suggesting no further changes in morphology after 45 s . In this case, phase inversion occurred earlier than in the TPVs made with the other PPs. One

possible explanation is the high gel content ( 65wt. % ) observed at 45 s ; another is the large difference between the viscosities and

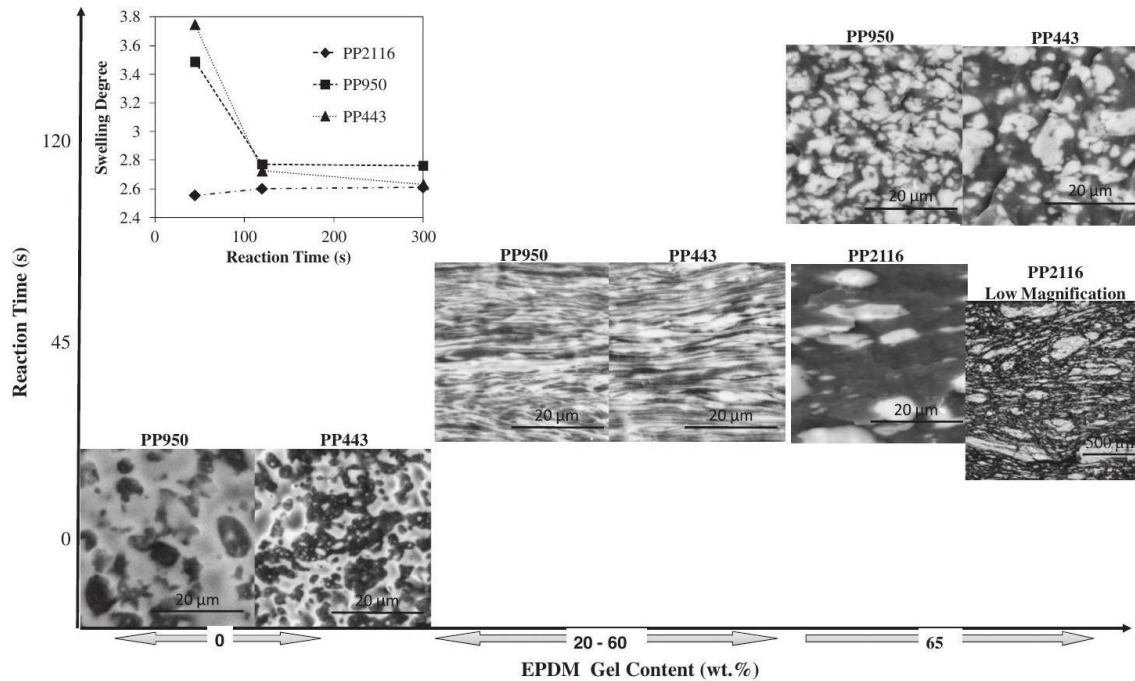


Fig. 6. EPDM3.4/PP TPVs with 50 wt.% PP: SEM-BSE micrographs at different reaction times in relation to EPDM gel content and swelling degree versus reaction time (inset plot).

elasticities of the EPDM and PP phases. As the EPDM viscosity began to increase due to the cross-linking reaction, the highly elastic PP was able to encapsulate the EPDM phase. Therefore, EPDM was encapsulated before being well stretched and a coarse morphology (as can be seen in the low-magnification micrograph of Fig. 6) resulted for these TPVs. These results provide evidence that the viscosity ratio affects morphology development during dynamic vulcanisation.

## Morphological-development mechanism

The results presented above yielded information on the effects of the Mw of the EPDM, the blend composition, the viscosity ratio and the EPDM gel content on morphology development. However, for more detailed insight into the morphological-development mechanism during dynamic vulcanisation, samples were collected at smaller time intervals after adding the cross-linking system ( 30,60, 90, 120 and 300 s). As the use of low-Mw EPDM allowed to decrease the cross-linking degree, EPDM3.4/PP950 with 50wt.%PP was chosen to investigate the mechanism of morphological development in more detail, including phase inversion driven by cross-linking. Moreover, the initial morphology of this blend consisted of dispersed PP instead of a co-continuous structure and, thus, complete phase inversion could be observed. The same experiment was performed with a conventional rubber used in TPV production (EPDM1648/PP950 with 50wt.%PP ) to compare the results in both cases.

Fig. 7 shows the TEM micrographs of the EPDM1648/ PP950 TPV collected before ( 0 s ) and after adding the cross-linking agents ( 30,60 and 90 s). General views of the morphologies are shown in the micrographs at the top (at low magnification), and more detail is provided in the micrographs below (at higher magnification); the EPDM gel contents and the equilibrium swelling degrees are also given below each micrograph. Initially ( 0 s ), the morphology was co-continuous; 30 s after adding the cross-linking agents, EPDM is dispersed and continuous. Some elongated EPDM domains, sometimes connected by thin threads, were observed, similarly to the morphology obtained above at 45 s (Fig. 4). These kinds of structures can also be observed at 60 s . At 90 s , the cross-linked EPDM particles were mainly dispersed in the PP matrix, and, after that, no more changes in morphology were detected. The swelling degree remained practically unchanged after 30 s, confirming that, afterward, no significant morphological changes took place. The EPDM gel contents, 61% at 30 s and 76% at 60 s , indicate that the cross-linking reaction had proceeded to quite an extent even at 30 s . Most probably, the elongated structures observed (at 30 and 60 s) resulted from further deformation of the EPDM domains formed in the early stages of cross-linking by the breakdown of the co-continuous structure. Despite the results obtained, the cross-linking degree with the high-Mw EPDM is higher and the morphological development in the initial stages of cross-linking could not be monitored.

The morphology of the samples collected during dynamic vulcanisation of the EPDM3.4/PP950 blend are shown in Fig. 8. At 0 s , the PP phase was dispersed in the EPDM matrix. After cross-linking began ( 30 s ), the initial structure was strongly elongated; the EPDM matrix broke down and the PP coalesced, leading to the formation of

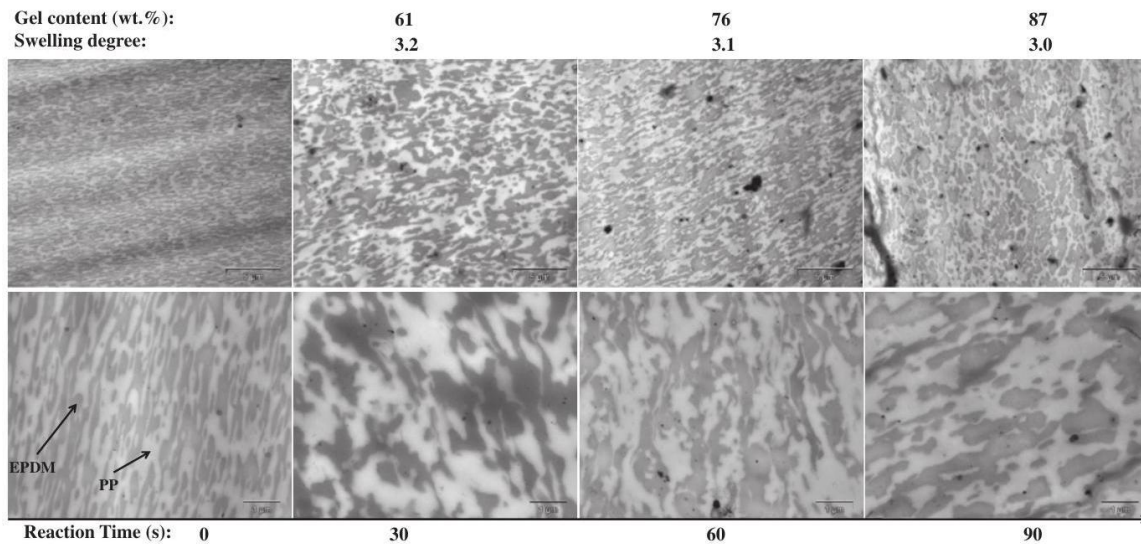


Fig. 7. Morphology development of EPDM1648/PP950 with 50 wt. % PP during dynamic vulcanisation.

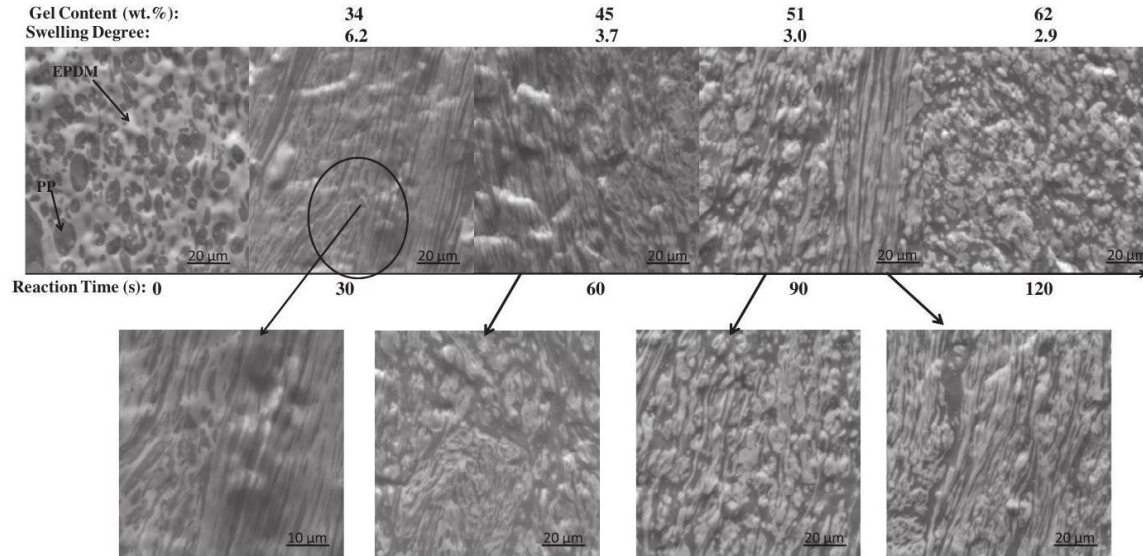


Fig. 8. SEM micrographs of EPDM3.4/PP950 samples with 50wt%PP collected during dynamic vulcanisation. At 0 s, elongated EPDM and PP domains, appearing as a lamellar structure. At 30 s, elongated EPDM and PP domains, appearing as a lamellar structure. At 60 s, different types of morphologies, such as PP dispersed in the EPDM phase, lamellar structures, elongated EPDM particles and dispersed EPDM particles were observed. This heterogeneity of TPVs morphology remained until 90 s. At this time, the EPDM appeared more as the dispersed phase and PP more as the continuous phase. EPDM fully dispersed in the PP phase was obtained at 120 s. After this, no further changes in morphology were detected. Judging by the swelling degree, the main changes in the morphology (phase inversion) occurred between 30 and 60 s because a decrease from 6.2 to 3.7 was observed; after 60 s of reaction time, it remained approximately constant.

Comparing the morphology development of both TPVs, it can be observed that the morphology of EPDM1648/PP950 was stable at 90 s whereas for EPDM3.4/PP950 it only became stable at 120 s. This may be related to the faster cross-linking reaction of the EPDM1648 and the viscosity ratio of the blend components. Another difference between the TPVs was the EPDM gel contents at which the morphology stabilizes, which were 62% (at 120 s) for TPV made with EPDM3.4 and 87% (at 90 s) for TPV made with EPDM1648. In the latter, even though the PP phase was the matrix at 30 s, an evolution of the EPDM phase (from connected to dispersed EPDM domains) was observed up to 90 s, and the EPDM gel content varied from 61% to 87%. In the case of the TPV made with EPDM3.4, at 120 s the EPDM gel content was 62% and no morphology refinement (further deformation and breakup of the dispersed EPDM phase) was seen. It seems that as soon as the PP950 encapsulated the EPDM3.4, no refinement of the morphology occurs; this may be related to the high elasticity of the PP950 relative to the EPDM3.4 (while the elasticity of PP950 is smaller than that of EPDM1648). Although cross-linking enhances the melt viscosity and melt elasticity of the EPDM phase, it was shown in a previous study [28] that the melt-complex viscosity and storage modulus of the cross-linked low-molecular-weight EPDM (at a cross-linking degree around the gel point) remained smaller than the PP phase. This suggests that PP (with higher elasticity) encapsulates the EPDM phase and no further deformation and break-up occur. The same behavior was also observed in the case of the EPDM3.4/PP2116 TPV, where phase inversion was observed to occur much earlier than in the other TPVs, after which no refinement of morphology was observed (Fig. 6). This can be explained by the Van Oene theory [29,30], which states that

the interfacial tension under dynamic conditions will be lower in a system where the highly elastic material is the matrix and the less elastic material is the dispersed phase.

From the above results, it is clear that the phase-inversion process and morphology refinement during dynamic vulcanisation occurs through the formation of elongated EPDM structures. The formation of elongated EVA structures was also observed by Deyrail and Cassagnau [31] in EVA/PDMS TPVs using a hot optical-shear device. They observed that droplet deformation decreased when the crosslinking level increased and, even though major deviations of the droplet deformation near the gel point were not noticed, it was possible to observe deformation of the EVA phase for cross-linking levels higher than the gel point. Radusch [9] also proposed that deformation of the rubber phase would be possible in the initial stages of cross-linking through the stresses transferred by the viscous thermoplastic matrix. According to Radusch, the initial co-continuous morphology is stretched more and more after the addition of the cross-linking system by the shear and elongation stresses, which increase as the viscosity of the rubber phase increases due to cross-linking. Then when a critical stress is reached, the stretched rubber phase will break apart into small particles and, after that, only distribution of the cross-linked particles occurs [9]. In the present work, it was observed that the stretched continuous EPDM structure first broke into EPDM threads, which were further elongated by the thermoplastic matrix and then broke up into small particles. Even in the case of the EPDM1648/ PP950, where it was not expected that the low-viscosity PP matrix would be able to deform the already cross-linked

EPDM phase, elongated EPDM domains were observed. Bhadane et al. [10] studied the effects of dynamic vulcanisation on the phase continuity and co-continuity of EPDM/PP blends using focused-ion-beam (FIB) etching of the sample surface followed by topological investigation of the sample surface using tapping-mode atomic-force microscopy (TMAFM). They reported the formation of a much finer and more extensive EPDM network (i.e., a continuous structure) upon dynamic vulcanisation of the coarse EPDM network in the initial uncross-linked EPDM/ PP blend. They suggested that the cross-linking reaction starts at the outer envelope of the EPDM phase and works its way towards the center. Consequently, due to the viscosity mismatch created between cross-linked and uncrosslinked EPDM and in response to the dynamic mixing conditions, the microgel particles detached from the initial network pull entangled chains of non-cross-linked EPDM, resulting in a refined continuous structure [10].

According to the above discussion, it is expected that cross-linking enhances the deformation and breakup of the EPDM structures, not only due to the increase of the shear and elongation stresses but also because of the viscosity mismatch created between the cross-linked and non-cross-linked EPDM particles. Once EPDM threads are formed, they seem to break up according to a Raleigh mechanism applied to polymers by Tomokita [32], as can be observed in the micrographs of Fig. 9. According to Tomokita, a thread surrounded by another polymer will break up due to instabilities driven by the interfacial tension. He suggested that the breakup of threads is related to the distortion of the elongated thread that runs sinusoidally. Therefore, the breakup of threads occurs when a critical distortion amplitude is reached. Although these relations were developed under quiescent conditions and for a Newtonian system, Elmendorp [33] found a good agreement for viscoelastic polymers.

This present study also shows that phase inversion, mainly with the low-Mw EPDM, is a rather heterogeneous process, suggesting that EPDM domains in the same sample have different levels of cross-linking. Indeed, it is anticipated that upon addition of cross-

linking agents to the EPDM/PP blend they are not instantaneously well distributed by the batch mixer, resulting in microscopically different levels of cross-linking. As the gel content measured is an average value of the macroscopic sample, thus

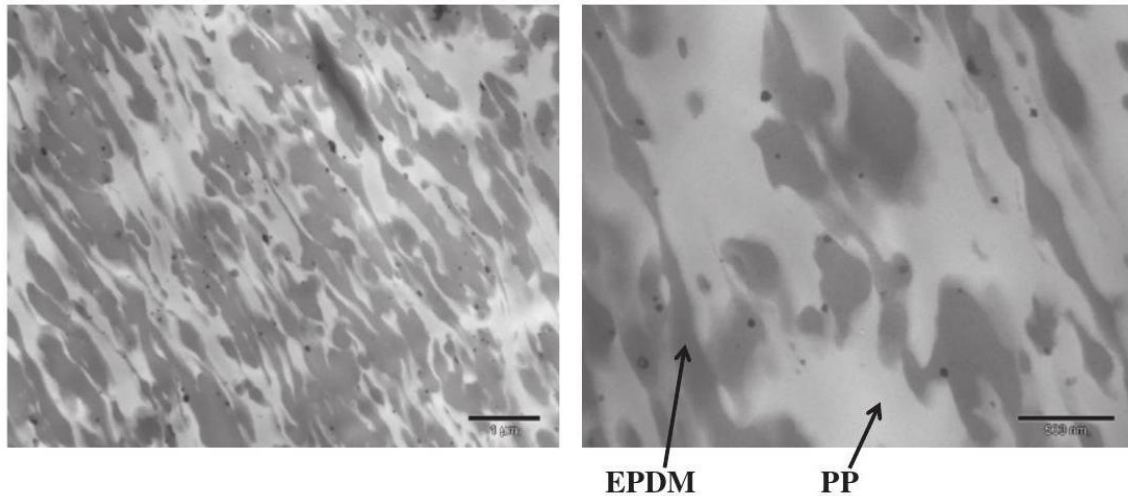


Fig. 9. TEM micrographs of a sample of the EPDM1648/PP950 TPV collected at 45 s .

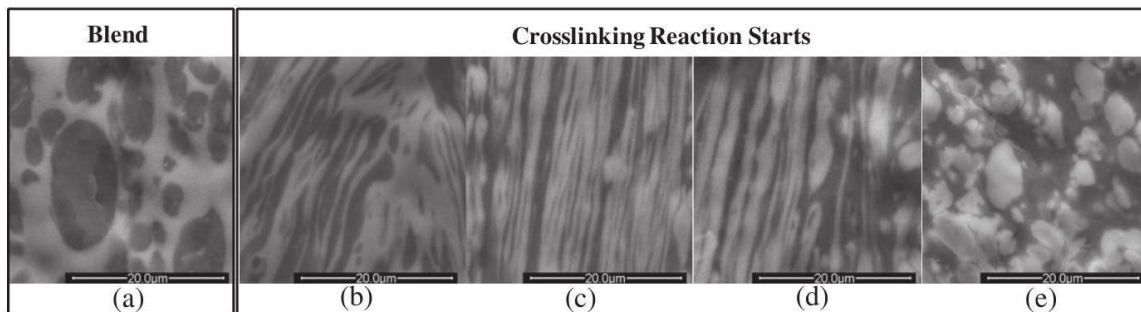


Fig. 10. Morphological-development mechanism proposed for phase inversion during dynamic vulcanisation. it is not representative of the cross-linking degree at a microscopic scale. Deyrail et al. [34] showed that the dispersion of the reagents in the EVA phase obtained in the batch mixer was very heterogeneous from a microscopic point of view. They showed that even when the cross-linking extent in the bulk corresponds to an 85% insoluble product (where deformation is not expected), some EVA droplets in a PDMS matrix were strongly deformed under shear flow, suggesting low levels of cross-linking. These results might also explain the elongated domains observed in the EPDM1648 product even at high degrees of cross-linking. Thus, the sort of structures observed in the micrographs at early reaction times are a consequence of the different kinetic stages of the EPDM phase resulting from the heterogeneous distribution of the cross-linking agents in the melt.

According to the results and the discussion above, a mechanism for phase inversion driven by cross-linking is proposed and is shown schematically Fig. 10. The mechanism can be described by the following steps (which correspond to each micrograph of Fig. 10):

- Before adding the cross-linking system, PP is dispersed in the EPDM matrix (Fig. 10a).
- Upon addition of the cross-linking system, as soon as the cross-linking agent comes into contact with EPDM, the reaction starts immediately:
- EPDM microgel particles formed start to effect the deformation of the EPDM matrix, which begins to break up, and PP starts to coalesce and become continuous (Fig. 10b).
- PP becomes more continuous (a highly viscous material in this case) and cross-linking advances; the shear and elongation stresses increase, resulting in further elongation of both phases, leading to the formation of a lamellar/fibrillar structure (Fig. 10c).
- As cross-linking proceeds, EPDM is further elongated and starts to break due to capillary instabilities (Fig. 10d).
- Finally, PP becomes the matrix and the cross-linked EPDM the dispersed phase (Fig. 10e).

## Conclusions

The morphology development during dynamic vulcanisation was investigated using an experimental plan consisting of vulcanising combinations of three rubbers and four PPs with different viscosities. It was demonstrated that the Mw of the EPDM has a significant effect on the cross-linking degree. At 45 s after adding the cross-linking system, the EPDM gel contents were 68%, 55% and 39% for the EPDM1648, EPDM53 and EPDM3.4 TPVs, respectively. As the cross-linking degree decreased using the low-Mw EPDM, the morphology development was also slowed, and it was possible to monitor the morphology development during TPV production. A stable morphology was achieved earlier for TPVs made with high-Mw EPDM. PP viscosity also plays an important role in both morphological development and phase inversion. A correlation between EPDM gel content evolution and morphology development was established.

The results obtained allowed to establish a general mechanism for morphology development during TPV production. Starting from PP dispersed in an EPDM matrix, at the early stages (EPDM gel content lower than 45% the EPDM matrix breaks down and the PP coalesces, leading to the formation of elongated EPDM and PP domains, appearing as a lamellar structure. As the EPDM gel content becomes close to 60%, different types of morphology, such as PP dispersed in the EPDM phase, lamellar structures, elongated EPDM particles and dispersed EPDM particles were observed. EPDM fully dispersed in the PP matrix is only achieved at gel content higher than 60%.

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<sup>a</sup> At 200°C, 65 s<sup>-1</sup> (estimated average shear rate in the internal mixer).