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Dynamic vulcanisation of EPDM/PE-based thermoplastic vulcanisates studied along the extruder axis

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Abstract

Simple blending and dynamic vulcanisation of EPDM/PE blends using the resol/$SnCl_2$ system was studied in an extruder using a series of sampling devices. The melting of the PE pellets occurs just in front of and in the first kneading zone. Upon complete melting of the PE phase, the EPDM/PE blends reach very quickly their final morphology. Crosslinking of the EPDM phase to high levels occurs already when the PE phase is not yet fully molten. The higher the EPDM content, the higher the viscous dissipation, the higher the melt temperature and, consequently, the higher the crosslinking rate. For the EPDM/PE (50/50; w/w) TPV a transition from continuous via co-continuous to fully dispersed EPDM is observed, which is driven by crosslinking. Although the degree of crosslinking of the EPDM rubber is very high, this does not prevent phase inversion of the blend. The EPDM/PE interface is rather blurred, because PE crystalline lamellae are growing into the EPDM domains, probably because of the high compatibility between PE and EPDM (60 wt% of ethene). This study shows that dynamic vulcanisation in extruders proceeds quite differently from that in batch kneaders, where melting, mixing and crosslinking are separated in time. In extruders mass and heat transport, melting of the thermoplastic, morphology development (including dispersion and phase inversion), distribution and dissolution of (crosslinking) chemicals and crosslinking of the rubber do not occur as independent phenomena, but mutually and/or continuously interact.

Keywords: Dynamic vulcanisation; Morphology; EPDM

1. Introduction

Thermoplastic elastomers (TPEs) combine the elastic and mechanical properties of thermoset crosslinked rubbers with the melt processability of thermoplastics. Today, TPEs comprise the fastest growing rubber market. TPEs can be processed by a variety of techniques, such as extrusion, blow moulding, injection moulding, vacuum forming and calandering. In addition, production scrap and waste after use can be recycled. Thermoplastic vulcanisates (TPVs) are a particular family of TPEs [1–3], which are produced via dynamic vulcanisation of non-miscible blends of a rubber and a thermoplastic, i.e. the selective crosslinking of the rubber while simultaneous melt mixing with the thermoplastic. As a result, the products obtained consist of crosslinked rubber particles dispersed in a thermoplastic matrix. The thermoplastic matrix explains the melt processability of TPVs, while the crosslinked elastomer particles, 'glued' together by thermoplastic inter-layers, explain the elasticity. Crosslinking during blending is essential for producing TPVs products with optimum properties. In comparison to simple, non-crosslinked blends, TPVs have enhanced elasticity and oil resistance. In addition, dynamic vulcanisation is a way to disperse rather large amounts of elastomer in the thermoplastic matrix, resulting in TPVs with a low hardness, and to prevent coalescence, resulting in a refined morphology. Most commercial TPVs contain substantial amounts of extender oil for lowering the hardness and increasing the melt processability. A very broad range of TPVs can be produced by varying the composition and the crosslink density. Most commercial TPVs are based on ethene/propene/diene terpolymers (EPDM), because of its stability against high temperatures, oxygen and ozone, thus giving to the corresponding TPVs good heat, oxidation and ozone resistance. EPDM-based TPVs are usually crosslinked with resols, because resol crosslinks the unsaturated

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elastomer phase selectively, is effective at the temperatures during extrusion and yields thermo-stable crosslinks. Main applications of EPDM-based TPVs are automotive sealings and bellows, soft touch for tool grips, etc.

A large number of experimental studies has been published on the production of TPVs [1–4]. TPV properties are usually interpreted in terms of blend composition, crosslink density and morphology. In some studies the morhology of dynamicallly vulcanised blends of the thermoplastic and the elastomer has been compared with that of the corresponding physical blends of the two polymers [5–7]. It has been demonstrated that crosslinking during mixing is driving the elastomer to become the dispersed phase, even when it is the major blend component, a process which is usually called phase inversion. However, the actual process of phase inversion as it is occurring inside the extruder has not been studied up to now, because of the inaccessability of the melt material inside the extruder. Clearly, screw pulling experiments suffer from too many artefacts (continued crosslinking, coalescence of dispersed phase, etc.) to be of use in this respect. This probably explains why the morphology development during dynamic vulcanisation of rubber/thermoplastic blends has been mainly studied as a function of time in batch kneaders [8–14]. It was shown that EPDM/PP blends with equal amounts of EPDM and PP or some excess of EPDM usually have a co-continuous morphology before crosslinking. Upon dynamic vulcanisation with a $SnCl_2$-activated resol system the EPDM phase becomes dispersed even if it is the major phase, i.e. crosslinking drives phase inversion indeed which is in agreement with the black-box extruder studies. Thus, dynamic vulcanisation is essential for obtaining the morphology that is required for combining elasticity with melt processability.

The morphology of blends and TPVs can be rationalised by the combined effect of the viscosity ratio and the blend composition. Avgeropoulos was the first to show that for polymer blends the phase with the lowest viscosity and/or the highest volume fraction becomes the matrix and the phase with the highest viscosity and/or the lowest volume fraction the dispersion [12]. At similar viscosities and/or equal volume fractions a co-continuous morphology is obtained. Although refined theories have been developed in the last decade to predict blend morphologies [15–17], it is felt that the basic Avgeropoulos model is sufficient to explain phase inversion during TPV production. Romanini was the first to use this model to explain the morphology of TPVs [8]. Crosslinking of the rubber results in an increase of the viscosity of the rubber phase and, thus, in phase inversion. Abdou-Sabet and Patel gave experimental evidence by 'mapping' the Avgeropoulos plot for EPDM/PP blends with a large variation in composition and EPDMs with different viscosities [9]. Radusch and Pham developed a mathematical model predicting the morphology of TPVs by combining mixing, mass and heat transport with crosslinking kinetics [10]. Recently, several studies have shown that not simply the change in melt viscosity, but the change in elasticity of the rubber phase is the driving force for phase inversion [13,14].

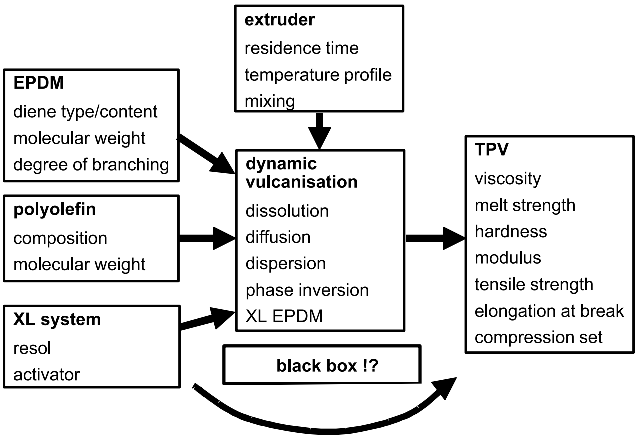

Fig. 1. Schematic representation of dynamic vulcanisation of rubber/thermoplastic blends, yielding thermoplastic vulcanisates.

Although these studies have provided new insights in the development of TPV morphology as a function of time in batch operation, it should be noted that on an industrial scale TPVs are preferably produced in twin-screw extruders, which allow continuous processing with high throughputs and with a large degree of process flexibility. Dynamic vulcanisation of TPVs on extruders is much more complex than that in batch kneaders, where the different steps of thermoplastic melting, rubber dispersion and crosslinking are separated in time. In extruders the elastomer and the thermoplastic are usually fed simultaneously through the hopper. Other ingredients, such as the crosslinking system, stabilisers, fillers, oil, etc. may be fed via the hopper and/or via side feeders. The thermoplastic has to melt, the elastomer and the thermoplastic have to mix, yielding a heterogeneous but finely dispersed blend, the extender oil that is often present has to redistribute over the two phases and the crosslink system has to dissolve and to crosslink the elastomer phase. These various processes will (partly) take place simultaneously and, in addition, will (partly) mutually interact. For example, crosslinking of the rubber phase will enhance the viscosity of the rubber phase and also affect the viscosity ratio of the blend, thus affecting the blend dispersion. Crosslinking may also limit the blend dispersion process, since it may already occur before the thermoplastic has been (fully) molten and/or fixate a non-equilibrium morphology. Similarly, the distribution of the oil will affect the volume fraction of the rubber and thermoplastic phases and also the viscosities of the two phases and, thus, the blend dispersion. To make matters even more complicated, the temperature and the flow field of the melt fluctuate along the extruder axis, thereby affecting the viscosities, the crosslinking kinetics, etc. At the end of the extruder usually de-venting is applied for removing gaseous and volatile products. The final melt strand coming out at the die of the extruder is cooled and pelletised.

Until now TPV product development and optimisation is performed in a ‘black box’ approach, which is characteristic for many polymeric compound developments in an industrial environment (Fig. 1). The blend recipe (type and content of various ingredients) and the processing conditions (screw lay-out, temperature, throughput and screw speed) are varied and the product is characterised. By correlating the output data with the input data, it is tried to optimise the process and the product without, however, having true insight in what is happening inside the extruder. Goal of this study is to de-black-box the process of dynamic vulcanisation of TPVs on extruders in order to have a better understanding of the process and to allow a more scientific process and product development and optimisation. The dispersion and crosslinking of HDPE/EPDM blends are studied along the axis of a twin-screw extruder during dynamic vulcanisation with resol. HDPE was chosen, since it can be replaced by a wide variety of other PE types (LDPE and VLLDPE) and/or ethene-containing polyolefins (like plastomers), allowing an extension of this work in future studies.

2. Experimental

TPVs were produced in a Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder with 29 *L/D* at a throughput of 5 kg/h, a screw speed of 290 rpm and a barrel set temperature of 200 °C. Tumble-mixed dry blends of milled, oil-extended EPDM (DSM Keltan® DE2322: 60 wt% ethene), PE (DSM Stamylex® 2H280 HDPE), stabiliser (Irganox 1010) and crosslinking system (resol and $SnCl_2 \cdot 2H_2O$) were fed to the extruder via the hopper. Simple EPDM/PE blends were studied without crosslinking with EPDM/PE ratios of 70/30, 50/50 and 30/70 (w/w) as references (Table 1). TPVs were prepared by dynamic vulcanisation of EPDM/PE blends with $SnCl_2$-activated resol with EPDM/PE ratios starting at 90/10 and going in steps to 10/90 (w/w). The amount of crosslinking chemicals is kept constant relatively to the amount of EPDM, viz. 1.5 parts per hundred rubber (phr) resol and 1 phr $SnCl_2$, but thus varies in wt% for each blend/TPV. The amount of stabiliser is 0.15 wt% relatively to the total amount of polymer (EPDM plus PE). Note that the EPDM content of the blends refers to the actual rubber content; the extender oil is not included.

Samples were taken along the screw axis using a series of sampling devices at *L/D* is 8, 9, 10, 15, 20, 25 and 29 (extrudate) (Fig. 2), which allow rapid sampling (∼5 s) of sufficient melt sample (∼2 g) for further characterisation and have been used in previous studies on polymer modification and reactive blending [18,19]. The average melt temperature was measured by sticking a pre-heated, needle-type, fast-response (time constant ∼1 s) Coleparmer type K thermocouple into the freshly collected sample. Melt samples for further characterisation were collected along the screw axis and from the extrudate and then quenched in liquid nitrogen in order to freeze in the morphology and stop the crosslinking reaction. Dynamic mechanical analysis (DMA) was performed with a Perkin–Elmer DMA7 in the tensile mode at room temperature on $1.8 \times 0.3\ mm^2$ samples, prepared by compression moulding, to get a first, qualitative impression of the physico-chemical phenomena along the screw axis. Extractions using cyclohexane were used to determine the EPDM content as a measure for the crosslink density of the EPDM phase. Approximately 2 g of sample was stirred in 100 ml cyclohexane (Riedel) for 48 h (the cyclohexane was refreshed after 24 h) at room temperature. The EPDM gel content was calculated assuming that the EPDM residue consists of PE and crosslinked EPDM only. Transmission electron microscopy (TEM) with a Philips CM200 (120 kV) on ∼100 μm cry-coupes, stained for 24 h in a RuO_4 solution, was used to study the morphology. Bulk staining was used instead of vapour staining, because the latter results in TEM micrographs with little contrast between the EPDM and

Table 1
Composition of EPDM/PE blends without and with crosslinking

Coding	EPDM (wt%)	PE (wt%)	Irganox 1010 (wt%)	Resol (wt%)	$SnCl_2$ (wt%)
Blends (no crosslinking)					
70/30	70	30	0.15	0	0
50/50	50	50	0.15	0	0
30/70	30	70	0.15	0	0
TPVs (with crosslinking)					
90/10	90	10	0.15	1.35	0.9
80/20	80	20	0.15	1.2	0.8
70/30	70	30	0.15	1.05	0.7
60/40	60	40	0.15	0.9	0.6
50/50	50	50	0.15	0.75	0.5
40/60	40	60	0.15	0.6	0.4
30/70	30	70	0.15	0.45	0.3
20/80	20	80	0.15	0.3	0.2
10/90	10	90	0.15	0.15	0.1

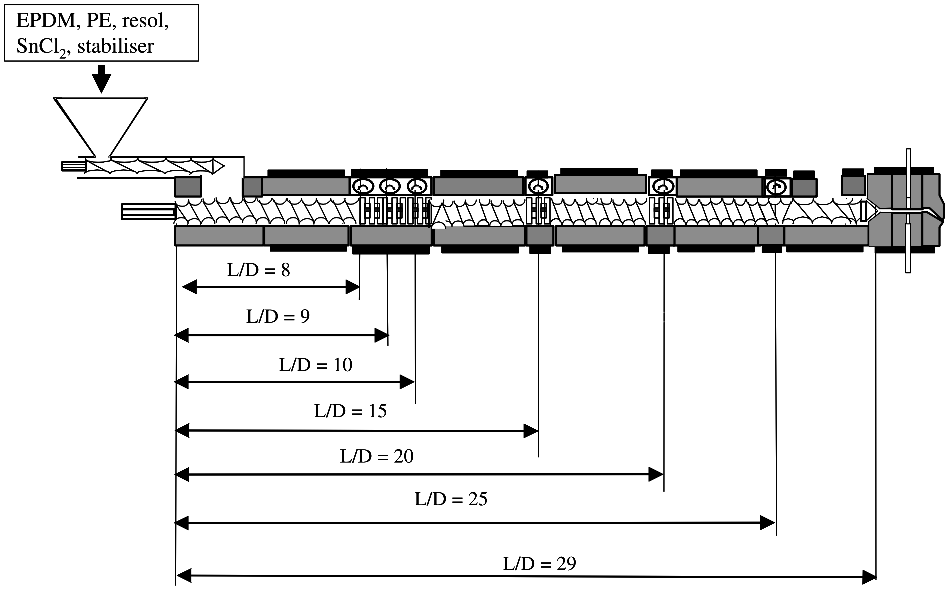

Fig. 2. Twin-screw extruder lay-out with positions of sampling devices (in *L/D*).

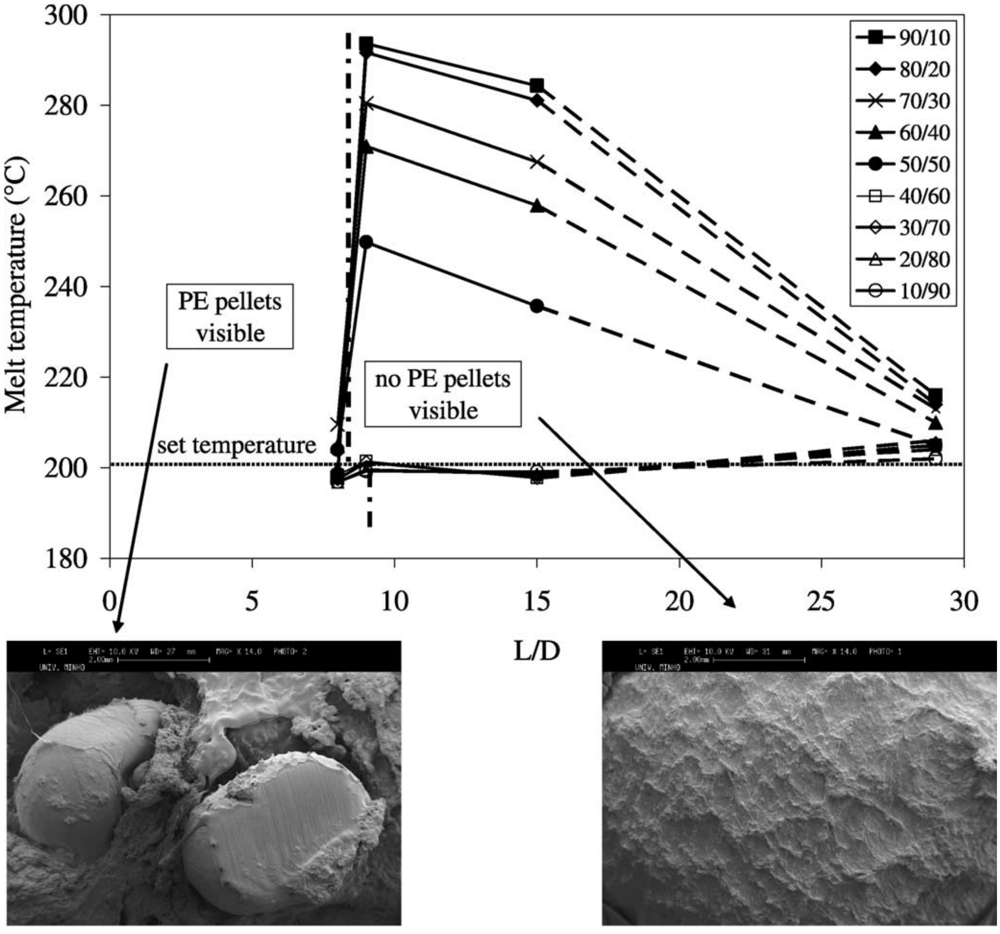

Fig. 3. Melt temperature of EPDM/PE TPVs with crosslinking along screw axis (note that drawn lines are just a guide to the eye, but do not represent the temperature profiles).

PE phases and hardly visible PE crystalline lamellae. For DMA, extractions and TEM care was always taken to avoid the presence of non-molten PE pellets in the samples. An Alpha Technologies MDR 2000E rheometer was used to determine the rate of $SnCl_2$-activated resol crosslinking of gumstock EPDM as a function of time at different temperatures (150, 175, 200, 225 and 250 °C). The torque is commonly viewed as a direct measure for the crosslink density [20].

3. Results and discussion

Various characteristics will be addressed in this study, i.e. the melt temperature, the presence of non-molten PE, the storage modulus, the gel content and the morphology. First the results for the simple EPDM/PE blends without crosslinking will be discussed, then those of the EPDM/PE blends which are dynamically vulcanised. Note that the former will be simply referred to as blends and the latter as TPVs, although the latter are actually not truly TPVs but TPVs in development.

3.1. Temperature

The temperature of the samples collected along the screw axis was measured several times, yielding an average value with a scatter of about ±5 °C. For the blends without crosslinking the melt temperature is within experimental error equal 200 °C, i.e. the barrel set temperature, independently of the blend composition and the sampling position. Obviously, for this type of relatively small laboratory extruder heat transfer to and from the barrel and screw is dominating over the heat generated as a result of viscous dissipation. For the TPVs with crosslinking the melt temperature shows a completely different behaviour (Fig. 3). At $L/D=8$ the melt temperature is still close to the set temperature of 200 °C for all TPVs. However, for the EPDM-rich TPVs (90/10 to 50/50; w/w) the melt temperature jumps to 250–290 °C at $L/D=9$ and then slowly decreases again to 205–215 °C, but does not reach the level of the barrel set temperature. For the EPDM-poor TPVs (40/60 to 10/90; w/w) the melt temperature remains equal within experimental error to the set temperature all along the extruder axis, as for the blends without crosslinking. It is noted that the true temperature profile is not simply a curve through the experimental data, since the melt temperature will increase in the kneading zone at $L/D=15$ and the zone with reverse kneading elements at $L/D=25$ and at the die, resulting in strong temperature fluctuations. Nevertheless, the curves shown in Fig. 3 give an impression of the temperature profile. Obviously, the presence of the crosslinking system is the origin of the increase of temperature, which is enhanced upon increasing the EPDM content of the TPVs. As will be discussed below, the EPDM-rich TPVs have a (co-)continuous EPDM phase. In the presence of resol and $SnCl_2$, the EPDM phase is crosslinked, resulting in a strongly increased viscosity, in its turn resulting in increased viscous dissipation and, thus, in a temperature rise. Note that the strong temperature increase for the EPDM-rich TPVs, the 90/10 (w/w) TPV being the most extreme case from 198 to 294 °C, occurs between the sampling devices at $L/D=8$ and 9, i.e. over a very short distance of only 3.4 cm.

3.2. Visual inspection

The samples collected along the screw axis have been visually inspected after quenching with liquid nitrogen. In some cases non-molten PE pellets are observed within the samples (Fig. 3). For the PE blends this is the case for all samples at $L/D=8$ and for the TPVs for all samples at

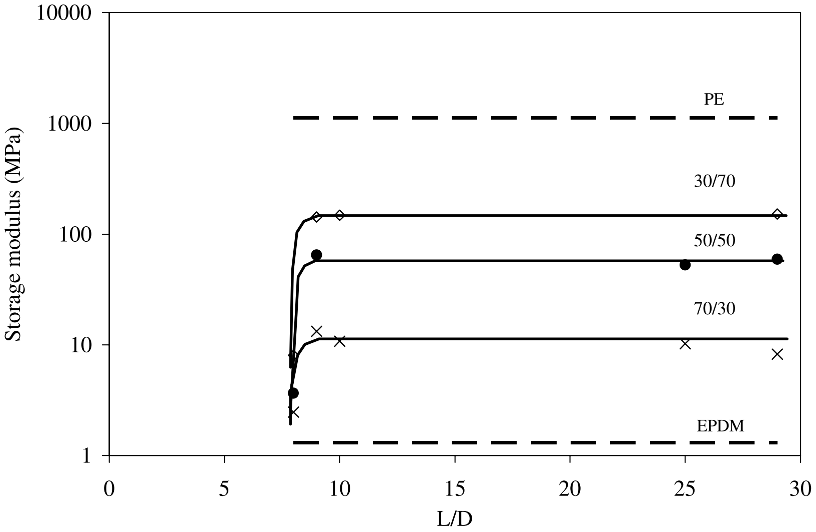

Fig. 4. Storage modulus measured at room temperature of EPDM/PE (70/30, 50/50 and 30/70; w/w) blends without crosslinking as a function of screw length.

$L/D=8$ and for the PE-rich TPVs (20/80 and 10/90; w/w) at $L/D=9$ (indicated by the dashed, vertical line in Fig. 3). However, substantial amounts of the PE pellets are molten at $L/D=8$, because the quenched melt samples feel rather rigid, indicating the presence of PE next to that of EPDM. Considering that the melting point of HDPE is about 120 °C, the presence of non-molten PE pellets at $L/D=8$ and 9, where melt temperatures of 200 °C and higher are measured, shows that the samples are not in equilibrium with respect to heat transfer. The higher the PE content of the TPVs (20/80 and 10/90; w/w), which also corresponds to the lower the melt temperature (∼200 °C), the longer it takes before the samples are homogeneous with respect to heat transfer (up to $L/D=9$).

3.3. Modulus

The storage modulus (E') of the samples was determined to get a first, general impression of the physico-chemical phenomena occurring along the screw axis during mixing (and dynamic vulcanisation) of the EPDM/PE blends. It is noted that the interpretation of E' is not straightforward, because E' of blends depends on several parameters such as the blend composition, the morphology and the moduli of the two blend components [21]. The modulus of the EPDM phase is determined by the degree of crosslinking. In addition, it is required to compression mould the samples before the actual modulus measurement, which will result in continued crosslinking especially in the samples collected at the beginning of the extruder.

Fig. 4 shows E' of the EPDM/PE (70/30, 50/50 and 30/70; w/w) blends without crosslinking as a function of the screw length. For all three compositions E' is relatively low at $L/D=8$, but increases strongly at $L/D=9$ and beyond that location reaches a constant level. It is no surprise that E' increases upon increasing PE content, since E' of blends of two polymers with a large difference in E' is first of all determined by the composition. Experimental E' values for PE and non-crosslinked EPDM are 1122 and 1.3 MPa, respectively. The sharp increase of E' between $L/D=8$ and 9 is not due to morphological changes, since the increase in E' is much too large for that. Considering that E' of these blends is dominated by the composition and that non-molten PE pellets are observed at $L/D=8$, but not at $L/D=9$, it is supposed that the sharp increase of E' is due to complete melting of all PE domains. Note that test plaques for DMA were always prepared from those parts of the collected samples, which do not contain solid PE.

Fig. 5 shows E' of the EPDM/PE (90/10 to 10/90; w/w) TPVs with crosslinking as a function of screw length. For all TPV compositions E' at $L/D=8$ is relatively low, increases at $L/D=9$ in particular for the PE-rich TPVs (50/50 to 10/90; w/w) and then levels off at $L/D=10$–15, more or less similar to the blends without crosslinking. Again it is no surprise that E' increases upon increasing PE content. E' of the TPVs is significantly lower than E' of the blends at corresponding compositions, which may be due to subtle differences in morphology, oil distribution (crosslinking will lower the oil content of the rubber phase) and low crystallinity of the PE phase. The (sharp) increase of E' between $L/D=8$ and $L/D=10$–15 is not due to crosslinking, since crosslinking of the rubber phase has only a small effect on E' according to the Kerner model. The increase is also not due to dramatic morphological changes, since these do not occur between $L/D=8$ and 9 (cf. below). As for the blends without crosslinking, it is supposed that the increase of E' of the TPVs between $L/D=8$ and $L/D=10$–15 is because of the complete melting of all PE domains.

The development of E' for the EPDM/PE blends and TPVs was initially studied to get a general impression of the physico-chemcial phenomena along the screw axis. However, it turned out that E' is dominated by the melting behaviour of PE and not by crosslinking of the EPDM phase nor by morphological changes. Therefore, the EPDM gel

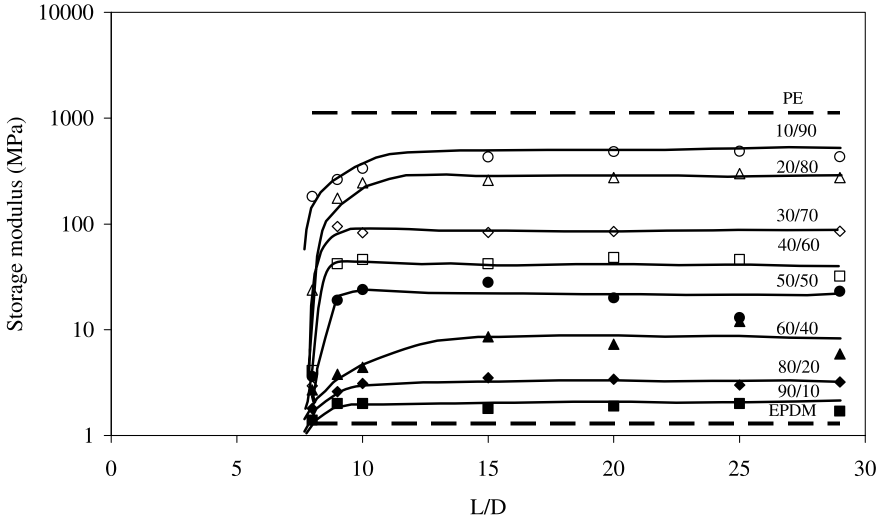

Fig. 5. Storage modulus measured at room temperature of EPDM/PE (90/10 to 10/90; w/w) TPVs with crosslinking as a function of screw length.

content was used to study the degree of crosslinking along the screw axis, and TEM was used to determine the actual morphology.

3.4. EPDM gel content

The EPDM gel content is used in this study as a measure for the degree of crosslinking of the EPDM phase. There are other (more sophisticated) techniques to probe the degree of crosslinking, such as swelling measurements, DMA, solid state NMR relaxation, etc. But these all suffer from the fact that the composition of the TPVs, i.e. the EPDM/PE ratio, also affects the experimental outcome. As a result, these techniques do not allow a fair comparison of the degree of crosslinking of the EPDM phase of the various TPVs, whereas the EPDM gel content does. It was shown that the EPDM dissolves fully in cyclohexane at room temperature, whereas the PE does not dissolve at all. The EPDM gel content for the EPDM/PE blends without crosslinking was close to 0% at *L*/*D*=8 and close to 1% at *L*/*D*=9 up to 29. These very low values agree with the absence of any crosslinking of the EPDM phase and show also that all EPDM is extractable even when the EPDM phase is dispersed as in the EPDM/PE (30/70; w/w) blend. It is noted that in some cases the EPDM gel content is well above 100%, which is not possible from a theoretical point of view. This can be probably due to linking of the resol to the rubber and incomplete extraction of the extender oil from the rubber network.

Fig. 6 shows the EPDM gel content of the EPDM/PE (90/10 to 10/90; w/w) TPVs with crosslinking as a function of screw length. For the EPDM-rich TPVs (90/10 and 80/20; w/w) the gel content is approximately 100% all along the screw axis. This shows that all EPDM chains are already part of a crosslinked 3D rubber network at *L*/*D*=8, even before all PE domains are fully molten and even before complete blend dispersion is achieved (see below). It should be realised though, that these results do not indicate that the crosslinking reaction is already completed at *L*/*D*=8, since the EPDM gel content is not sensitive for variations in the degree of crosslinking at high degrees of crosslinking. When all rubber chains are part of the network, further crosslinking does not affect the gel content anymore (the gel content cannot increase above 100%). For the TPVs with EPDM/PE ratios between 70/30 and 30/70 (w/w) the gel content increases between *L*/*D*=8 and 9 especially for the PE-rich TPVs (40/60 and 30/70; w/w), but then levels off again at about 100%. For the 20/80 and 10/90 (w/w) TPVs the increase is less steep and continues up to *L*/*D*=10 and 20, respectively. As discussed above, the melt temperature of the TPV samples increases strongly upon increasing the EPDM content, which explains most probably the strong increase of the crosslinking rate upon increasing the EPDM content. Fig. 7 shows rheometer curves for the static vulcanisation of EPDM rubber with $SnCl_2$-activated resol as a function of temperature. The crosslinking rate strongly increases upon increasing the temperature from 150 to 250 °C. At 150 °C the crosslinking is completed in ~25 min, at 200 °C in ~1.5 min and at 250 °C in ~1 min. The latter value is probably an upper estimate, because at 250 °C heat transfer is limiting the crosslinking, since it takes ~1 min. for the rheometer cell and rubber sample to reach the set temperature of 250 °C. Another explanation for the decreasing EPDM crosslinking rate upon increasing PE content is that the diffusion of the resol crosslinker from the abundant PE phase to the relatively small amount of EPDM phase may limiting.

3.5. Morphology

Before discussing the TEM micrographs of the EPDM/PE blends and TPVs a general discussion on TPV morphology is in its place. In contrast to the morphology of non-crosslinked blends, consisting of a regular dispersion of

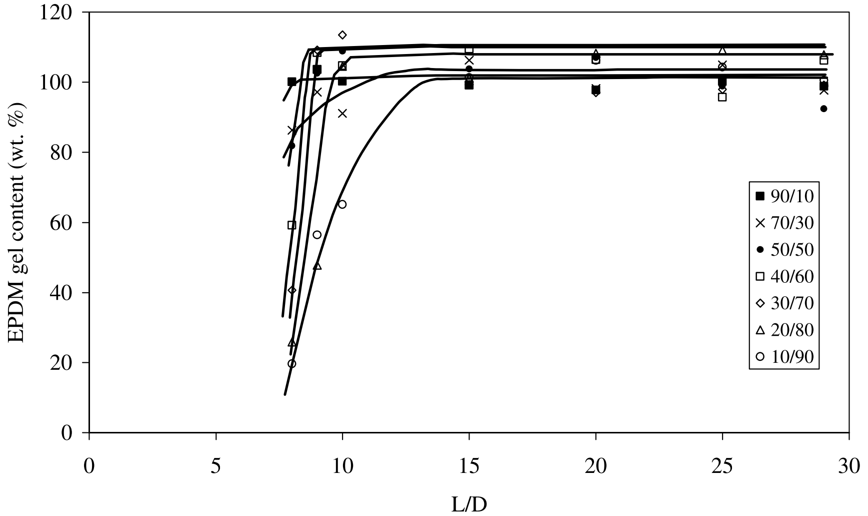

Fig. 6. EPDM gel content of EPDM/PE (90/10 to 10/90; w/w) TPVs with crosslinking as a function of screw length.

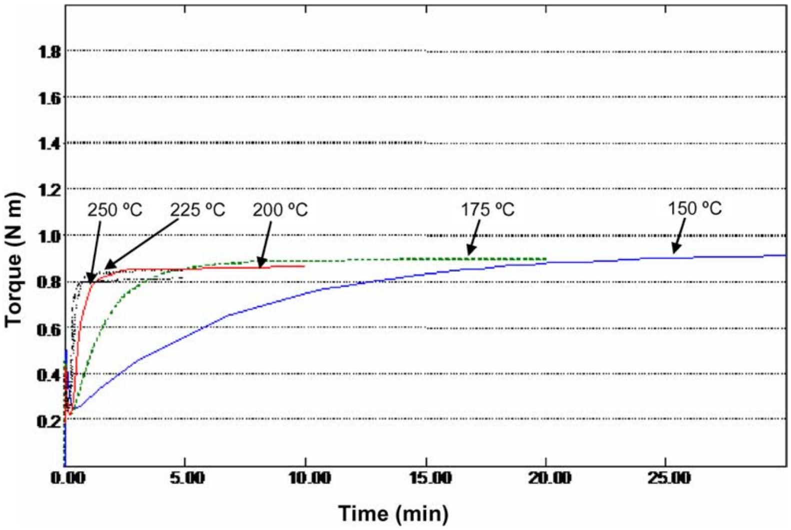

Fig. 7. Rheometer curves for thermoset crosslinking of EPDM with $SnCl_2$-activated resol at different temperatures (150, 175, 200, 225 and 250 °C).

spherical droplets in a matrix, the morphology of TPVs consists usually of irregularly shaped rubber particles, which can hardly be distinguished from each other because of actual interfacial contact and/or microscopy artefacts. The latter may be because the rubber is the dispersed phase, despite the fact that it is the major phase. The rubber particles have a rather broad distribution in size and, in addition, the morphology of TPVs is often rather heterogeneous in space. Upon cooling down TPV samples from the melt, the thermoplastic phase crystallises and the extender oil will redistribute. It was recently shown for EPDM/PP based TPVs that the oil is more or less evenly distributed over the rubber phase and the amorphous PP fraction [22]. As a result, the interpretation of TPV morphologies as obtained by TEM is far from trivial and at best only qualitative statements on the actual morphology in the melt can be made. The study of the morphology of the EPDM/PE blends and TPVs is even more complicated, because the interface between the EPDM and PE phases is difficult to observe. Fig. 8 shows representative TEM

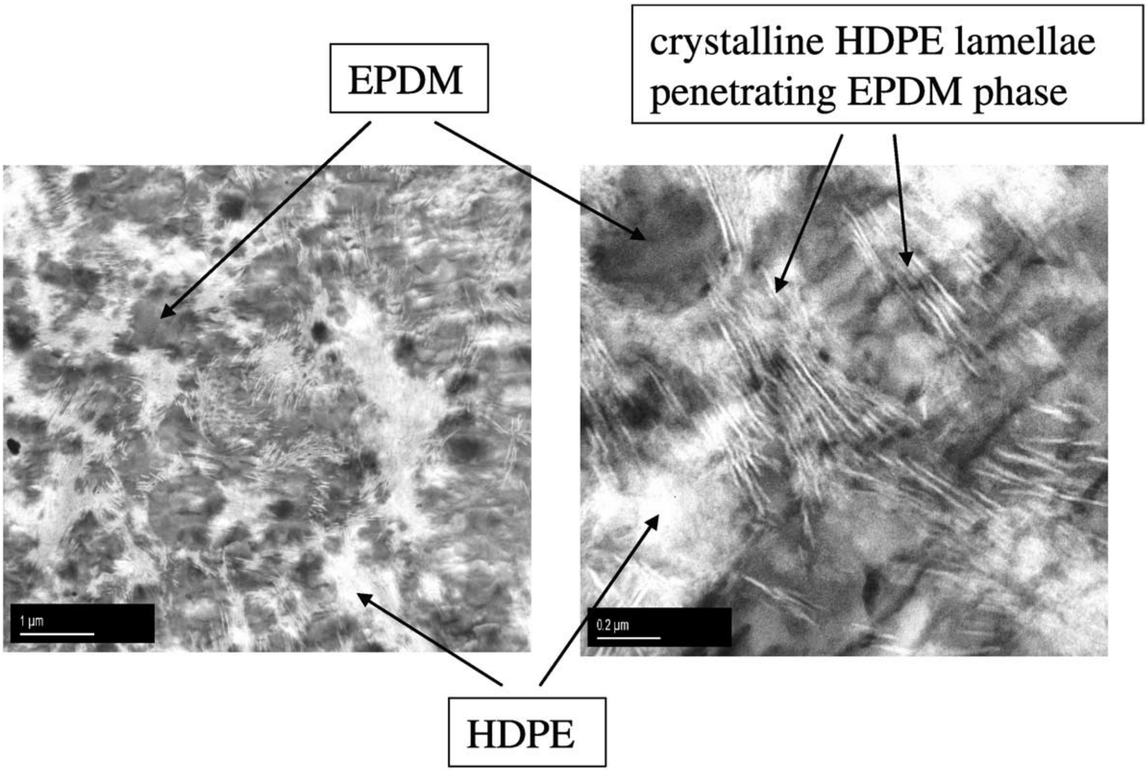

Fig. 8. TEM micrographs of EPDM/PE (50/50; w/w) TPV at *L*/*D* 8 at different magnifications.

micrographs with different magnifications. It is difficult to distinguish the 'dark' EPDM and 'white' PE phases, because there are no sharp boundaries. The PE phase is not fully 'white', because crystalline PE lamellae are present, which give some darkening effect. At higher magnification it becomes clear that these crystalline PE lamellae penetrate the EPDM phase, thus blurring the interface. This is probably because of the high compatibility between the PE phase and the EPDM phase with a high ethene content (60 wt%) and/or co-crystallisation of long ethene sequences of EPDM with PE chains.

Figs. 9–11 show the TEM micrographs of the 20/80, 80/20 and 50/50 (w/w) TPVs with crosslinking along the screw axis. From the visual inspection of the samples for all three TPVs it has become clear that not all PE pellets are molten at $L/D=8$ and for PE-rich TPVs not even at $L/D=9$. The TEM micrographs for all TPVs at $L/D=8$ and 9 show morphologies, consisting of 'white' PE and 'dark' EPDM phases, indicating that part of the PE has already been molten though. For all TPVs it looks as if the amount of 'white' PE phase is increased between $L/D=8$, 9 and/or 10 and then remains constant along the screw axis. This is again related to the complete melting of all PE domains between $L/D=8$ and $L/D=9$ and/or 10 in combination with the fact that the TEM cryo-coupes were always cut from those parts of the samples that do not contain solid PE pellets. For the 20/80 (w/w) TPV the morphology changes from a coarse EPDM dispersion in a PE matrix at $L/D=8$, via a finer EPDM dispersion but still with areas in the PE matrix without any EPDM at $L/D=9$ to a nicely dispersed EPDM phase at $L/D=10$, which is not further refined at $L/D=15$ (Fig. 9). For the 80/20 (w/w) TPV there is only

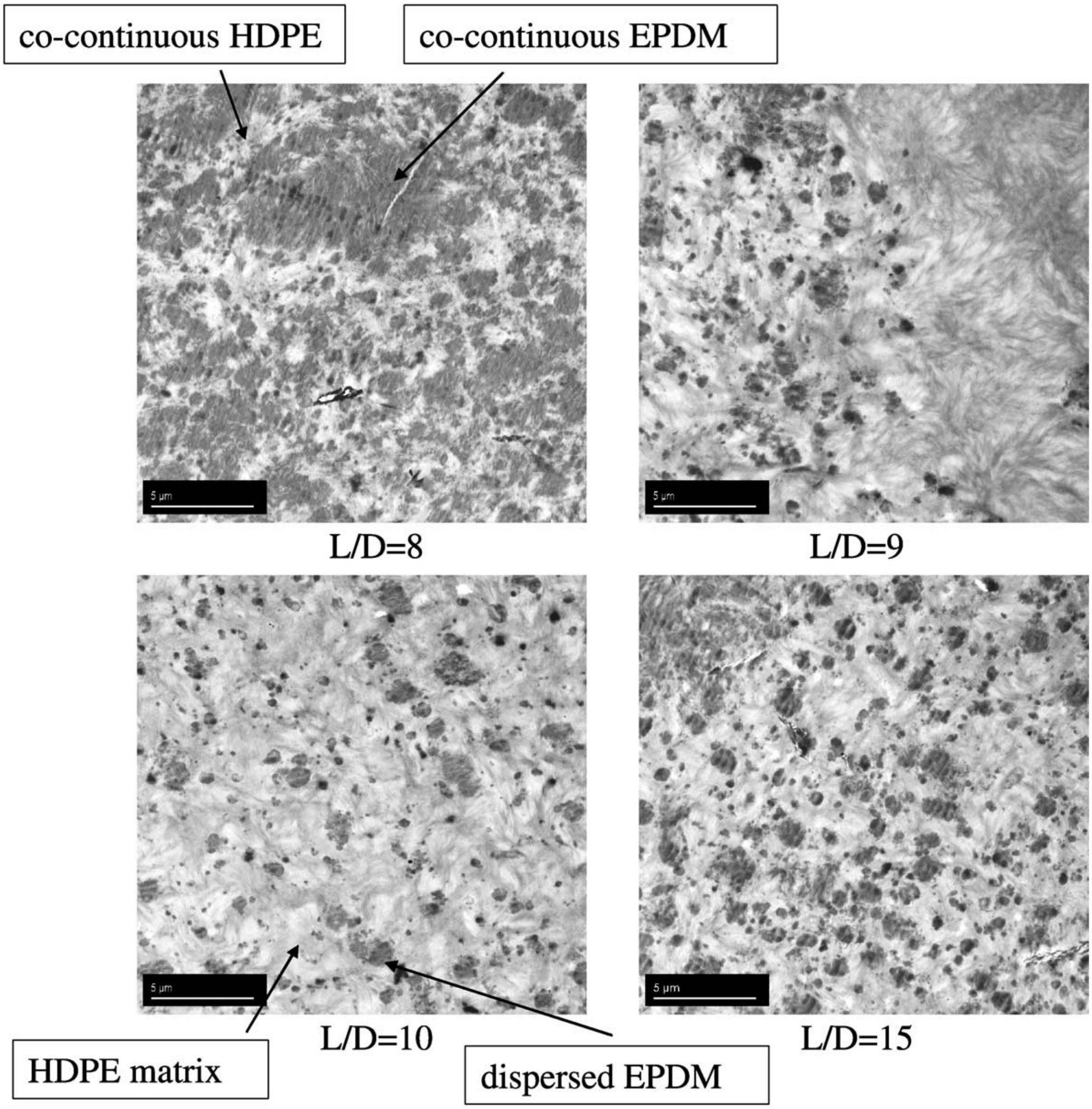

Fig. 9. TEM micrographs of EPDM/PE (20/80; w/w) TPVs at $L/D=8$, 9, 10 and 15.

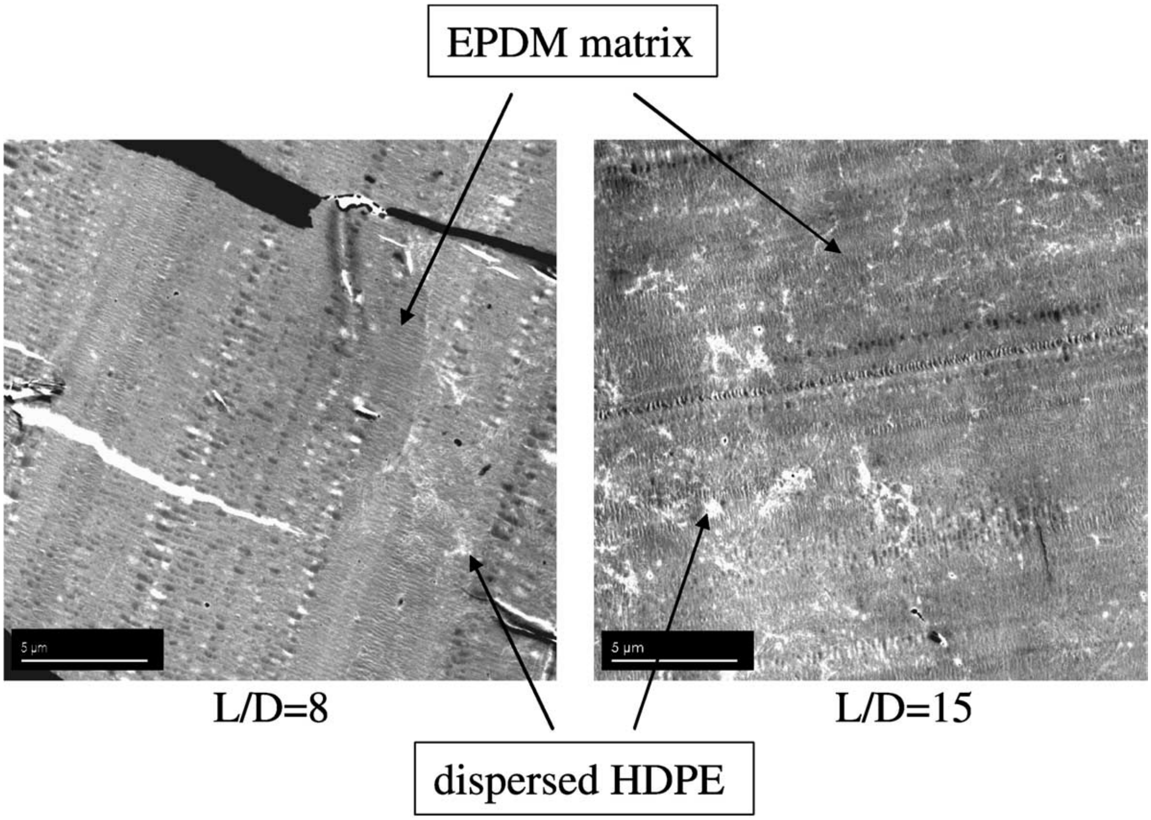

Fig. 10. TEM micrographs of EPDM/PE (80/20; w/w) TPVs at $L/D=8$ and 15.

some refinement of the morphology between $L/D=8$ and 9, but no significant changes after $L/D=9$ (Fig. 10). Note that the dispersed PE domains in the 80/20 (w/w) TPVs are not spherical, as is usually observed for polymer blends, but have a sort of spider-like structure. The EPDM-rich TPVs (80/20; w/w) have always a continuous EPDM phase, whereas the PE-rich TPVs (20/80; w/w) have always an EPDM dispersion, which is in agreement with the Avgeropoulos model [12]. It is concluded that complete dispersion from the mm level to the micrometer level occurs in a few seconds, which confirms the conclusions of earlier studies [23–25] and that the high degrees of crosslinking do not interfere with the morphology development.

Fig. 11 shows the TEM micrographs of the 50/50 (w/w) TPVs. At $L/D=8$ an EPDM matrix with a 'woven' PE lamellar structure and small areas (<1.5 μm) of irregularly shaped PE domains is observed. At $L/D=9$ there seems to be a mixture of two types of morphologies, viz. one which consists mainly of EPDM and the other one consisting of a PE matrix with an EPDM dispersion (1–5 μm) with PE lamellae growing inside. At $L/D=10$ both PE and EPDM phases are co-continuous. Larger and smaller EPDM domains are visible. Finally, at $L/D=15$ the PE phase has become the matrix with small and large dispersed EPDM domains. In agreement with previous studies [9,10] it appears that crosslinking is the driving force for phase inversion. Fig. 12 shows the Avgeropoulos plot [12]. The center arrow in this plot represents the increase in viscosity (or elasticity) as a result of crosslinking of the EPDM phase as the driving force for phase inversion. For the 80/20 (w/w) TPVs phase inversion as a result of crosslinking will not occur, because EPDM is already the dispersed phase (right arrow). For the 20/80 (w/w) TPVs PE is the continuous phase at all sampling positions, i.e. the increase in viscosity (or elasticity) as a result of crosslinking is insufficient to result in phase inversion (left arrow).

4. Conclusions

Clearly, the use of the series of sampling devices along the extruder axis allowed a detailed investigation of the physico-chemical phenomena during blending of EPDM with PE without and with crosslinking (dynamic vulcanisation). For all compositions melting of the crystalline PE takes place just in front of and in the first kneading section. As soon as part of the PE has become molten, it is intimately mixed with the rubbery EPDM. The dispersion from millimetre pellets to micrometre domains takes place in the first kneading zone, which confirms the conclusions of previous studies [23–25]. The high degrees of crosslinking do not interfere with the morphology development. In the case of the blends without crosslinking the temperature along the screw axis remains more or less equal to the set

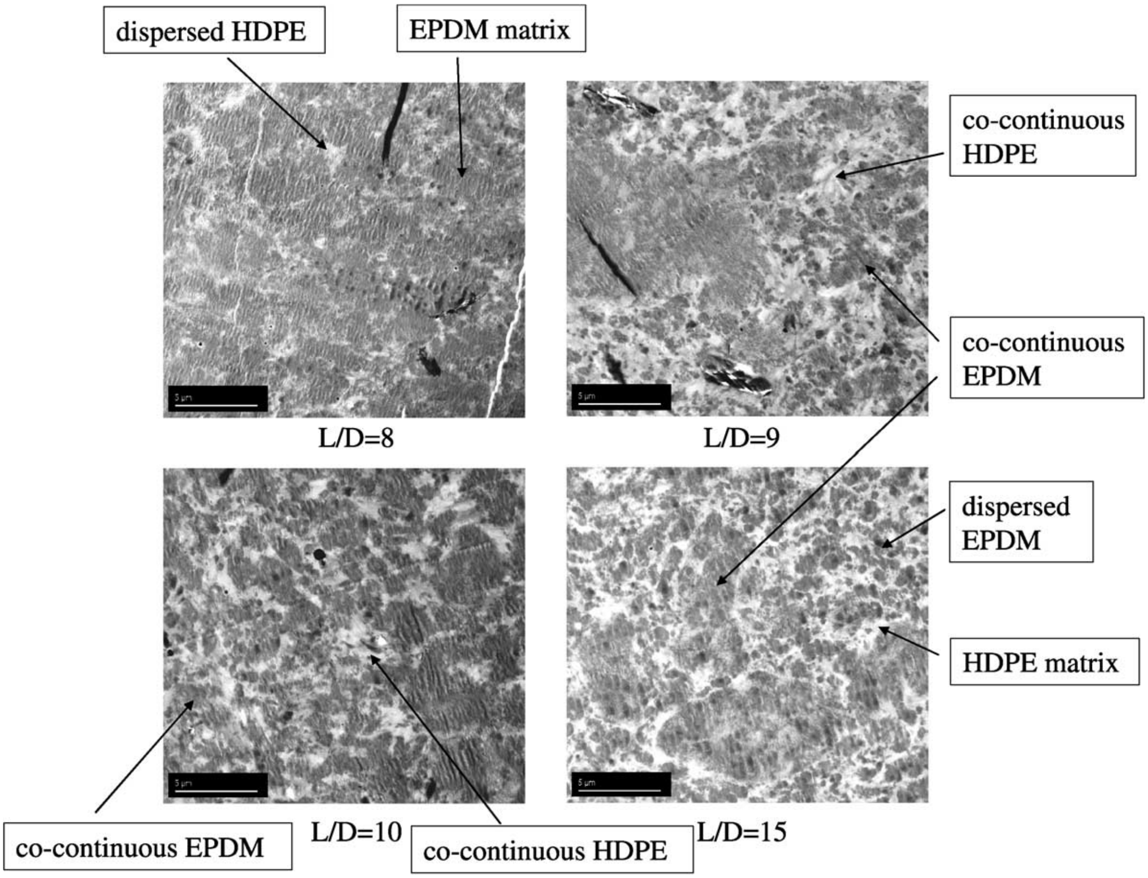

Fig. 11. TEM micrographs of EPDM/PE (50/50; w/w) TPVs at *L*/*D* = 8, 9, 10 and 15.

temperature. For the TPVs high degrees of crosslinking are already observed in the first kneading section. As a result, the EPDM viscosity increases strongly and, consequently, the melt temperature increases to values (far) above the barrel set temperature. The higher the EPDM content of the TPVs, the higher the viscous dissipation during extrusion, the higher the rise of the temperature and, thus, the higher the crosslinking rate. So, there is a reciprocal interaction between the melt temperature and crosslinking. Only for the PE-rich blends, which are characterised by relatively low melt temperatures, a less steep crosslinking profile towards 100% EPDM gel is observed. As predicted by the Avgeropoulos model, EPDM-rich systems yield continuous EPDM matrices, whereas PE-rich systems yield EPDM dispersions. For the 20/80 (w/w) TPVs the crosslinking just fixates the EPDM dispersion. For the 50/50 (w/w) TPVs crosslinking drives phase inversion from continuous via co-continuous to an EPDM dispersion. Although the degree of crosslinking of the EPDM rubber is very high, this does not prevent phase inversion of the blend. For the 80/20 (w/w) TPVs crosslinking is insufficient to enforce phase inversion and a TPV with a crosslinked EPDM matrix is collected at the die.

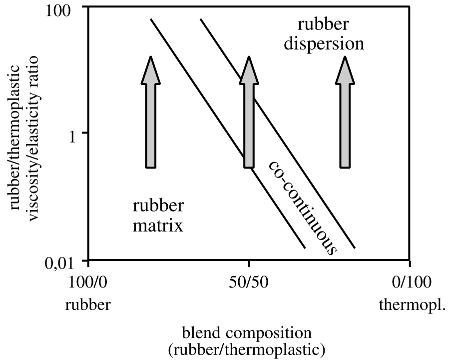

Fig. 12. Morphology of EPDM/PE blends as a function of viscosity (or elasticity) ratio versus blend composition; crosslinking of EPDM phase results in phase inversion for 50/50 (w/w) composition only.

In summary, dynamic vulcanisation of rubber/thermoplastic blends in a continuous extrusion process is rather complicated. Mass and heat transport, melting of the thermoplastic, morphology development (including dispersion and phase inversion), distribution and dissolution of (crosslinking) chemicals and crosslinking of the rubber do not occur as independent phenomena, but mutually and/or continuously interact. In that respect, studies performed in batch operation [9–14] do give fundamental insight in dynamic vulcanisation, because some of these phenomena are decoupled, but clearly do not approach the complexity of continuous extrusion. In a follow up, the mutual interaction of mixing and crosslinking will be investigated in more detail.

Finally, insight in a process such as dynamic vulcanisation is not a goal by itself, but merely a tool to optimise the process and the TPVs produced. A surprising conclusion is that melting, dispersion, crosslinking and phase inversion are complete, for most TPV compositions, in the first part of the extruder. This means that the throughput could be substantially increased, which is of obvious economic interest by itself, but also the residence time and temperature could be lower, thus limiting polymer degradation.

The properties of the TPVs as collected at the die of the extruder during this study will be presented in detail in a second paper and will be interpreted in terms of composition, morphology and crosslink density. It suffices here to note that the TPVs with a crosslinked, continuous rubber phase, i.e. those with a high EPDM content (90/10 to 70/30; w/w), on the one hand are highly elastic, but on the other hand are hardly processable. The TPVs with a PE matrix, i.e. those with a high PE content (30/70 to 10/90; w/w), are easily processed in the melt, but have poor elasticity. The TPVs with intermediate compositions (60/40 to 40/60; w/w) combine both melt processability and elasticity, thus providing the best products. The ultimate goal is to shift the TPV compositions towards higher EPDM contents in order to have TPVs with enhanced elasticity, while maintaining melt processability by adjusting the blend composition (molecular weight of PE, level of crosslinking chemicals) and processing conditions.

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