Phase Inversion of EPDM/PP Blends: Effect of Viscosity Ratio

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Abstract

EPDM/PP blends and TPVs with and without crosslinking, respectively, were prepared, in a batch mixer, using three different EPDM rubbers. EPDM/PP based TPVs were dynamic vulcanised using the resol /$SnCl_2$ system. Samples were collected along the time in order to get information on the morphology evolution and crosslinking density during dynamic vulcanisation. The morphology was studied by SEM and the crosslink density by gel content. In the case of low viscosity EPDMs, crosslinking of the EPDM phase was retarded due to its low crosslinking efficiency. This delay on crosslinking reaction enables the observation of the various stages of the morphological mechanism that takes place during dynamic vulcanisation. It could be observed that phase inversion takes place via lamellar mechanism. More detailed insight on phase inversion mechanism during dynamic vulcanisation was accomplished.

Keywords: Rheology, Crosslinking, Viscosity, Dynamic vulcanization.

INTRODUTION

Thermoplastic vulcanisates (TPVs) are a particular class of TPEs, which are obtained via dynamic vulcanization and combine rubber-like properties and thermoplastic processability in a single product. Most commercial TPVs are based on a crosslinked ethylene propylene diene monomer (EPDM) phase that is dispersed in a polypropylene (PP) matrix. These materials are produced by selective crosslinking of EPDM upon melt-mixing with PP. The crosslinking enhances the viscosity and elasticity of the rubber phase and, as a consequence, the final TPVs morphology consists of crosslinked rubber particles dispersed in a thermoplastic matrix, even if large amount of rubber are used [1-3].

Although this morphology explains the melt processability of TPVs, the elastic properties of TPVs suggest some continuity of the rubber phase [4,5].

The high concentration of the rubber phase and the irregularly shaped of the rubber particles make the morphological characterization difficult. Thus, TPVs morphology is a topic under discussion and is far from trivial. Several authors have been made continues efforts in order to understanding the morphology development during dynamic vulcanization. It has been shown that if the rubber is partially crosslinked a co-continuous morphology is established [6], even if the initial blend consists in thermoplastic phase dispersed in the rubber phase. EPDM/PP-based TPVs have been also study as a function of time in batch mixers and the results obtained shown that crosslinking is a very fast process. As a consequence the TPVs morphology is quickly achieved, after adding the crosslinking system [7-9], becoming hard to monitor the morphology development. According to Radush et al. [9], the formation of finely rubber particles dispersed in the thermoplatisc phase, at high contents of rubber is only achieved if initial co-continuous blend morphology exists before the addition of the crosslinking system. It has been proposed that the co-continuous structure is deformed by the action of shear and elongation stresses, although the particles become thinner, the co-continuous morphology remains stable. When the selective crosslinking of the rubber starts, the shear and elongation increases as the crosslink density increases, then, when a critical stress is reached, the rubber phase will break up into small particles [9]. In EVA/PP based TPVs, Verbois et al. [10] showed that PP changes from dispersed phase into matrix during dynamic vulcanization via a co-continuous structure. The formation of the co-continuous structure was observed at gel content around 60%, which suggested that phase inversion takes place at this point.

The present study aims to give more insight on TPV production, therefore the morphology development during dynamic vulcanization, its correlation with initial viscosity ration and with the crosslinking density will be investigate.

EXPERIMENTAL

Materials

Three different EPDMs (EPDM1: $160\ \mathrm{kg.mol^{-1}}$; EPDM2: $47\ \mathrm{kg.mol^{-1}}$; and EPDM3: $7.2\ \mathrm{kg.mol^{-1}}$) from DSM Elastomers and an isotatic PP homopolymer (MFI of $2\ \mathrm{g/10\ min}$ at $230^{\circ}\mathrm{C}$ with 2.16 kg) from Sabic were used.

The crosslinking system was composed by octylphenol-formaldehyde resin (SP1045, Schenectady International, USA) called resole (5 phr), and a combination of stannous chloride $(\mathrm{SnCl_2.2H_2O})(1.5\mathrm{phr})$ and zinc oxide $(\mathrm{ZnO})(1.8\mathrm{phr})$ as activators (both from Aldrich). Irganox 1076 from Aldrich was used as a stabilizer ($0.25\mathrm{wt\%}$ relative to the total amount of polymer (EPDM and PP)).

Processing

TPVs were produced in a Haake batch mixer (Rheocord 90; volume 60 ml), equipped with two rotors running in a counter-rotating way. The rotor speed was 80 rpm and the set temperature was $200^\circ C$. Each blend and respective TPV was prepared using $50/50(w/w)$ of EPDM/PP. The PP pellets were first introduced into the hot mixer, after melting the stabilizer was added, and then the EPDM rubber was mixed in. When the torque reached a constant value, indicating the formation of a homogenous melt, the rotors were stooped and a sample was taken from the mixer using a spatula, which took about 5 s . After that ZnO , resol and $SnCl_2$ were added in this order (which takes about 5 s). The instant when $SnCl_2$ was added was defined as time zero. At 45 s and 120 s samples were collected by the same procedure describe before. At 300 s the total sample was removed. In order to stop the crosslink reaction and to avoid morphological changes, all the samples collected from the mixer were cooled between two metal plates.

Materials Characterization

The rheological characterization of the PP and EPDM polymers was carried out on a stress-controlled rotational rheometer from AR-G2 (TA Instruments) using parallel-plate geometry. Samples with a diameter of 25 mm and a thickness of 1 mm were compression molded at $200^\circ C$ under a pressure of 30 tons. Because samples of the EPDM2 and EPDM3 are a syrupy liquid at room temperature, they were placed directly on the rheometer plate. The frequency sweep experiments were performed in a range of $0.1 - 100 rad.s^{-1}$ at $200^\circ C$. For each material, a stress sweep was carried out from 0.5 to 5000 Pa at frequencies of 1 and 10 Hz to determine the linear viscoelastic region.

EPDM gel content experiments were performed, as a measurement of the crosslink density, by EPDM extraction in cyclohexane at room temperature. Approximately 200 mg of TPV sample was weighted and, then, immersed in cyclohexane during 48 h under gentle stirring, which was refreshed after 24 h . After drying the sample, in a vacuum oven at $100^\circ C$ during 12 h with nitrogen purging, the weight was determined. The EPDM gel content was calculated assuming that the residue consists of only PP and crosslinked EPDM. The degree of equilibrium swelling was also measured, the procedure is the same as used for the gel content experiments, but before drying the sample swollen, it was weighted in a sealed glass bottle after wiping off the surplus cyclohexane with a tissue. The swelling degree is calculated as the ratio of the weight between the swollen and dry samples. The morphology were analysed by SEM in back-scattering mode using a Leica Scanning Electron Microscope. Samples were fractured in liquid nitrogen and, then, vapour stained by ruthenium tetraoxide during 120 minutes. The morphology of the EPDM higher-Mw was also characterized by TEM using a Philips CM120 Transmission Electron Microscope (TEM). Samples were cryomicrotoming to 100 nm thin sections at $-130^\circ C$ and then they were vapour stained by ruthenium tetraoxide for a period of 20 minutes.

RESULTS AND DISCUSSION

Dynamic rheological measurements were performed to characterize EPDM/PP blends in terms of melt viscosity ratios of EPDM and PP polymers at the applied processing conditions (i.e., set temperature and shear rate). Figure 1 represents the complex viscosity of the various EPDMs and PP at $200^\circ C$, as a function of frequency. High viscosity rubber (EPDM1) shows shear thinning behaviour over the complete range of frequencies. However, low viscosity rubbers (EPDM3 and EPDM1) display a Newtonian plateau over most whole frequency ranges. Shear thinning behaviour is observed only at high frequencies. PP shows pseudo-plastic behaviour with a Newtonian plateau at lower frequencies and shear thinning behaviour at higher frequencies.

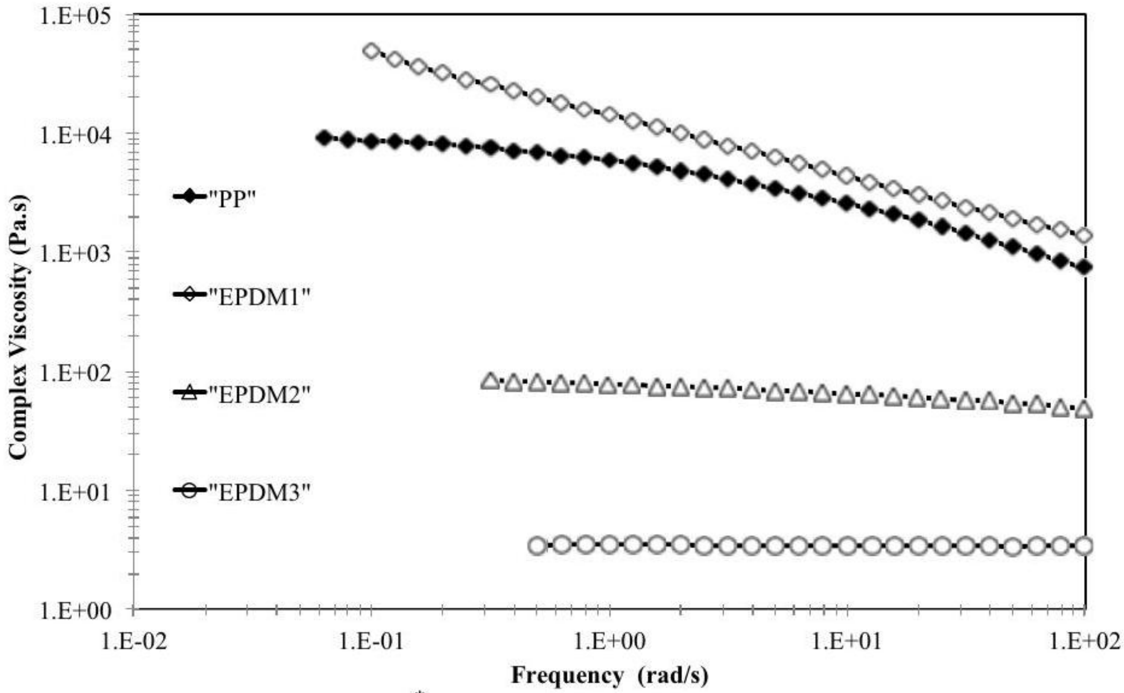

FIGURE 1. Complex viscosity (η^*) of various PP and EPDM polymers at 200°C as a function of frequency.

Because PP and EPDM are known to follow the Cox-Merz rule, it is assumed that the shear rate dependence of the steady shear viscosity is equal to the frequency (rad. $^{-1}$) dependence of the complex viscosity. Table 1 provides the melt viscosity ratio of the EPDM and PP polymers at 200°C and at an average shear rate of 65 s^{-1}.

TABLE 1. Melt viscosity (p_η) ratio of EPDM and PP polymers at a shear rate of 65 s^{-1} and temperature of 200°C.

EPDM	$p_\eta = \frac{\eta_{EPDM}}{\eta_{pp}}$
1	1.7
2	5.6×10^{-2}
3	3.6×10^{-3}

Figure 2 shows the EPDM gel content and the swelling degree as a function of reaction time for the EPDM/PP (50/50, w/w) TPVs made with the different three rubbers. In general, the rubber gel content increases with time, indicating an increase in crosslinking density. Moreover, the degree of equilibrium swelling decreases with the time, which is associated with an increase of crosslinking density. As expected the samples collected before adding the crosslinking system have a gel content of 0%, with an absolute error of ±5%, (corresponding to the gel content at time zero in the plot, Figure 1). The absolute error in the values of the EPDM gel content for all the systems is about ±5% at 45 s and ±2% at 120 s and 300 s . The larger error obtained at 45 s can be explained by the heterogeneous crosslink system distribution and thus, the heterogeneity in crosslinking of the samples at the early stages of mixing. In case of the swelling degree, the larger absolute error found was ±0.09. It is observed that EPDM gel content is higher, for the TPV made with the EPDM1 (higher viscosity EPDM), which is in according with literature [6]. The gel content is about 10% higher than the TPVs made with two low EPDMs viscosity (EPDM2 and EPDM3). These two TPVs, after 120 s , display similar values of gel content. At early stage of mixing (45 s) the crosslinking is going on and probably not homogeneous in the system, thus the sample collected may not be representative of the all system.

Since the gel content increases as the viscosity of EPDM increases (Figure 2), it seems that when low viscosity EPDMs are used the crosslinking reaction is retarded. The values of equilibrium swelling confirm the trends of gel content at the end of mixing. However, during dynamic vulcanization, special for two low viscosity EPDMs, the values of swelling degree are not in accordance with the values of the gel content. A possible explanation is that the degree of equilibrium swelling is not only determined by the degree of crosslinking but also by morphology. Thus, swelling can be used as a first indication of phase inversion. As observed in Figure 2, a significantly decrease of the swelling, especially for the two low viscosity EPDMs, is observed between 45 s and 120 s , which can be associated with morphological changes.

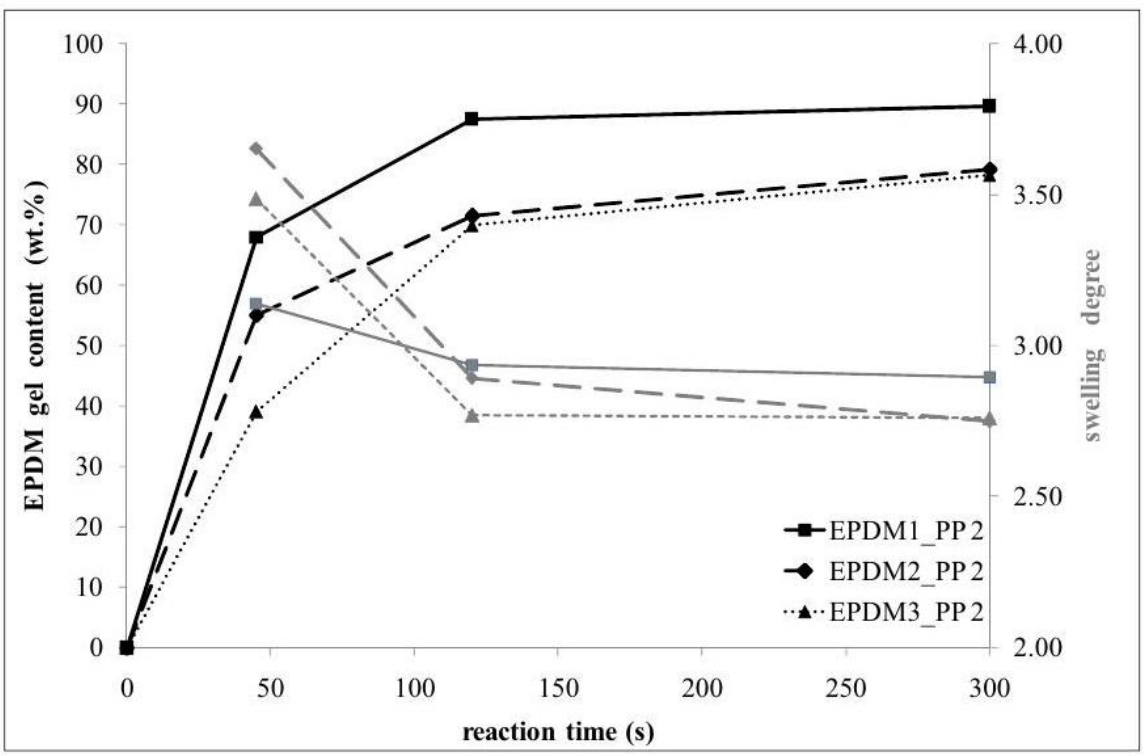

FIGURE 2. EPDM gel content (black lines) and swelling degree (grey lines) for 50/50TPVs composition made with different EPDMs.

TEM is the most common technique for study TPVs morphology because it provides high-resolution micrographs, that allows to obtain some details on the microstructure, which cannot be obtained easily by other conventional technique like SEM, LVSEM and AFM. However, it has been demonstrated that sometimes the TEM image can be misleading, that becomes hard the interpretation. Since two of the EPDMs that were used did not provide such a fine dispersed phase, SEM analysis in back-scattering mode, allows to obtained detail information on morphology. Thus, the morphologies of the blends (samples collecting before adding the crosslinking system) and the TPVs were study using this technique. However, for the TPV made with the higher viscosity EPDM, TEM was required. The SEM micrographs of the blends are shown in Figure 3. The white regions in micrographs are assigned to the EPDM phase and the black regions to the PP phase. In case of EPDM1 (higher viscosity) it is clearly that both phases are continuous. For the EPDM2, although EPDM seems to be the matrix some continuity of the PP is observed. In case of EPDM3, PP seems to be dispersed in the EPDM matrix. These morphologies can be explained by the decrease of viscosity and elasticity of EPDM phase. However, a micrograph is a two-dimensional object and thus PP can be view as droplet, but it can be continuous in other plane. In addition it was observed that after extraction experiments (where all the EPDM is removed) all the samples do not disintegrate, suggesting that the PP phase is continuous even in the last case.

Figure 4-6 shows the morphology development at 45, 120 and 300 s after adding the crosslinking system. TEM images are presented in Figure 4 and thus the EPDM phase is the black regions and PP the white regions. In this case the morphology is practically established at 45 s , at this time only a few stretched EPDM particles are observed. The co-continuous morphology of the initial blend becomes in EPDM dispersed particles after dynamic vulcanization. Figure 5 and 6, show the morphology as a function of time for EPDM2 and EPDM3, respectively. In both Figures, at 45 s a lamellar structure as intermediate state can be detected. However, in case of the EPDM3 the process seems to be in an earliest stage than in case of EPDM2, because at some points is possible to observed that the EPDM matrix seems to be highly deformed and not completed "break up" in a lamellar structure. At 120 s , for both EPDMs, the morphology consists already in EPDM particles dispersed in a PP matrix. These results give a good correlation with the values of gel content obtained (see Figure 2). The morphology develops as the gel content increases. The results suggested that phase inversion occurs when the gel content reaches a value of circa 68% (gel content for EPDM1/PP TPV at 45 s).

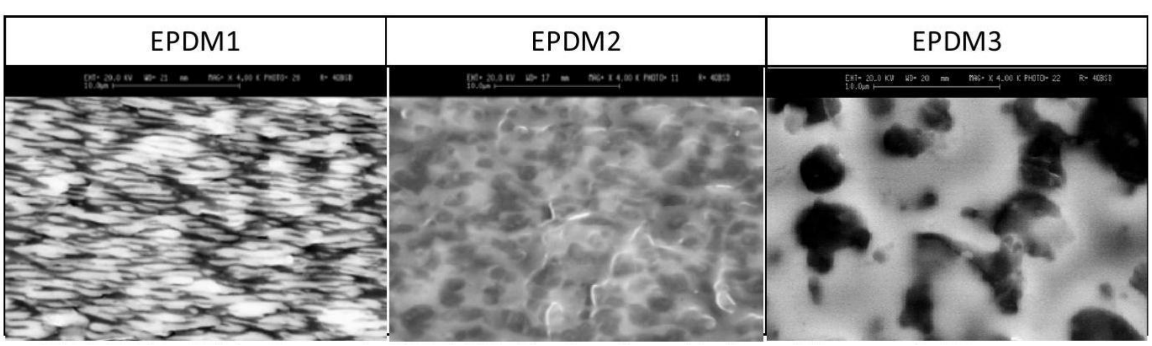

FIGURE 3. SEM micrographs EPDM/PP blends collected before adding crosslinking system.

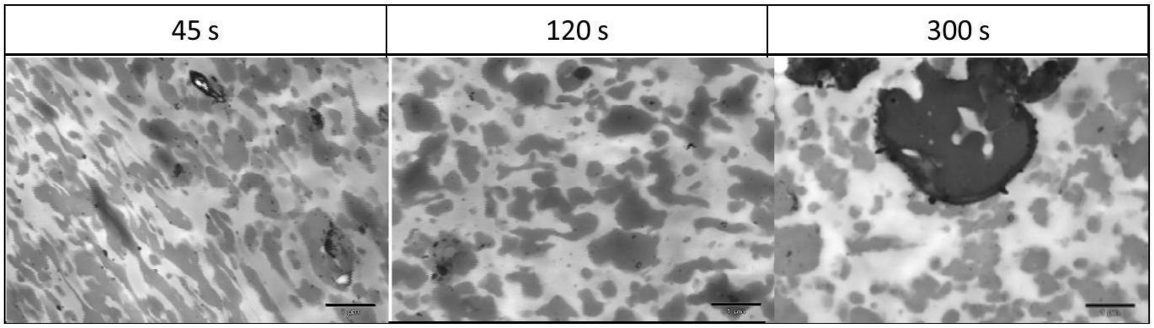

FIGURE 4. TEM micrographs EPDM1/PP TPVs collected at 45, 120 and 300 s after adding crosslinking system.

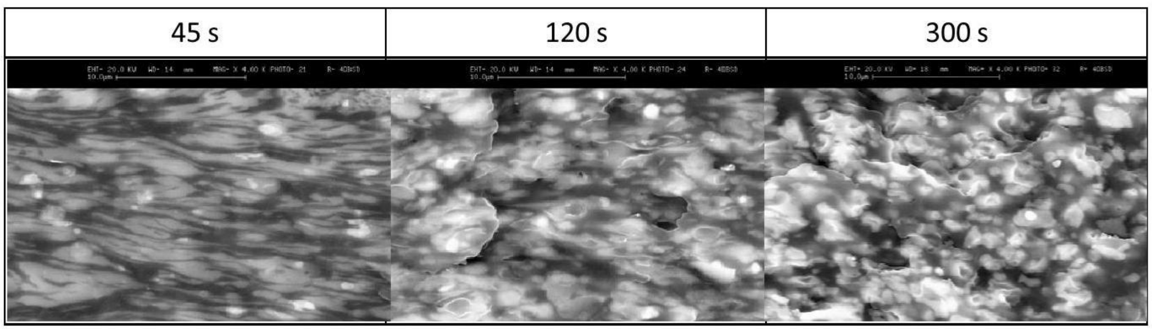

FIGURE 5. SEM micrographs EPDM2/PP TPVs collected at 45, 120 and 300 s after adding crosslinking system.

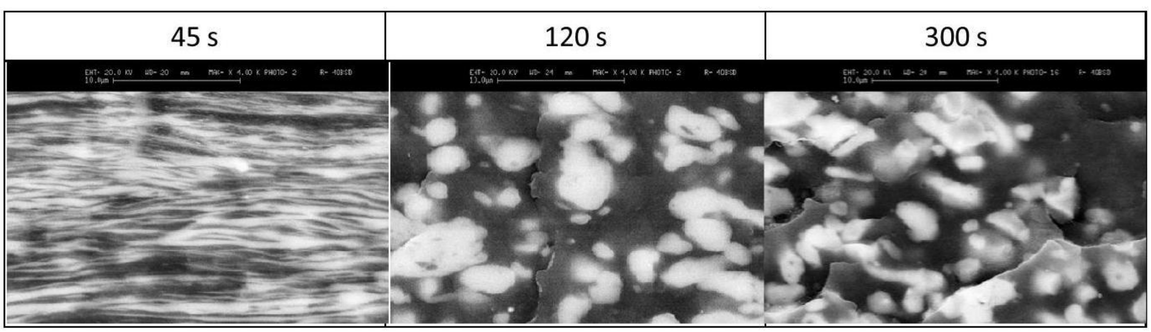

FIGURE 6. SEM micrographs EPDM3/PP TPVs collected at 45, 120 and 300 s after adding crosslinking system.

CONCLUSIONS

EPDM/PP- based TPVs were prepared via dynamic vulcanization, in a batch mixer, using a resol /$SnCl_2$ as crosslinking agent. Three EPDMs with different viscosity were used. Due to the faster crosslinking reaction for high viscosity EPDM, low EPDM gel content was obtained for samples collected at 45 s , in case of low viscosity EPDMs. The slower crosslinking process allowed to get information of an intermediate morphology state between the co-continuous structures and the matrix-dispersed particle driving by crosslinking. It was shown that phase inversion occurs via lamellar structure. A good correlation between gel content and morphology development was found.

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