DEGRADATION OF THE RUBBER NETWORK DURING DYNAMIC VULCANIZATION OF EPDM/PP BLENDS USING PHENOLIC RESOL

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Abstract

Physical blends and thermoplastic vulcanizates (TPVs) based on EPDM and PP were prepared in a batch mixer. Dynamic vulcanization of TPVs using resol//$SnCl_2$ was studied as a function of time. Static and dynamic vulcanization of EPDM in the absence of PP were also studied. Crosslinking of EPDM in the absence of PP is more efficient via static than dynamic vulcanization. For EPDM/PP-based TPVs the extent of crosslinking reaction versus time decreases as the amount of EPDM increases. Degradation of the EPDM network occurs during dynamic vulcanization, due to the combined action of shearing and high temperature, and increases as EPDM becomes more and more the continuous phase.

INTRODUCTION

Thermoplastics vulcanizates (TPVs) belong to the family of thermoplastic elastomers (TPEs), and, like other TPEs, combine the melt processability and recyclability of thermoplastics with the elasticity and the mechanical properties of thermoset rubbers. [1–3] TPV products can be melt processed by conventional techniques, such as extrusion, blow moulding, injection moulding, vacuum forming and calendaring. Most commercial TPVs are based on heterogeneous blends of isotactic polypropylene homopolymer (PP) and ethylene-propylene-diene (EPDM) rubber, because of the relatively high melting point of the former and the excellent oxygen, ozone and heat resistance of the latter. [4] TPVs usually contain large amounts of extender oil to improve processability and to lower hardness.

TPVs are produced via dynamic vulcanization, where the rubber is selectively crosslinked during its melt mixing with the thermoplastic. The final TPV morphology consists ideally of finely divided crosslinked rubber particles dispersed in a thermoplastic matrix. If large amounts of rubber are used to produce low-hardness TPVs, the initial blend morphology usually consists of a dispersion of PP particles in a rubber matrix or a co-continuous morphology. Several studies have demonstrated that crosslinking provokes drastic changes of the viscosity and the elasticity of the rubber phase. [5−7] Upon the high-shear dynamic vulcanization of low-hardness TPVs, the morphology changes from a (co-) continuous EPDM phase to crosslinked particles of EPDM dispersed in the PP matrix, i.e. crosslinking is the driving force for the occurrence of phase inversion. According to Coran et al. [8] the typical elastomeric properties of TPVs are only obtained if the rubber is highly vulcanized and if the size of the crosslinked rubber particles is small (approximately 1μ m). According to Bhadane et al., [9] the interfacial tension of EPDM/PP blends is very low. It is estimated to be around $0{,}3 \mathrm{mN/m}$ at a melt blending temperature of $190^{\circ}\mathrm{C}$ and, consequently, EPDM/PP blends are partially miscible in the melt. This explains the very fine morphologies of EPDM/PP-based TPVs even in the absence of a compatibilizer. The TPV morphology can be modified by changing the initial EPDM/PP viscosity ratio. According to Wu[10] an increase of the EPDM/PP viscosity ratio of the blend results in larger particles; a minimum particle size is obtained when the viscosity ratio is close to unity. It was shown by Sengputa et al. [11]

that hardness, Young's modulus and tensile strength of TPVs decrease with a decrease of the PP viscosity, which is related to an increase of the EPDM particle size.

TPV properties can be adjusted by varying the EPDM structure, the blend composition and the crosslinking degree. It has been demonstrated by Datta [12] that low-molecular-weight EPDM with low ethylene and diene contents results in TPVs with better compression set properties. Nevertheless, high-molecular-weight EPDM with high ethylene and diene content results in TPVs with better tensile and tear properties. Coran et al. [8] were the first to show that improved properties, such as tensile strength, modulus and compression set, are obtained if the rubber phase is highly crosslinked. Sabet et al. [13] have shown that high-molecular-weight EPDM results in a higher crosslinking degree.

Resols are the most commonly used crosslinking systems for EPDM in TPVs, despite the inconvenience of discoloration and black speck formation. They provide TPVs with good mechanical properties and processing characteristics, and yield thermally stable crosslinks. [14] The chemistry of resol crosslinking has been studied using low-molecular-weight models for EPDM rubber first by Lattimer [15] and later by van Duin et al. [16,17] Stannous chloride is usually used as activator; the acidic stannous chloride activates the degradation of resol into mono-phenolic units with benzylic cations, which eventually will connect two EPDM chains via methylene and/or chroman crosslinks.

Although TPVs have been already commercially available from the 1970's and a large number of scientific studies have been published, they are still produced in a somewhat empirical fashion. The relationships between the production process, the structure and the final properties are still not fully understood. [18] The general goal of our studies aims at understanding the physical and chemical phenomena, which take place during dynamic vulcanization of TPVs. In this particular study emphasis will be on the occurrence of network degradation during crosslinking. Further papers will be published on the relationship between crosslinking and morphology development, including phase inversion.

EXPERIMENTAL

MATERIALS

The EPDM rubber (K2340A: 53wt. % ethylene and 6 wt . % ENB; Mooney viscosity (1+4) at 125 °C : 25) used in this study was supplied by DSM Elastomers BV. As the thermoplastic phase, three different grades of isotatic PP homopolymer, supplied by Sabic Europe, with different melt flow indices (531P: MFI = 0.3; 524P: MFI = 2; and 579S: MFI = 47 g/10 min at 230 °C/2.16 kg) were used. Octylphenol-formaldehyde resin (SP1045, Schenectady International, USA) called resol in this work, stannous chloride and zinc oxide (Aldrich) were used as a crosslinking system. Irganox 1076 from Aldrich was used as a stabilizer. Physical blends without crosslinking and crosslinked TPVs were prepared for each PP grade using EPDM/PP ratios of 70/30,50/50 and 30/70(w/w). The amount of crosslinking agents was kept constant relative to the amount of EPDM and is expressed in parts per hundred rubber (phr). The crosslinking system was composed of resol crosslinker (5 phr) and a combination of $SnCl_2 . 2H_2O$(1.5phr) and ZnO(1.8phr) as activators. Irganox 1076 was used at 0.25wt. % relative to the total amount of polymers (EPDM and PP).

RHEOLOGICAL CHARACTERIZATION OF RAW MATERIALS

The rheological behavior of raw materials (PP and EPDM) was characterized by dynamic rheological measurements in a stress-controlled AR-G2 (TA Instruments) rotational rheometer, using a parallel-plate geometry (diameter = 25 mm; gap = 1 mm). All measurements were performed at 200 °C in a frequency range of 0.1 – 100rad/s. The complex viscosities of EPDM and

PP at a shear rate of 65 s^{-1} (the average shear rate estimated for the batch mixer at 80 rpm using the model developed by Bousmina et al.) [19] are given in Table I.

Table I
Dynamic Viscosities of the EPDM and PP at 200°C (Shear Rate of 65 S^{-1})

Material	MFI (g/10 min at 230°C/2.16 kg)	Dynamic viscosity, (Pa.s)
EPDM	-	1648
PP	0.3	2116
PP	2.0	950
PP	47	184

PREPARATION OF BLENDS AND TPVs

Physical blends and TPVs were prepared in a Haake batch mixer (HAAKE Rheomix 600 OS; volume 69 ml) equipped with two counter-rotating rotors. The rotor speed was 80 rpm and the set temperature was $200^{\circ}C$. The following mixing sequence was used. First, PP pellets were introduced into the hot mixer, after melting the stabilizer was added, and then the EPDM rubber. When the torque reached a constant value, which took about 3 minutes, and indicated the formation of a homogenous melt, ZnO , resol and $SnCl_2$ were added in this order (which took about 5 s). The instant when $SnCl_2$ was added is defined as time zero. At 45 s and 120 s the rotors were stopped and samples, weighing approximately 1.5 g , were taken from the mixer using a spatula, which took about 5 s , and then the mixing was continued. At 300 s the total sample was removed. In case of physical blends (without crosslinking) samples were only collected at 300 s , after the torque reached a constant value.

Dynamic vulcanization of EPDM rubber in the absence of PP was performed in the same way as for the TPVs at different temperatures (170,200 and $220^{\circ}C$). In order to prepare vulcanized EPDM via static vulcanization, EPDM rubber, ZnO , resol and $SnCl_2$ were pre-blended in the internal mixer at $80^{\circ}C$ during approximately three minutes at a rotor speed of 80 rpm . The crosslinking reaction does not occur at this low temperature. Then the EPDM mixture was vulcanized in a hot press at different temperatures (170,200 and $220^{\circ}C$). All the samples collected from the mixer and the hot-press (at 45, 120 and 300 s) were cooled between two metal plates in order to stop the crosslinking reaction and to avoid morphological changes.

SAMPLE CHARACTERIZATION

The EPDM gel content was determined as a measure of the crosslinking degree by extraction in cyclohexane at room temperature and in boiling xylene. For extractions in cyclohexane, approximately 200 mg of TPV sample was weighed and then immersed in cyclohexane for 48 h under gentle stirring; the cyclohexane was refreshed after 24 h . After drying the sample in a vacuum oven at $100^{\circ}C$ for 12 h with nitrogen purging, the weight was determined. The EPDM gel content was calculated assuming that the residue consists of insoluble PP, ZnO, resol, $SnCl_2$ and crosslinked EPDM. For extractions in xylene, approximately 500 mg of TPV sample was weighed and placed in a 80μ m mesh stainless-steel cage, the cage was also weighed, and then immersed in boiling xylene for 48 h . The samples were dried using the same conditions as used for the cyclohexane extractions. The EPDM gel content was calculated assuming that the residue consists of insoluble crosslinked EPDM and resol and corrected for the presence of ZnO . The degree of equilibrium swelling was also measured to confirm the trends of crosslinking determined with extractions. The procedure was the same as described previously for the determination of EPDM gel content via cyclohexane extraction. However, in this case before drying the swollen sample, it was weighed in a sealed glass bottle after carefully removing the surplus cyclohexane with a tissue. The swelling degree was calculated as the ratio of the weights of the swollen and dried samples.

The morphology was studied by scanning electron microscopy (SEM) in the back-scattering mode using a Leica Scanning Electron Microscope. Samples were fractured in liquid nitrogen and vapor-stained with ruthenium tetroxide for 120 minutes.

RESULTS AND DISCUSSION

TORQUE AND TEMPERATURE

Figure 1 shows the torque and temperature curves upon dynamic vulcanization of a 50/50 (w/w) EPDM/PP (MFI 0.3) blend in the batch mixer. The first and second peaks in the torque curve correspond to the introduction of PP and EPDM into the mixer, respectively. The torque reaches more or less a constant value, indicating complete melting of PP and full homogenization of the EPDM/PP blend. The addition of the crosslinking system produces an immediate decrease of the torque, which is attributed to lubrication of the blend system by the molten resol and $SnCl_2$. Then, the torque increases steeply and reaches a maximum at approximately 85 s after adding the crosslink system, which is related to drastic changes in the viscosity and elasticity of the EPDM phase due to crosslinking. The next two interruptions in the torque curve are the result from stopping the rotors in order to take samples at 45 and 120 s after adding the crosslinking system. Upon prolonged mixing the torque shows a moderate but continuous decrease. In the temperature curve a decrease from 198 to 181°C is observed when the polymers are fed due to the introduction of a cold mass in the mixer and the melting of PP. Upon addition of the high-molecular-weight EPDM a continuous temperature increase up to 220°C is observed, due to viscous dissipation, which is enhanced as a result of crosslinking. Both the torque and temperature curves are similar to the ones reported in other studies for dynamic vulcanization of EPDM/PP blends.[11,20,21]

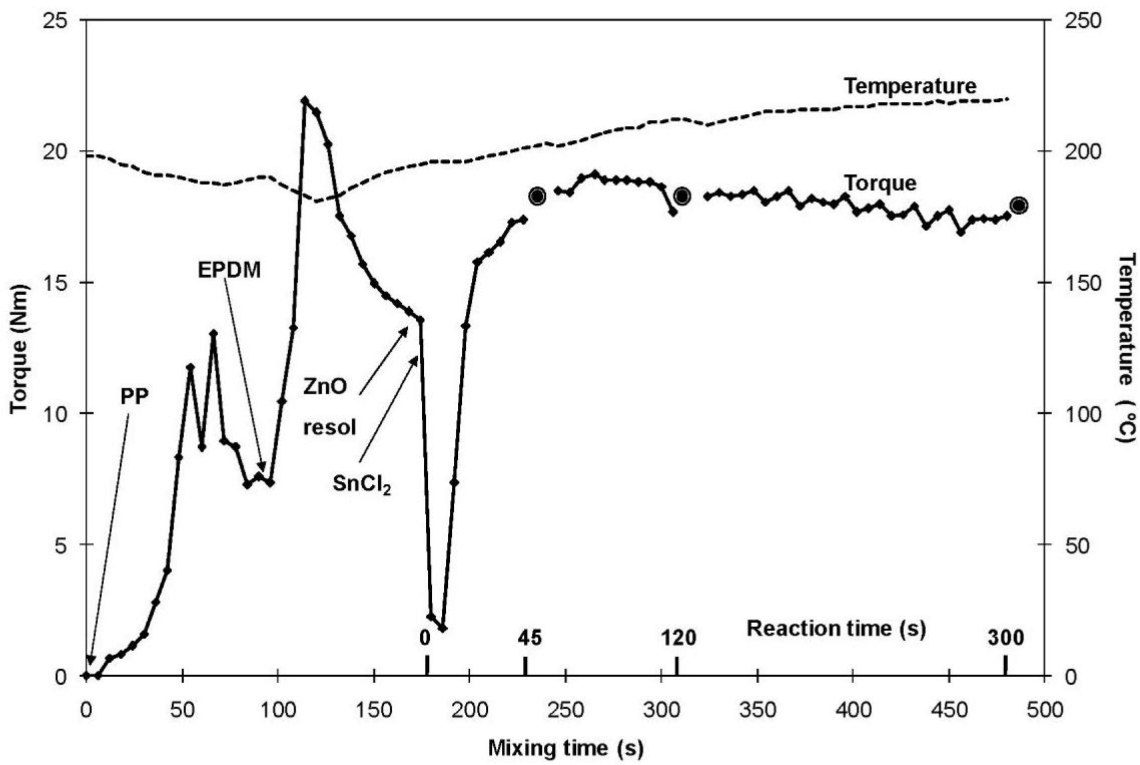

FIG. 1. - Evolution of torque and temperature as a function of mixing time for 50/50(w/w) EPDM/PP, MFI 0.3 TPV. The arrows indicate the instants of addition of the various ingredients. The filled circles indicate the time of sampling.

Since the mixing torque represents the overall viscosity of the blend and the melt temperature is influenced by viscous dissipation, it is expected that both torque and temperature could be correlated. Table II shows the values of the mixing torque and melt temperature at different mixing times for all studied compositions. The torque value corresponding to a reaction time of 0 s was registered just before adding the crosslinking system. The torque values at 45, 120 and 300 s were taken just before stopping the rotors to collect the samples. Independently of the blend composition and the reaction time, it is observed that the mixing torque and the melt temperature increase when the PP molecular weight increases, which contributes to an increase of the viscous dissipation. An increase of the EPDM content also results in an increase of both torque and temperature; the largest relative increase in torque is noted for PP MFI 47 at high reaction times. The mixing torque increases up to a certain level at 45-120 s and then it decreases. This could be explained by the occurrence of phase inversion. Since after phase inversion the viscosity of the molten TPV will be determined by the PP matrix where crosslinked rubber particles are dispersed. Temperature increases approximately 5°C with an increase of the EPDM content from 30 to 70%. The increase in torque and temperature is explained by the fact that the EPDM melt viscosity is higher than those of PP MFI 47 and 2, and is further increased by crosslinking. In the case of PP MFI 0.3 at low reaction times, an increase in the EPDM content actually results in a decrease of the torque and temperature because the EPDM viscosity is somewhat lower than that of PP MFI 0.3. At high reaction times crosslinking of the EPDM phase will be completed and the viscosity of EPDM phase will be higher than that of all PPs. Finally, for all TPVs, the melt temperature shows increases from 17 to 27°C upon prolonged mixing time up to 300 s , due to viscous dissipation.

The decrease in torque, after going through a maximum, once the crosslinking system was added, has been explained in terms of morphological changes. [5,21] However, for the 30/70 (w/w) EPDM/PP compositions with PP MFI 0.3 and 2, where phase inversion is rather improbable because the initial morphology already consists of a continuous PP phase (see below), the torque still goes through a maximum. Thus, a more probable explanation for the final decrease of the torque might be the degradation of PP and/or the EPDM network.

Table II
Mixing Torque (Γ) and Melt Temperature (T) Recorded During Dynamic Vulcanization of EPDM/PP Blends

Sample		Reaction time (s)							
		0		45		120		300	
EPDM/PP w/w	PP MFI	Γ, Nm	T, °C	Γ, Nm	T, °C	Γ, Nm	T, °C	Γ, Nm	**T, °C**
70/30	0.3	12.5	194	18.0	202	18.6	214	18.4	221
70/30	2	10.0	191	13.0	196	15.9	207	14.8	216
70/30	47	6.3	190	9.8	194	10.9	203	9.8	209
50/50	0.3	13.6	196	17.4	201	18.6	212	16.5	220
50/50	2	10.0	188	13.4	195	13.3	204	11.1	212
50/50	47	4.9	186	6.2	192	7.2	200	6.6	206

30/70	0.3	13.4	201	18.7	206	17.0	213	15.4	218
30/70	2	9.3	188	11.3	196	10.5	203	9.3	210
30/70	47	3.4	186	3.3	192	3.3	197	3.6	203

EFFECT OF PP MFI AND BLEND COMPOSITION ON DYNAMIC VULCANIZATION

Resol /$SnCl_2$ is the most common system used for dynamic vulcanization of PP/EPDM blends. [18] The resol reacts only with unsaturation, i.e. only the EPDM phase will be affected (crosslinking). Reaction of the resol with PP, such as graft EPDM/PP copolymer formation, as suggested by Sabet et al. [22] is highly improbable.

The crosslinking degree of the EPDM phase was measured by determination of the EPDM gel content in cyclohexane and xylene and by the degree of equilibrium swelling in cyclohexane. The EPDM gel content, determined by extraction in boiling xylene, is not affected by the EPDM/PP ratio, since PP dissolves in refluxing xylene and the residue consists only in crosslinked EPDM, resol, and ZnO. Thus, it will allow a fair comparison of the crosslinking degree of the EPDM phase in different TPV compositions. Since at early stages of mixing, crosslinking may proceed during extraction due to the high boiling temperature of xylene and unreacted resol is still present, xylene extractions were only performed for physical blends and for TPV samples collected after 5 min . In the case of the EPDM gel content determined by extraction in cyclohexane, the PP phase does not dissolve. Thus, in TPVs with PP-rich compositions, where PP might be the matrix and EPDM the dispersed phase, the solvent should not be able to remove all the uncrosslinked EPDM efficiently. Still, the cyclohexane gel content was measured in order to follow the evolution of the crosslinking as a function of time at least in a qualitative way. Since the presence of rigid PP limits the swelling of the (crosslinked) EPDM phase, the degree of swelling in cyclohexane is not only determined by the crosslinking degree, but also by the composition and the morphology of the TPVs. In addition, at high EPDM levels micro-gel rubber particles were observed in the solvent. Although, the degree of swelling was measured for all samples and it decreases for all compositions as a function of time, suggesting an increase of the crosslinking degree, these data will not be discussed in detail, because the interpretation is not straightforward.

Figure 2 shows the gel content in cyclohexane as a function of the reaction time for the various TPVs with different EPDM/PP compositions and PP MFIs. The values at 0 s were measured for the physical blends. The PP-rich compositions, 30/70 (w/w) EPDM/PP, show gel content values between 40-50% at 0 s , significantly different from zero. Since no crosslinking system was presented, this can be related to the inefficiency of the solvent to remove all EPDM, as explained above. The absolute error in the values of the EPDM gel content for TPVs samples at 120 and 300 s is less than $\pm 2\%$, while at 45 s it is close to $\pm 5\%$. The larger error for data at 45 s can be explained by the heterogeneous distribution of the crosslinking system in the early stages of mixing, resulting in crosslinking heterogeneity.

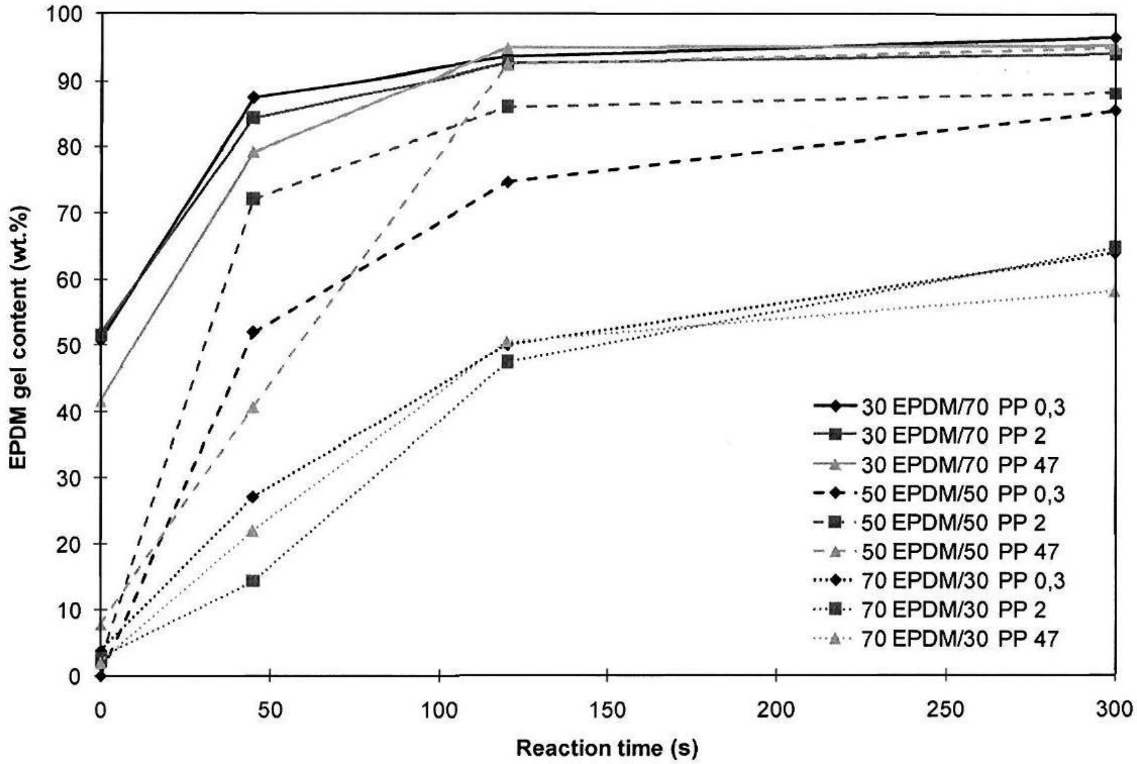

FIG. 2. - EPDM gel content of the various EPDM/PP compositions (different lines) and PP MFI (different symbols) as a function of reaction time, determined via cyclohexane extraction.

In general, the rubber gel content increases with time, indicating an increase in crosslinking degree. The curves of the gel content versus time for each EPDM/PP composition are more or less similar and independent of the PP MFI. For 70/30 (w/w) EPDM/PP TPVs compositions the rate of crosslinking is slow: gel content at 0 s is close to 0%, at 45 s it is below 30% and even after 300 s of mixing the values are only around 65%, i.e. far below to the theoretical maximum of 100%. For 50/50 (w/w) EPDM/PP compositions, crosslinking proceeds somewhat faster. Gel content at 0 s is again close to 0%, then it varies between 40 – 75% at 45 s and at 300 s it is between 85-95 %. Mainly in case of the two high-molecular-weight PPs (PP MFI 0.3 and 2), gel content values are significantly less than 100%. A decrease of the PP molecular weight yields higher gel content at higher reaction time. For 30/70 (w/w) EPDM/PP compositions, the evolution of crosslinking is similar for all PPs. The gel content is around 50% at 0 s , above 80% at 45 s and close to 100% at 300 s . Although, these values may be overestimates, it is reasonable to presume that for this PP-rich composition the crosslinking degree reaches higher levels than for others compositions.

In summary these results indicate that PP molecular weight does not have a major influence on the crosslinking of the EPDM phase. Since the amount of crosslinking chemicals was kept constant relatively to the amount of EPDM, more or less similar trends of gel content for all three EPDM/PP compositions were expected. However, comparing the actual gel content data for the different TPV compositions indicates that gel content decreases as the EPDM content increases; the lowest values are obtained for the 70/30 (w/w) EPDM/PP compositions. Due to the limitations of cyclohexane extractions as discussed above, some extractions in refluxing xylene were performed. The gel content values determined by xylene extraction of TPVs collected at 5 min are shown in Table III. The gel content was also determined for physical blends and the values obtained were 0% for all compositions, as expected. EPDM-rich 70/30 (w/w) EPDM/PP compositions show similar gel content values, remaining below 50% for all PPs. For 50/50 (w/w) EPDM/PP compositions, gel content increases from 51 to 92% as the PP MFI increases. For PPrich 30/70 (w/w) EPDM/PP compositions, it is also observed that gel content increases from 63 % to 84 % as the PP MFI increases.

Table III
EPDM Gel Content by Xylene Extraction For TPVs Collected at 300 S

Composition EPDM/PP	PP MFI (g/10 min at 230°C/ 2.16 kg)	EPDM gel content (wt. %)
70/30	0.3	42
50/50		51
30/70		63
70/30	2.0	44
50/50		68
30/70		73
70/30	47	42
50/50		92
30/70		84

Comparing these xylene extraction results with those obtained by cyclohexane, it can be noticed that the general trends are the same, although the gel content data obtained by xylene extraction are smaller. The latter can be explained, as discussed before, by the fact that in case of cyclohexane extraction the PP is not dissolved and, consequently, the solvent is not able to remove all the non-crosslinked EPDM, especially when PP is the matrix. During xylene extractions, PP is also dissolved and, thus, removal of the non-crosslinked EPDM by the solvent is more efficient. Most probably these trends in gel content, determined via both cyclohexane and xylene extractions, are related to differences in morphology of the EPDM/PP blends. To investigate this in more detail, scanning electron microscopy (SEM) in the back-scattering mode was performed on non-crosslinked blends. The micrographs of the various compositions are depicted in Figure 3. White regions in the micrographs are assigned to the EPDM phase and black regions to the PP phase. The morphology of the corresponding TPVs were also studied, but it will be discussed separately in a detailed study on morphology development during dynamic vulcanization with emphasis on phase inversion. [23] The morphology of the EPDM/PP blends can be explained in terms of the viscosity ratio and the blend composition, as it has been shown previously by several authors. [13,20,24,25] The morphologies, obtained for blends with the highest amount of

EPDM (70 wt. %) and PPs with different MFIs, consist mainly of an EPDM matrix with a dispersed PP phase (Figure 3). An increased tendency towards co-continuity of the PP phase is observed as the PP MFI increases, because the phase with the lowest viscosity in general has a preference to become the matrix. Morphologies obtained for 50/50(w/w) compositions indicate some sort of co-continuity for all 3 PP MFIs. For the blend with high molecular weight, PP MFI 0.3, the EPDM phase seems to be more continuous than in the blend with PP MFI 2. For the blend with the low molecular weight, PP MFI 47, the EPDM phase seems to be dispersed in the PP matrix, although some EPDM particles seem to be connected. These differences are again related to the increase of EPDM/PP viscosity ratio. For the blends with the lowest amount of EPDM (30 wt.%), PP is always the matrix. Nevertheless, with the two high molecular weight PPs (MFI 0.3 and 2) the dispersed EPDM particles are elongated and sometimes seem to be connected. For all blend compositions, it is noticed that the size of the EPDM particles increases as the EPDM/PP viscosity ratio increases, i.e. becomes larger than 1 , which is in accordance with the study by Wu et al.[10]

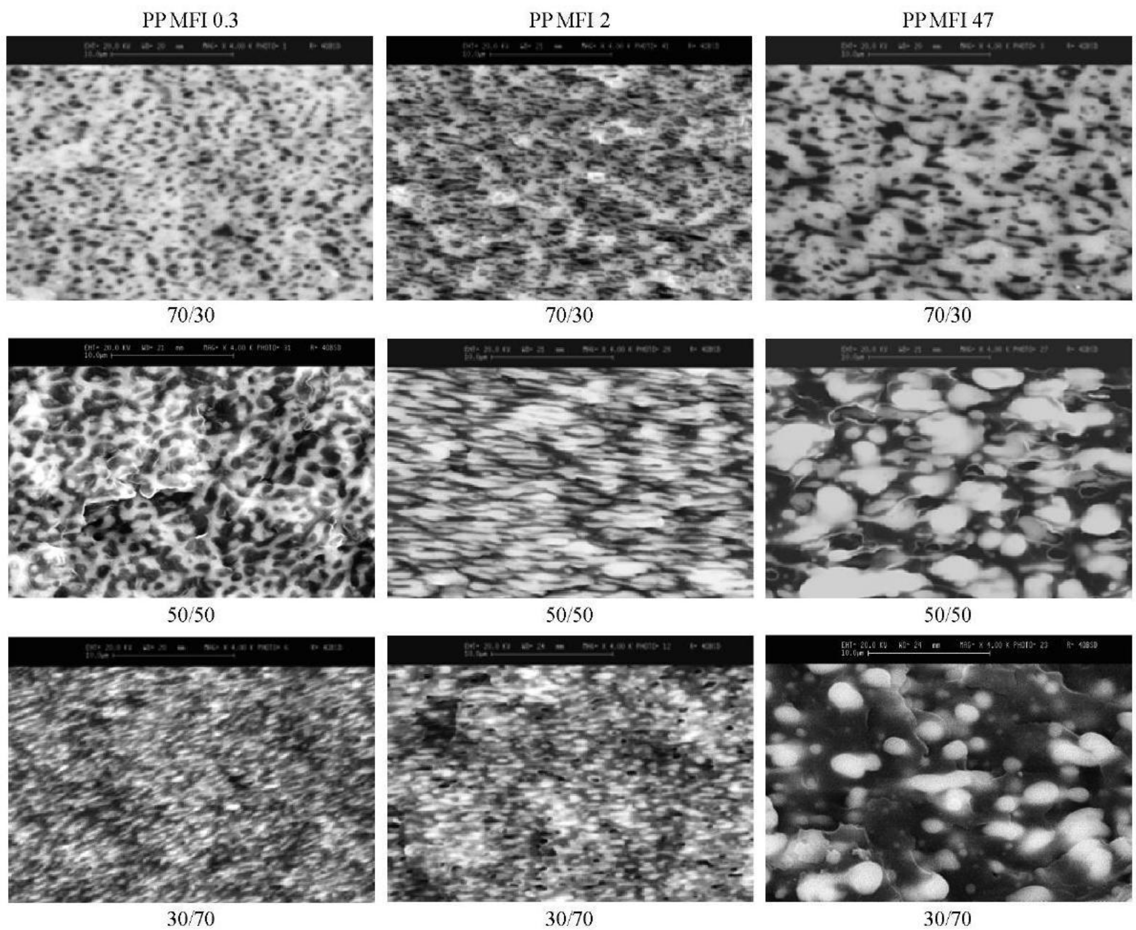

FIG. 3. - SEM images of non-crosslinked EPDM/PP blends. (EPDM is the light phase and PP is the dark phase).

For EPDM-rich 70/30 (w/w) EPDM/PP compositions, it is shown that PP is mainly the dispersed phase and, thus, the crosslinking system will end up initially in the EPDM phase and it is able to react immediately with the rubber. For PP-rich, 30/70 (w/w) EPDM/PP compositions, it is shown that the morphology consists mainly of EPDM domains dispersed in the PP phase and, thus, the crosslinking agents have first to migrate through the PP matrix, before reaching and crosslinking the EPDM phase. Surprisingly, for the latter TPVs, the highest values of the gel content are obtained. This shows that the decrease of the crosslinking degree upon increasing the rubber content in the TPV formulation is not related to the localization or migration of the crosslinking agents, but may be related to the fact whether EPDM is the matrix or the dispersed phase. The increase in the gel content values, both in cyclohexane and xylene, upon increasing the PP amount (with the exception of TPVs based on PP 47 as will be explained below), may be explained by the occurrence of degradation of the EPDM network during dynamic vulcanization, mainly when EPDM is the continuous phase and is more sensitive to high shear and elongation stresses. In addition, it seems that EPDM degradation is not only an outcome of shear and elongation stresses applied directly to the EPDM phase, but may also occur when shear and elongation stresses are transferred via PP matrix to the dispersed EPDM phase. Since shear and elongation stresses increase as the viscosity of the matrix increases, this explains the decrease of the rubber gel content as the PP molecular weight increases, i.e. as PP MFI decreases, in the cases of 50/50 and 30/70 (w/w) EPDM/PP compositions. For PP MFI 47 a decrease of the crosslinking degree, determined by xylene extraction, is observed when the PP amount increases from 50 to 70wt. % (see Table III). This suggests that shear and elongation stresses, transferred by this low viscous PP, are not strong enough to cause degradation of the EPDM network.

To validate if degradation of the EPDM network occurs during dynamic vulcanization of EPDM/PP blends, static vulcanization of EPDM/PP blends was performed in the batch mixer by stopping the rotors after adding the crosslinking system. However, due to the high melt temperature the crosslinking reaction has already proceeded significantly before the crosslinking chemicals were well dispersed. Therefore, both static and dynamic vulcanization of EPDM in the absence of PP was investigated.

STATIC AND DYNAMIC VULCANIZATION OF EPDM IN THE ABSENCE OF PP

Figure 4 shows the EPDM gel content and the degree of equilibrium swelling upon crosslinking EPDM in the absence of PP in a hot press as a function of the curing time and temperature (static vulcanization). The gel content increases both with time and temperature. The rate of the crosslinking reaction is low at 170°C, the gel content at 45 s is below 30% and at 300 s it is only 80%. At 200°C the gel content is close to 80% at 45 s and then increases to 95 % at 300 s. Finally, at 220°C the gel content at 45 s is already 93% and is 97% at longer times. It should be noticed that the levelling off of the gel content at approximately 100% does not mean that crosslinking stops at prolonged reaction times at 200 and 220°C. At 100% gel all rubber chains are coupled to the 3D network by at least one link. Crosslinking probably continues, resulting in higher crosslinking densities, the rubber gel content has already reached its upper limit and cannot increase above 100%. However, at higher degrees of crosslinking the changes in crosslinking density can be studied by determining the degree of equilibrium swelling, which indeed decreases indicating that the crosslinking degree increases at longer times (Figure 4). The degree of swelling at low crosslinking degree (at 45 s and 170°C) cannot be determined accurately due to the presence of micro-gel rubber particles in the solvent. Generally, the equilibrium swelling data confirm the trends observed for the gel content. In summary, resol cure of just EPDM under static conditions proceeds as expected according to a normal Arrhenius behavior, i.e, the crosslinking reaction increases as the temperature increases.

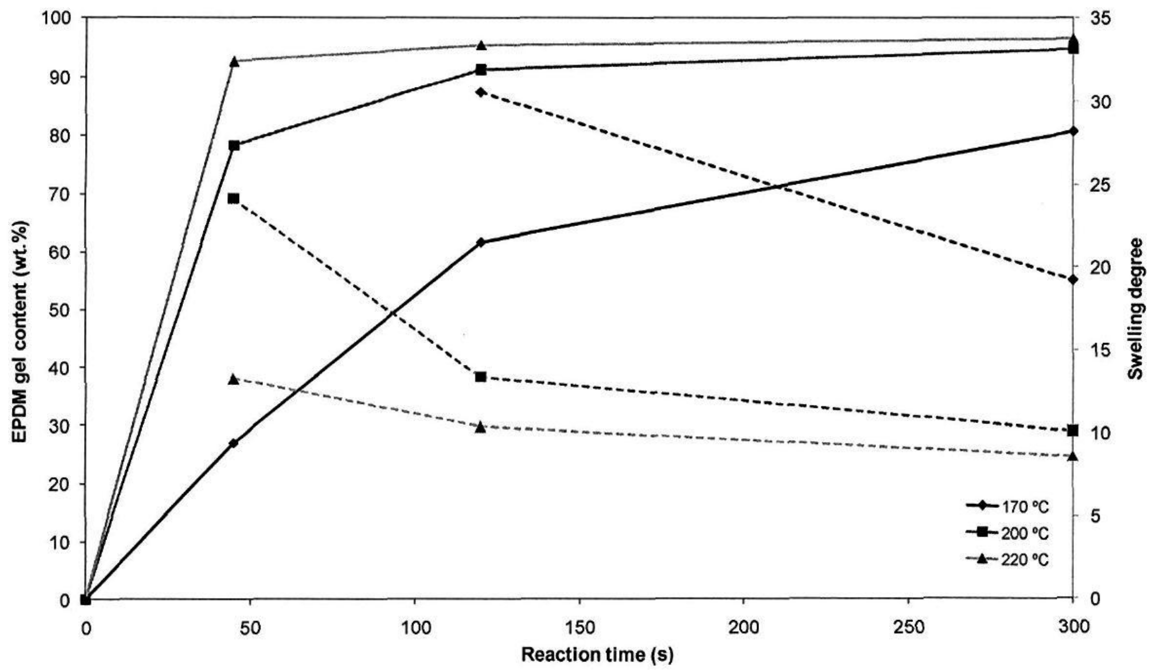

FIG. 4. - EPDM gel content (solid lines) and degree of equilibrium swelling (dashed lines), using cyclohexane, of EPDM statically vulcanized in the absence of PP at different temperatures in a hot press.

The torque curves obtained during dynamic vulcanization of EPDM in the absence of PP in the batch mixer at different temperatures (Figure 5) are in a way quite similar to those of the TPVs shown in Figure 1. In all cases, the first torque peak corresponds to the introduction of the cold EPDM rubber, which is homogenized after approximately 75 s . The corresponding torque level decreases as the set temperature of the batch mixer increases, which is due to the decrease of melt viscosity. Adding the crosslinking agents, first results in a torque decrease, due to lubrication, but then in a strong increase as a result of crosslinking. A maximum torque level is reached at approximately 225 s . For EPDM dynamically vulcanized at 170 °C, the maximum value in torque is followed by a rapid decrease, due to crumbling of the crosslinked rubber. The powdery rubber crumb is simply turned around in the mixing chamber and does not apply any mechanical force on the rotors. A different behavior was observed for EPDM samples dynamically vulcanized at 200 and 220°C. The torque remains practically constant when the maximum was reached, and at both temperatures the rubber mass remained a viscous melt. Again a lower torque level were obtained for high temperature. These results indicated that the crosslinking degree of the EPDM dynamically vulcanized at 170°C is larger than at 200 and 220°C, which is confirmed by the EPDM gel content measurements (Figure 6). EPDM gel content increases with time and temperature in a rather unexpected sequence: 170°C > 220°C > 200°C. Due to the low level of crosslinking at 45 s and 120 s , the degrees of equilibrium swelling could only be measured at the end of the dynamic crosslinking of EPDM at 200 and 220°C, being 22 and 18, respectively. This corroborates the trend obtained for the

EPDM gel content. For samples crosslinked at 170°C it was not possible to determine the degree of swelling, due to the crumb form of the product.

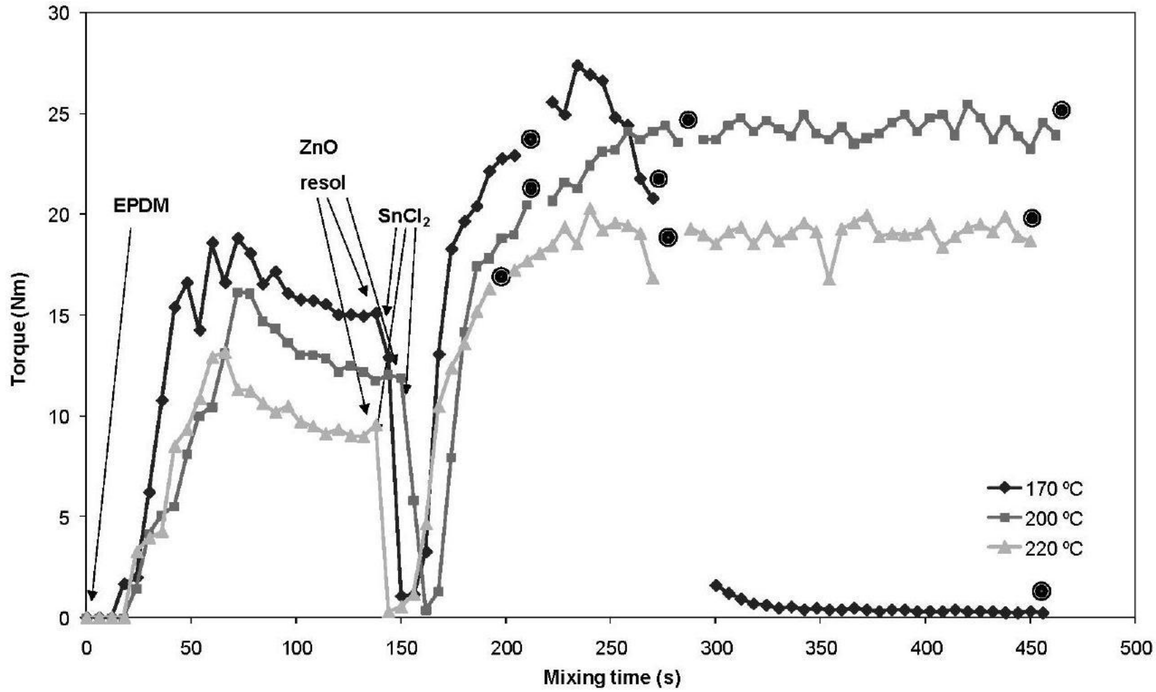

Fig. 5. - Evolution of torque as a function of mixing time for EPDM, dynamically vulcanized in the absence of PP at different temperatures in the batch mixer.

The comparison of Figures 4 and 6 show that the crosslinking degree at 170 °C for dynamic vulcanization is similar to that of static vulcanization. Crosslinking at this temperature is relatively slow, and no degradation as a result of shear seems to occur. At 200 and 220°C the crosslinking degree under dynamic conditions are significantly smaller when compared to those obtained under static conditions. It can be concluded that degradation of the EPDM network is indeed induced by high shear stress at elevated temperatures. The higher crosslinking degree achieved at a set temperature of 220°C compared to that at 200°C is explained by the faster crosslinking reaction and the lower viscosity at 220°C, the latter probably resulting in less shear degradation. Since the gel content of the EPDM melt at 220°C is 57% and that of the crumb obtained at 170°C and 120 s is 64%, it seems that the point where the transition from viscous melt to elastic solid occurs is around 60% gel.

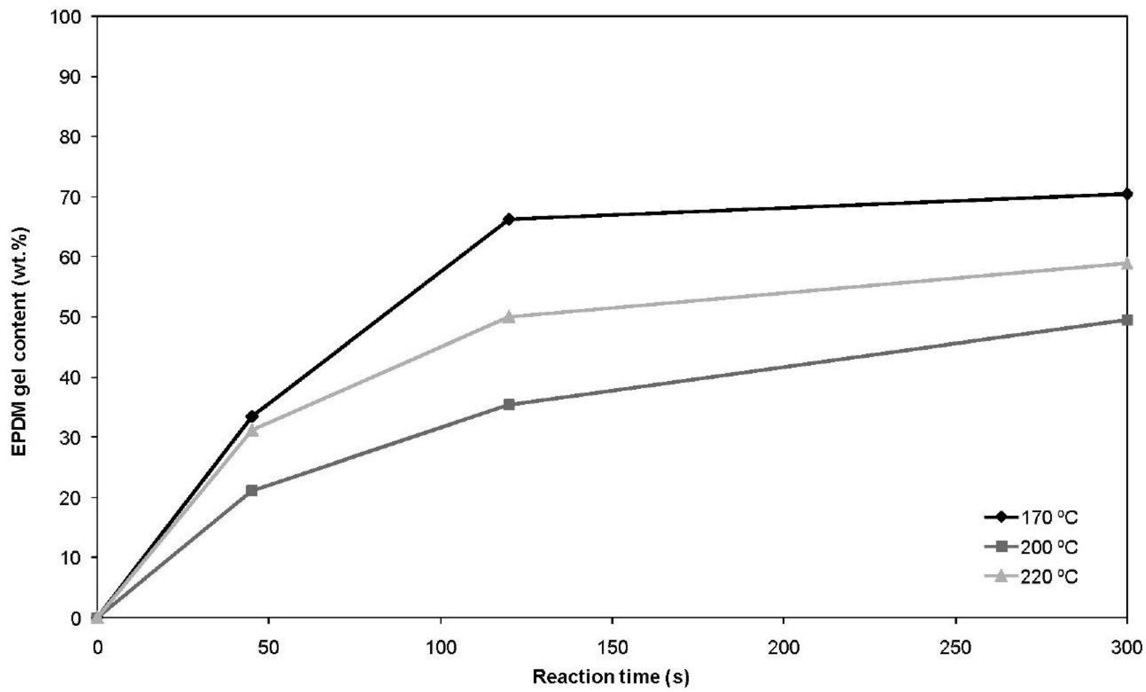

FIG. 6. - EPDM gel content as a function of time for EPDM in the absence of PP, dynamically vulcanized at different temperatures in the batch mixer.

The results of dynamic vulcanization of EPDM in the absence of PP at 200°C (Figure 6) are rather similar to those of dynamic vulcanization of 70/30 (w/w) EPDM/PP TPVs (Figure 2). Obviously, EPDM is the matrix in these EPDM-rich TPV and suffers significantly from degradation, similar to what occurs to EPDM in the absence PP. In case of PP-rich TPVs compositions and also for the 50/50 (w/w) EPDM/PP MFI 47 TPV composition, the gel content trend is similar to those obtained for the static vulcanization of EPDM. This supports the hypothesis that degradation of the EPDM (network) occurs during dynamic vulcanization, especially if EPDM is the matrix.

Actually, crosslinking and degradation are competing processes during dynamic vulcanization, while during static vulcanization only crosslinking occurs. Degradation is probably related to thermo-mechanical effects (high temperature and high shear). Oxidation due to the presence of oxygen can also occur. This phenomenon has not been reported in the literature on dynamic vulcanization of TPVs, although devulcanization under high shear flow of EPDM rubber, cured with sulphur or with peroxide, as a way of recycling has been reported. [27–29]

DYNAMIC VULCANIZATION OF TPVs AT DIFFERENT TEMPERATURES

Finally, in order to evaluate the effect of set temperature of the batch mixer on the extent of crosslinking during dynamic vulcanization of a full TPV formulation, experiments were performed at 170,200 and 220°C. The 30/70 (w/w) EPDM/PP composition with the PP MFI 47 was used, in order to have EPDM as the dispersed phase and to keep degradation of the EPDM (network) to a minimum. EPDM gel content in cyclohexane as a function of time and in xylene at 300 s as a function of temperature is presented in Figure 7. EPDM gel content determined with cyclohexane is hardly affected by the increase of temperature. At 45 s a slight increase of the crosslinking degree with increasing temperature is observed, which is probably related to the faster crosslinking at higher temperatures (see Figure 6). A comparison between dynamic vulcanization of EPDM in the presence of PP at 170°C with static vulcanization of only EPDM (Figure 6) shows that the former results in faster crosslinking and achieves higher gel content.

This is probably related to the more efficient heat transfer in the latter case due to mixing. These results are confirmed by xylene extraction on the 300 s samples. The EPDM gel content is similar at 170 and 200°C. At 220°C a slight decrease of gel content is observed. These data demonstrate that if EPDM is mainly dispersed in the low viscous PP matrix, degradation of the EPDM network does not occur to a significant extent.

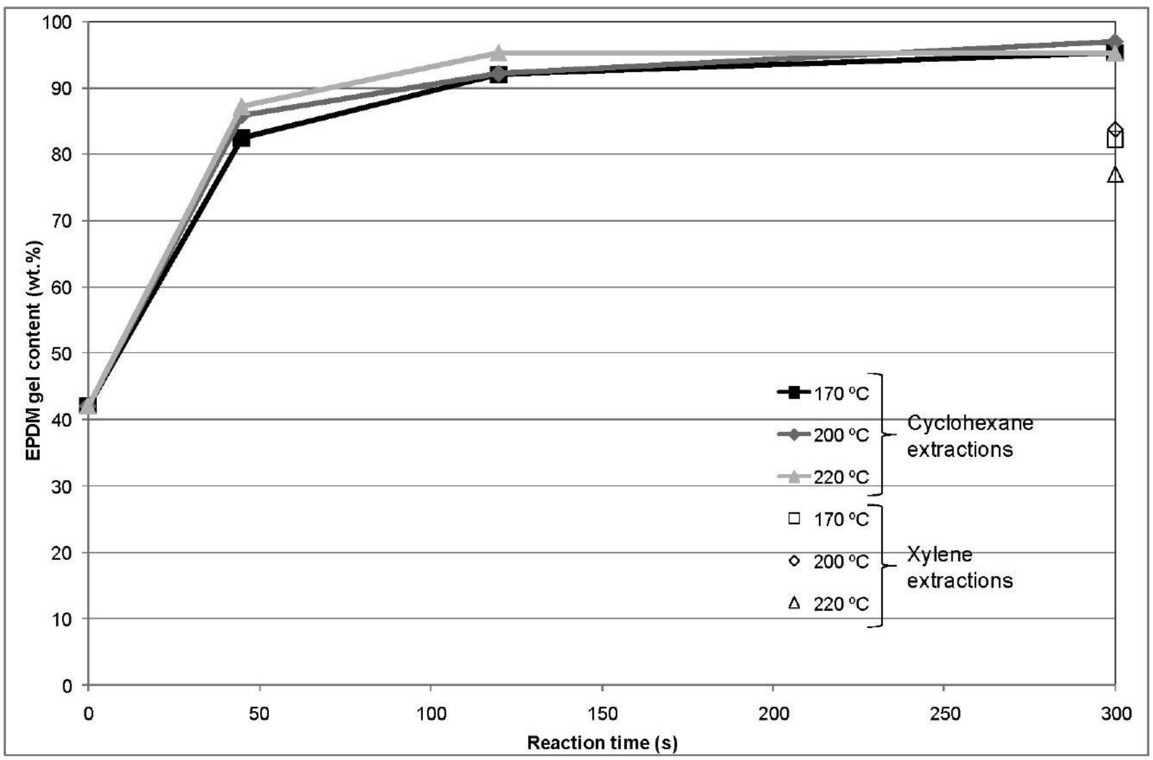

FIG. 7. - EPDM gel content of EPDM/PP (30/70; w/w) TPVs with PP MFI 47 as a function of reaction time at different temperatures (closed symbols - data from cyclohexane and open symbols - data from xylene only at 300 s).

CONCLUSIONS

EPDM/PP - based TPVs were prepared via dynamic vulcanization using resol/ $SnCl_2$ as the crosslinking system. Although the amount of the crosslinking agents was kept constant relative to EPDM amount, it was noticed that the evolution of crosslinking as a function of time decreases as the EPDM amount increases. In case of static vulcanization of only EPDM in the absence of PP the crosslinking reaction proceeds according to normal Arrhenius behavior and high degrees of crosslinking are obtained at higher temperatures.

Dynamic vulcanization of EPDM in the absence of PP results in relatively low levels of crosslinking. It could be concluded that degradation of the EPDM network occurs during dynamic vulcanization, due to the action of both high shear and elongation stresses and high temperature. Combining the gel content data for TPVs with the corresponding blend morphologies, it was shown that degradation of the EPDM network in a TPV formulation is minimized if EPDM is the dispersed phase and/or if the PP matrix has low viscosity.

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