

EPDM-based thermoplastic vulcanisates: Crosslinking chemistry and dynamic vulcanisation along the extruder axis

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Abstract

This paper presents new insights in the resole crosslinking chemistry of thermoplastic vulcanisates (TPVs) and in the production of TPVs on extruders. Low-molecular-weight olefins were used in combination with EPDM crosslinking experiments to investigate the resole crosslinking chemistry. The fact that enhanced substitution of the olefin/EPDM unsaturation enhances the reactivity towards the resole strongly supports the cationic character of SnCl_2 -activated resole crosslinking. Samples were collected along the extruder during TPV preparation to study the physico-chemical phenomena during compounding. It was observed that crosslinking of the EPDM phase takes place even when the PE phase is not yet fully molten. Upon complete melting of the PE phase the blend very quickly reaches its final morphology. Only for the (50/50; w/w) blend, a transition from continuous via co-continuous to fully dispersed EPDM is observed, which is driven by crosslinking.

Keywords: Crosslinking chemistry; Dynamic vulcanisation; Morphology; EPDM; TPV; Resole

Introduction

Thermoplastic elastomers (TPEs) combine the elastic and mechanical properties of thermoset crosslinked rubbers with the melt processability of thermoplastics. TPEs can be processed by a variety of techniques, such as extrusion, blow moulding, injection moulding, vacuum forming and calendaring. In addition, production scrap and waste after use can be recycled. Today, TPEs comprise the fastest growing rubber market.

Thermoplastic vulcanisates (TPVs) are a particular family of TPEs [1-3], which are produced via dynamic vulcanisation of non-miscible blends of a thermoplastic and

a rubber, i.e. the selective crosslinking of the rubber while 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 and the crosslinked elastomer particles, "glued" together by thermoplastic inter-layers, explain the elasticity. Crosslinking during blending is essential for producing TPV 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 phase in the thermoplastic matrix, resulting in products with a low hardness. 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. With respect to

TPV composition, one should realise that not only the type and the amount of elastomer, thermoplastic and oil can be optimised, but also additional fillers, stabilisers, flame retardants, colourants, etc. can be added for tuning the TPV for a particular application. On an industrial scale TPVs are typically produced on twin-screw extruders, allowing a large degree of process flexibility.

Most commercial TPVs are based on blends of polypropylene (PP) and ethene/propene/diene terpolymers (EPDM). PP is used because of its high melting point and high crystallinity, resulting in good TPV properties even at elevated temperatures. EPDM is used because of its stability against high temperatures, oxygen and ozone, thus giving the corresponding TPVs good heat oxidation and ozone resistance. As a result of the compatibility of PP and EPDM, TPVs based on PP/EPDM blends are characterised by a finely dispersed EPDM phase ($1 - 3\mu\text{m}$) without the need of a special compatibiliser. Of course, the relatively low price of PP/EPDM/oil-based TPVs in comparison to the block-copolymer TPEs explains part of the commercial success and the relatively high growth rate ($\sim 10\%$ /year) of TPVs. PP/EPDMbased TPVs are usually crosslinked with acid-activated resole systems. Resole crosslinking is used, since it: (i) crosslinks the unsaturated elastomer phase selectively, (ii) is effective at the temperatures during extrusion and (iii) yields thermo-stable crosslinks. The chemistry of resole crosslinking of EPDM has been studied using low-molecular-weight models (Fig. 1) [4-6]. It has been shown that the resole, a phenol/formaldehyde oligomer, is degraded into mono-phenolic units, which eventually connect two EPDM chains via chroman and/or methylene-bridged structures. SnCl_2 activates the scission of the dimethylol ether linkage of the resole, yielding benzyl cations that add to the EPDM unsaturation. A recent ^{13}C NMR study showed that for EPDM with 5-ethylidene-2norbornene (ENB) as diene only methylene/chroman crosslinks are formed [7]. Resole is still the "work horse" for TPV production, because of the excellent properties and the good processability of the corresponding TPVs and despite its disadvantages like black speck formation and discolouration.

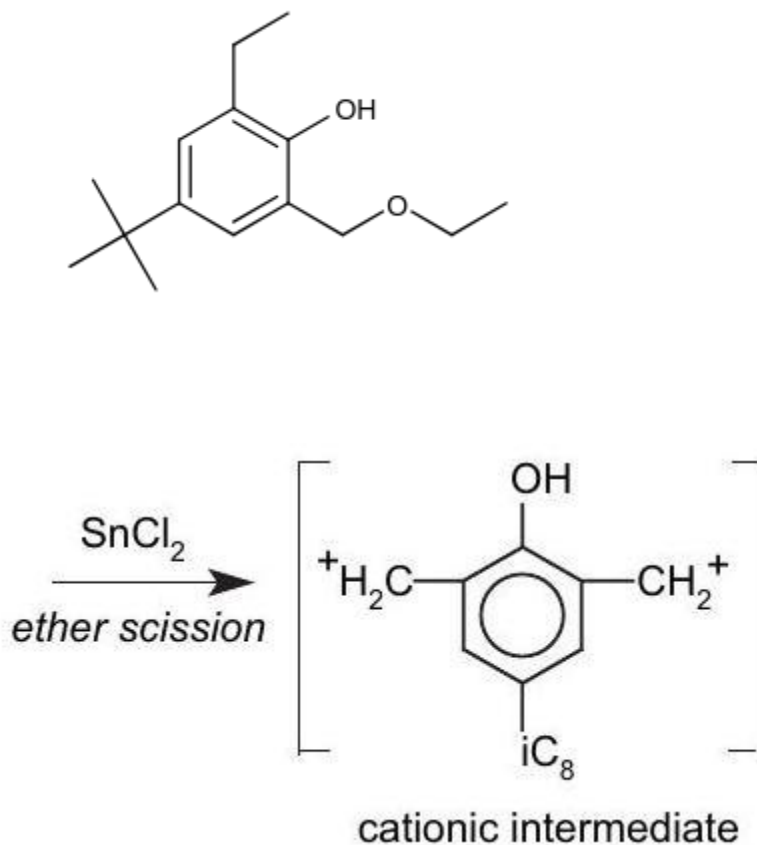
In this paper, the results of two recent experimental studies will be presented. First, the effect of the diene on the reactivity of EPDM rubber for resole crosslinking has been studied. Both low-molecular-weight model olefins were used, allowing an in depth mechanistic investigation, and crosslinking experiments were performed with EPDMs with various diene monomers. Secondly, the dispersion and the crosslinking of HDPE/EPDM blends are studied along the axis of an extruder during dynamic vulcanisation with

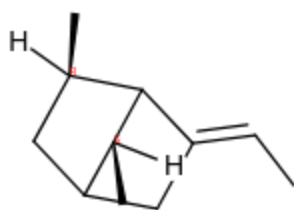
resole. HDPE was chosen, since it can be replaced by a wide variety of other PE types (LDPE and VLLDPE) and/or ethenecontaining polyolefins (like plastomers), allowing an extension of this work in future studies.

Experimental

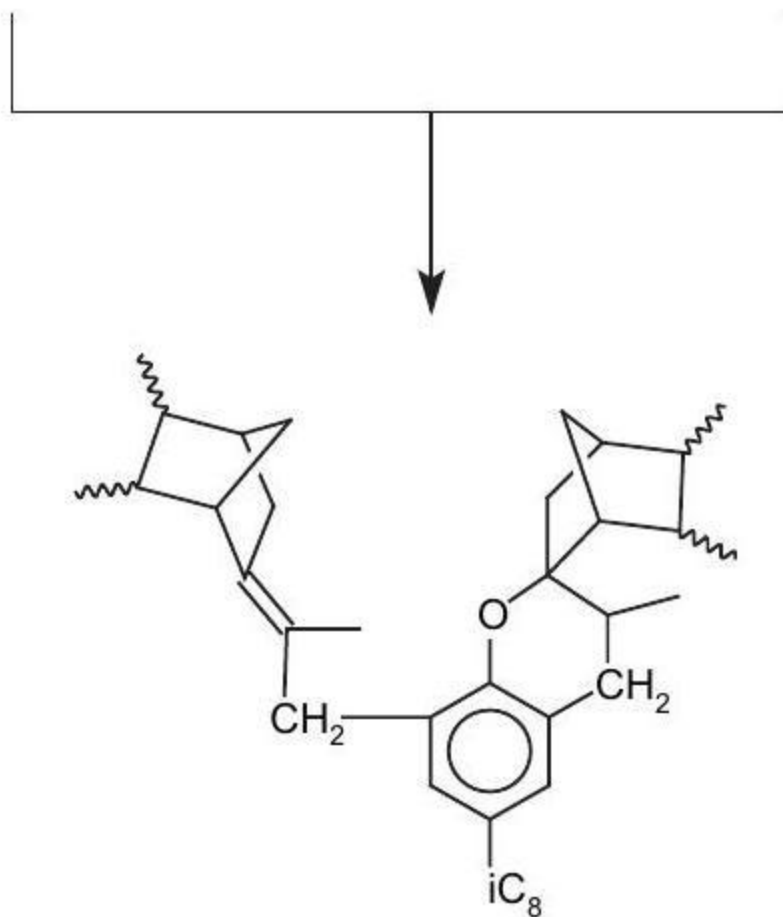
EPDM (model) crosslinking

For details of the set up of the low-molecular-weight model studies, see [5,6]. Salicylic alcohol (SA) was used as a model for the resole. As model olefins were used; 1-hexene (1H), cis and trans-3-hexene (*c/t*3H), 2-methyl-2-pentene (MP), 2,3-dimethyl-2-butene (DMB) - all commercially available - and the norbornene-hydrogenated





ENB-EPDM



methylene/chroman crosslink

Fig. 1. Simplified mechanism of SnCl_2 -activated resole crosslinking of ENB-EPDM [4-6]. products of ENB and dicyclopentadiene (DCPD), viz. ENBH and DCPDH, respectively, the latter two being representative models for EPDM. The reaction products were analysed with gas chromatography with a mass spectrometer detector (GC-MS). The number of hydroxyl groups of the reaction products is determined with GCMS after derivation with *N,O*-bis(trimethylsilyl)acetamide (BSA), allowing the distinction between chroman and methylene-bridged species. Note that GC-MS do not allow full quantification. The level of crosslinking of EPDM polymer was determined as a function of time on an Alpha

Technologies MDR 2000E rheometer at 175°C. For that purpose gum stock compounds were prepared by mixing EPDM with different dienes (DSM Keltan[®] 4802: 4wt. % ENB; Keltan^(R) 820: 4% DCPD; Nordel^(®) 1070: 2% 1,4-hexadiene [HD]; lab-scale EPDM: 4% 5-vinylidene-2-norbornene [VNB]) with resole (Schenectady[®] SP 1045) and SnCl₂ in a 50 cc Brabender kneader at low temperature.

Sampling during dynamic vulcanisation

A Leistritz LSM 30.34 intermeshing co-rotating twinscrew extruder with 29L/D was used at a throughput of 5 kg/h and 200 rpm with a barrel set temperature of 200°C. Tumble-mixed dry blends of milled, oil-extended EPDM (Keltan[®] DE2322: 60 wt. % ethene), PE (Stamylex[®] 2H280 : HDPE), resole and SnCl₂ · 2H₂O were fed to the extruder via the hopper. Samples were taken along the screw axis using a series of sampling devices (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 [8,9]. Dynamic mechanical analysis (DMA) using a Perkin Elmer DMA7 at room temperature in the tensile mode was performed to get a first qualitative impression of the physico-chemical phenomena along the extruder. Extractions using cyclohexane (supplied by Reidel) at room temperature during 48 h were used to determine the rubber gel content as a measure for the crosslink density of the EPDM phase. Transmission electron microscopy (TEM) with a Philips CM200 (120 kV) on cry-coups stained with RuO₄ was used to study the morphology.

Results and discussion

EPDM (model) crosslinking

The GC chromatograms of the model reaction products are quite complex with 20-40 different components, most of them being identified with MS. Three important clusters of reaction products are observed: (i) SA/ olefin condensation products ($M = M_{SA} + M_{olefin} - M_{H_2O}$), (ii) SA dimers and (iii) (SA dimer)/olefin condensation products ($M = M_{SA \text{ dimer}} + M_{olefin} - M_{H_2O}$). A summary of the GC-MS data is given in Table 1 in order of increasing yield of SA/olefin and (SA dimer)/olefin condensation products. It is evident that the yield is primarily dependent on the number of α -alkyl substituents on the carbocation of the intermediate and to a lesser extent on the number of β -alkyl substituents. This fully supports the cationic mechanism as shown in Fig. 1 and falsifies the occurrence of ene addition. Upon addition of the resole-derived benzyl cation to the unsaturation, a cationic intermediate is formed, which has an increased stability upon increasing substitution with electron-donating alkyl groups. For most olefins chroman structures are predominantly formed, which is in agreement with the study by Lattimer et al. [4], but for ENBH and, to a lesser extent, for MP methylene structures are formed too.

The rheometer experiments on resole-crosslinked EPDMs with various dienes confirm the results of the model study. For HD-EPDM, DCPD-EPDM and

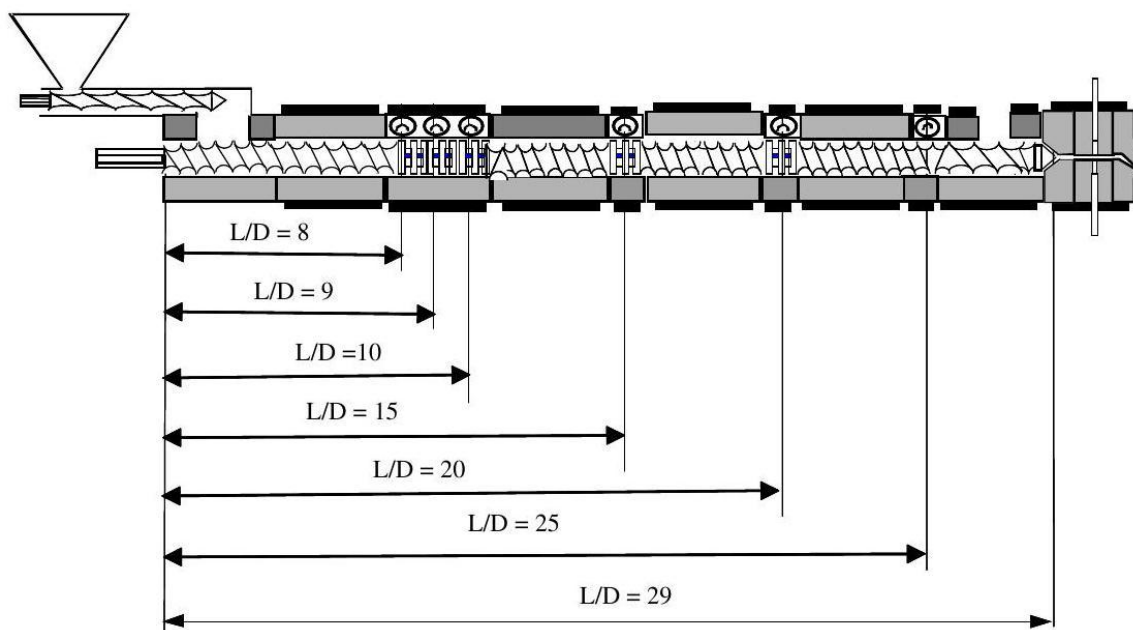


Fig. 2. Extruder lay-out with positions of the sampling devices.

Table
GC-MS results

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Olefin	Number of α, β -substituents ^a	Yield ^b	Selectivity for chroman (%)
1 H	2/2	0.02	95
<i>t</i> 3H	2/3	0.2	90
<i>c</i> 3H	2/3	0.5	95
DCPDH	2/4	0.9	100
MP	3/2	5	75
DMB	3/3	8	95
ENBH	3/5	12	45

^a α, β -Alkyl substituents on cationic intermediates.

^b Indicative value for formation of SA/olefin and (SA dimer)/olefin condensation products.

VNB-EPDM crosslinking hardly proceeds; the rheometer torque ($\Delta S = MH - ML$) remains below 0.3 Nm at 30 min . ENB-EPDM is by far the most reactive, both in terms of crosslinking rate and final crosslink density ($\Delta S = 0.5\text{Nm}$ at 10 min). Thus, the higher the degree of substitution of the intermediate cation, the higher the reactivity. The study by Baldwin et al. on resole crosslinking of 10 EPDMs with different dienes strongly points in the same direction, viz. all dienes which give cationic intermediates with three alkyl

substituents are effectively crosslinked with resole, whereas those with only two alkyl substituents are not [10].

Sampling during dynamic vulcanisation

As a typical example Fig. 3 shows the temperature, the modulus and the rubber gel content as a function of the position on the screw upon dynamic vulcanisation of the PE/EPDM (50/50; w/w) blend. The temperature at $L/D = 8$ is 245°C, which is far above the set temperature of 200°C, which can be attributed to the increase in viscosity due to the crosslinking reaction. At higher L/D the melt cools to 205°C, which is close to the set temperature of this relatively small extruder. In all samples taken at $L/D = 8$ and for some samples at $L/D = 9$, PE pellets could be distinguished visually, even though the melting temperature of HDPE used is

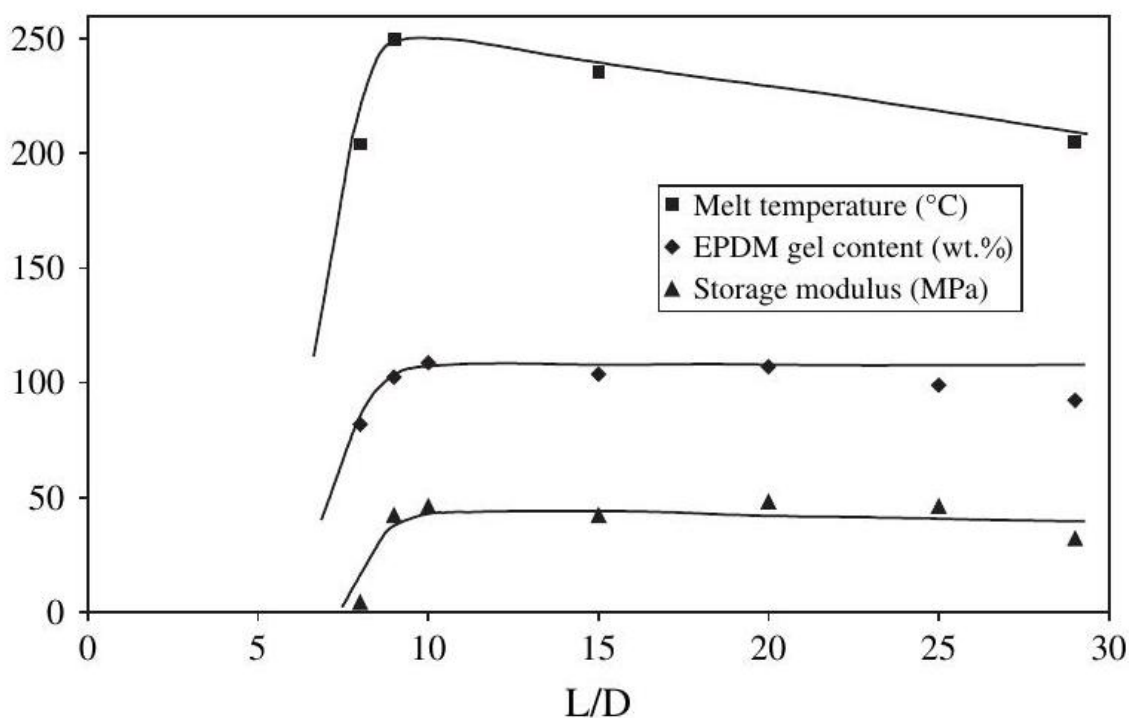


Fig. 3. Temperature, modulus and rubber gel content upon dynamic vulcanisation of PE/EPDM (50/50; w/w) blend along the screw axis. ~ 120°C. This shows that at the beginning of the first kneading zone melting of PE does occur, but is not yet completed, at $L/D = 10$ no pellets could be observed anymore.

TEM allows not only a distinction between the PE (light) and EPDM (dark) phases, but also crystalline PE lamellae are observed (Fig. 4). The interfaces between the PE and EPDM phases are blurred due to PE crystalline lamellae growing into the EPDM phase (Fig. 5), which can be attributed to the high ethene content (60wt. %) of the EPDM. For the PE/EPDM (50/50; w/w) blend at $L/D = 8$ an EPDM matrix with a "woven" PE lamellar structure and small areas ($< 1.5\mu\text{m}$) of irregularly shaped PE domains is seen. At $L/D = 9$ it 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 μ m) with PE lamellae growing inside. Since all PE have molten at $L/D = 9$ and, thus, the lowest dilution of the EPDM phase has been reached, TEM shows a relatively larger amount of PE phase in comparison to $L/D = 8$. 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 [11] it appears that crosslinking is the driving force for phase inversion. The morphology does not change significantly beyond $L/D = 10$. In other words, the final morphology is established as soon as all PE has become molten, i.e. within a few seconds.

The modulus of the PE/EPDM (50/50; w/w) blend as a function of L/D shows a strong increase at $L/D = 8$, levels off at $L/D = 9$ and then decreases again somewhat towards the end of the extruder (Fig. 3). It is known that the modulus of thermoplastic/rubber blends depends first of all on the blend composition (PE/EPDM ratio) and, next, in a more subtle way on the blend morphology (EPDM dispersion in PE matrix or the other way around) and the modulus of the EPDM phase (crosslink density) [12]. The strong increase of the modulus at $L/D = 8$ is probably because of complete melting of the PE phase, which then can fully contribute to the overall modulus. At higher L/D the modulus reaches a constant value, because upon PE melting the morphology is very quickly established and the crosslink density also does not change anymore, as witnessed by TEM and extraction data, respectively. The rubber gel content at $L/D = 8$ is 80%, indicating that crosslinking of the EPDM phase already occurs when the PE phase is not yet fully molten. The increase of the gel content up to $L/D = 9$ shows that the crosslinking reaction continues up to this point. The gel content between $L/D = 9$ and 20 is within error equal to 100%, i.e. all rubber chains have become part of the 3D rubber network.

Similar phenomena are observed for the blends with other PE/EPDM ratios. However, for the PE/EPDM

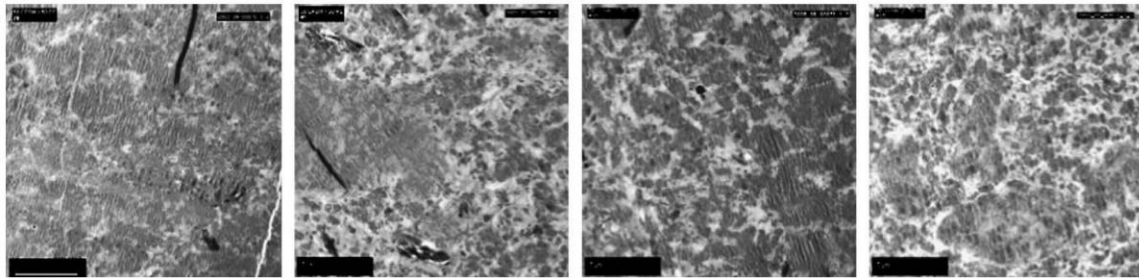


Fig. 4. TEM micrographs of samples taken at $L/D = 8, 9, 10$ and 15 upon dynamic vulcanisation of PE/EPDM blend (50/50; w/w).

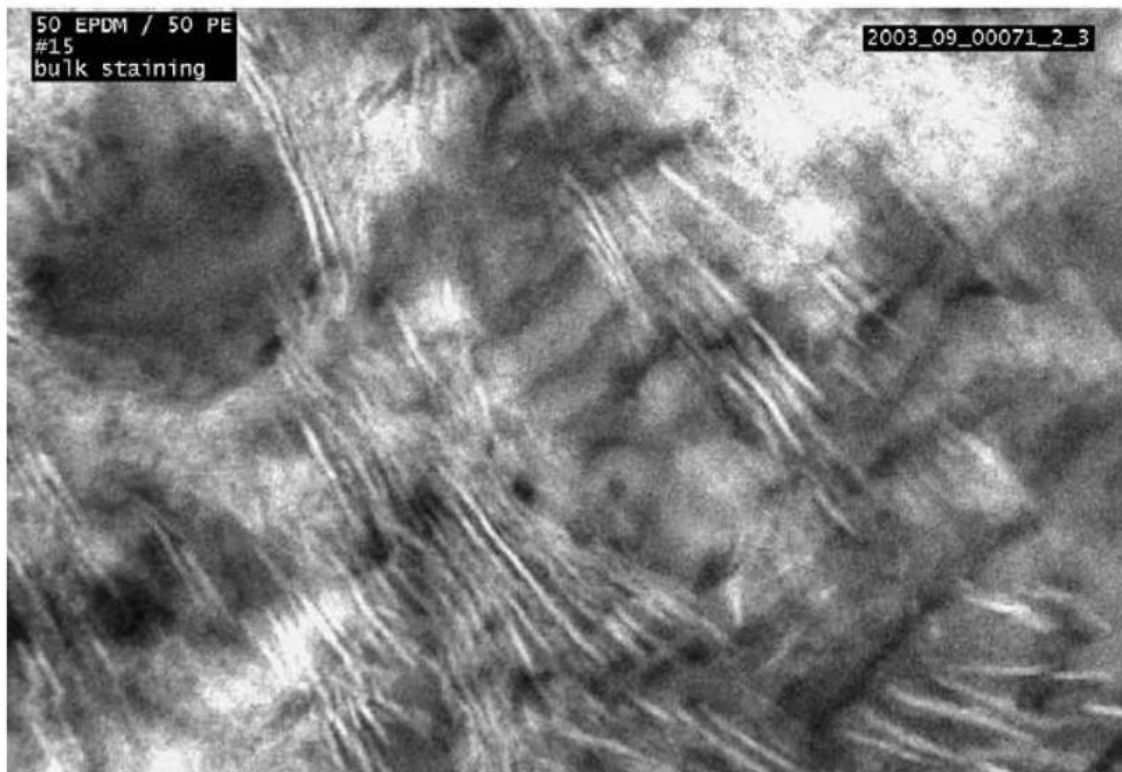
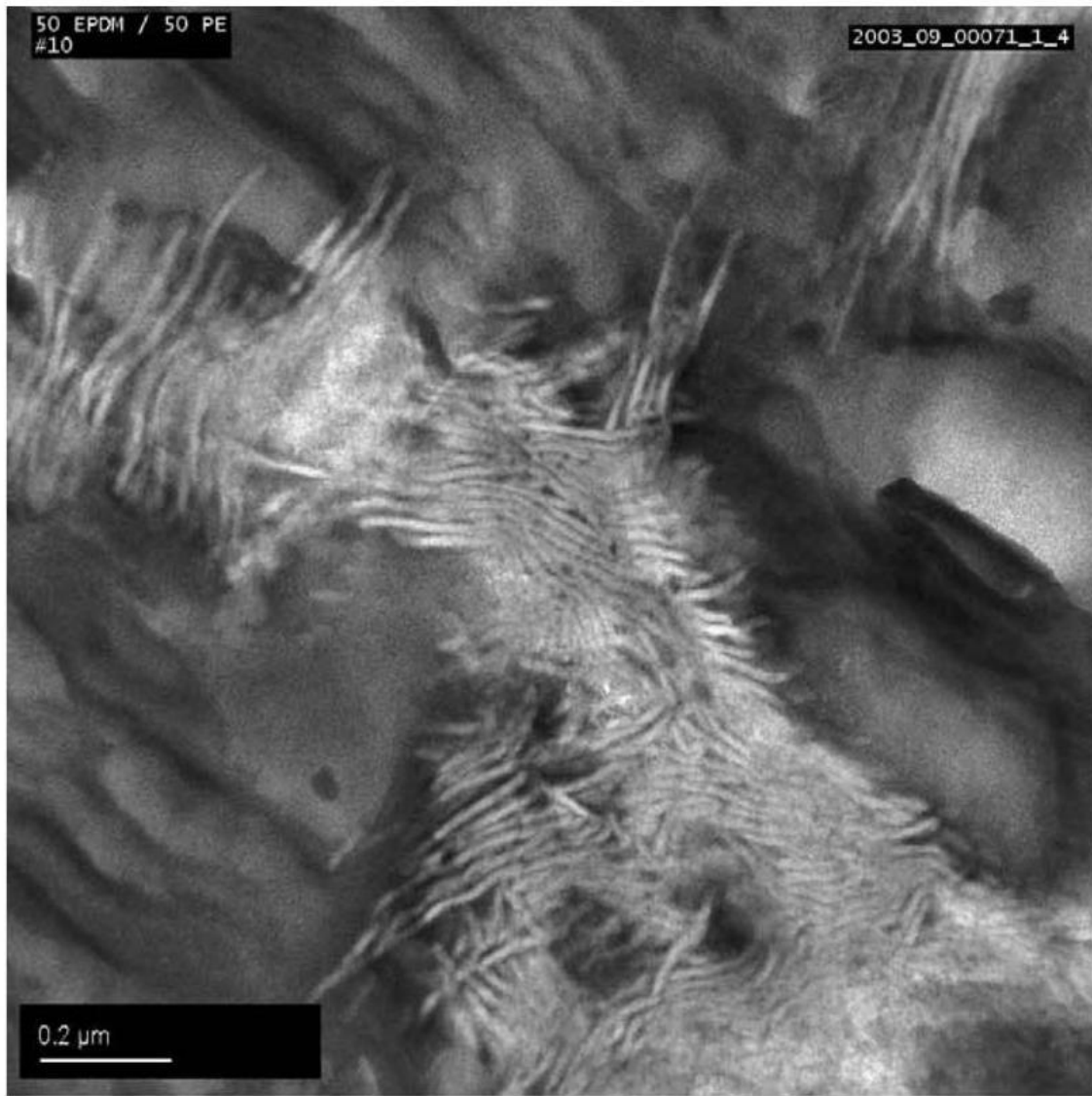


Fig. 5. TEM micrographs of samples taken at $L/D = 10$ and 15 upon dynamic vulcanisation of PE/EPDM blend (50/50; w/w) using higher magnification.

(80/20; w/w) blend the crosslinking reaction proceeds up to $L/D = 25$. This may be explained by the relatively low temperature of this PE-rich blend (200°C) or by the limiting diffusion of the resole crosslinker from the PE-rich phase to the relatively small amount of EPDM phase. For the PE/EPDM (80/20; w/w) blend PE is the continuous phase at all sampling positions, i.e. phase inversion driven by crosslinking does not occur. On the other hand, for the (20/80; w/w) blend the EPDM is always the continuous phase.

Conclusions

Both the low-molecular-weight model studies and the EPDM crosslinking experiments strongly support the cationic character of SnCl_2 -activated resole crosslinking. Increasing the number of alkyl substituents on the cationic intermediate results in increased reactivity for resole crosslinking. During dynamic vulcanisation of PE/EPDM blends using the resole/ SnCl_2 system in the extruder it was shown that crosslinking of the EPDM phase already occurs when the PE phase is not yet fully molten. Upon complete melting of the PE phase the blend very quickly reaches its final morphology. Only for the (50/50; w/w) blend, a transition from continuous via co-continuous to fully dispersed EPDM is observed, which is driven by crosslinking. This shows that dynamic vulcanisation in extruders proceeds quite differently from that in batch kneaders [13], where melting, mixing and crosslinking are separated in time.

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