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Recent Developments for EPDM-Based Thermoplastic Vulcanisates

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Summary: An overview will be given on thermoplastic vulcanisates (TPVs). Like other thermoplastic elastomers, TPVs combine the elastic and mechanical properties of thermoset cross-linked rubbers with the melt processability of thermoplastics. Emphasis will be on general-purpose TPVs, based on resol-cross-linked EPDM/PP/oil blends. The following recent scientific developments will be discussed in detail: resol cross-linking chemistry, extruder dynamic vulcanisation, TPV morphology, oil distribution, TPV elasticity model and TPV rheology. A series of scientific questions and technological problems, which are challenging future TPV developments, will be put forward at the end.

Keywords: cross-linking; dynamic vulcanisation; elasticity; morphology; TPV

Introduction

Like other thermoplastic elastomers (TPEs), thermoplastic vulcanisates (TPVs) combine the elastic and mechanical properties of thermoset cross-linked rubbers with the melt processability of thermoplastics.[1–3] Note that TPVs in contrast to most other TPEs are not based on block-copolymers but on polymer blends. TPVs are produced via dynamic vulcanisation of non-miscible blends of a rubber and a thermoplastic, i.e. the selective cross-linking of the rubber while melt mixing with the thermoplastic. As a result, products are obtained which consist of cross-linked rubber particles dispersed in a thermoplastic matrix, which explains both the elasticity and melt processability of TPVs. 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 ethene/propene/diene (EPDM) terpolymers (saturated main chain, explaining the excellent stability against heat, oxygen and ozone of the corresponding TPVs) and polypropene (PP: high melting point and high crystallinity, explaining the rigidity and the high heat and oil resistance). In addition, commercial TPVs contain large quantities of extender oil in order to improve the melt processability and to lower the hardness. Cross-linking of the rubber phase of TPVs is essential for preventing coalescence and for achieving optimum elasticity, tensile properties and oil resistance. EPDM/PP-based TPVs are traditionally cross-linked with acid-activated resol, but because of the consequent off-white colour and the formation of black specks other cross-linking systems have been developed, such as platinum-catalysed hydrosilane and peroxide/co-agent. White fillers are used to some extent and other additives like anti-oxidants, UV-stabilisers, pigments etc. are used at a low level only. TPVs can be processed in the melt by a variety of techniques, such as extrusion, blow moulding, injection moulding, vacuum forming and calandering. Production scrap and waste after use can be recycled. Typical applications are in the automotive (airbag cover, interior foils and bellows; recently, the first full TPV sealing system was commercialised), building and construction (door and window profiles), industrial (cable and wire, tubing and seals) and

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consumer (soft touch, i.e. grips and handles) markets. TPVs compete with TPEs based on reactor PP/EPM blends and compounds based on styrenic block-copolymers on the low end of the market and with polyester-based TPEs at the high end of the market. Today, TPVs comprise the fastest growing rubber market (~150 kton; ~8%/year), explaining the entrance of a large number of compounding companies into the market in addition to the traditional TPV producers like Exxon/AES, DSM and Mitsui, who have a strong raw materials (read: EPDM) position.

Resol Cross-Linking Chemistry

Although resol cross-linking is hardly used for thermoset elastomers with the exception of butyl rubber, which explains why the cross-linking chemistry is hardly studied, it is the "workhorse" for TPVs. Resols are condensation polymers of an alkylphenol with formaldehyde with dimethylene ether bridges connecting the phenolic units. In the presence of acid activators ether scission occurs and the formed benzyl cations add to the EPDM unsaturation. Low-molecular-weight model compound studies and ^{13}C NMR spectroscopy on resol-cross-linked ^{13}C-labeled EPDM have demonstrated the formation of chroman and/or methylene-bridged intermediates and, eventually, mono-phenolic cross-links (Figure 1).[4–6] EPDM with ethylidene norbornene (ENB) as diene monomer is more reactive towards resol cross-linking than EPDM with dicyclopentadiene (DCPD), 1,4-hexadiene (HD) or vinylidene norbornene (VNB), because of the high degree of substitution of the residual ENB unsaturation and, consequently, the relatively high stability of the cationic intermediate.[7] Most probably, the resol does not react with PP, because of the absence of unsaturation.

Dynamic Vulcanisation along the Extruder Axis

Production of TPVs on large-scale, twin-screw extruders is a rather complicated process with melting, dispersion, dissolution,

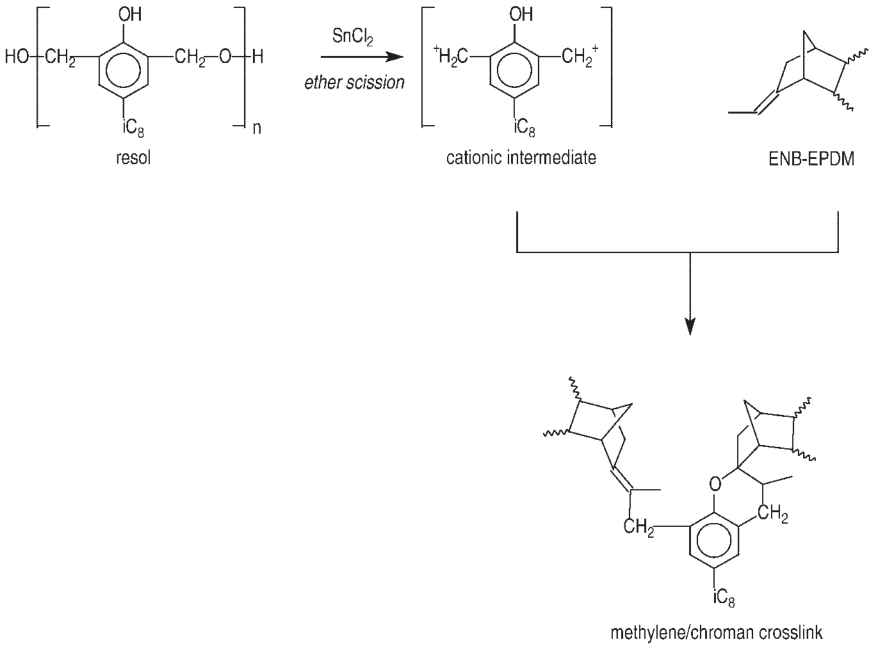

Figure 1.
Resol cross-linking of EPDM.

diffusion, cross-linking and phase inversion occurring and mutually interacting within 1 minute at temperatures between 200 and 300 °C. Until recently, the development of TPVs was a black-box approach with the TPV properties being interpreted in terms of blend formulation (type and content of ingredients) and extrusion process variables (throughput, rpm, set temperatures etc.), but without true insight in the physico-chemical phenomena occurring inside the extruder. Although several studies have been performed in the past using batch kneaders, these are clearly not representative for continuous extruder operation. An extruder equipped with a series of sampling devices, allowing fast and representative collection of melt samples for further off-line analysis,[8] was used to study the dynamic vulcanisation of TPVs based on EPDM, high-density polyethene (HDPE) and oil.[9] It was shown that the melt temperature increases very rapidly in the first kneading zone (especially for high EPDM levels because of viscous dissipation: ~280 °C), but that melting of the HDPE pellets lacks behind (Figure 2). Actually, the EPDM chains have already formed a rubber network (the rubber gel content is close to 100%) before melting of the HDPE is completed. Still, a transition of EPDM from the continuous phase at $L/D = 8$ via a co-continuous phase at $L/D = 9$ and 10 to a dispersion at $L/D \geq 15$ is observed along the screw axis for a 33/33/33 (w/w/w) EPDM/HDPE/oil TPV, i.e. phase inversion of EPDM is driven by a combination of completed melting of the HDPE phase and continued cross-linking of the EPDM phase.

Morphology

The morphology of TPVs is usually discussed in terms of a cross-linked rubber phase dispersed in a thermoplastic matrix, which explains the melt processability of TPVs in a satisfactory way. However, it is noted that the interpretation of transmission electron microscopy (TEM) images of TPVs is not that straightforward, since i) the oil redistributes when the sample is quenched from the melt and the PP partly crystallises, ii) the TEM cryo-coupes are usually quite thick in comparison to the rubber particle size (~100 vs. ~2 μm), iii) it is often quite difficult to distinguish between rubber particles that overlap or make contact versus true co-continuity, especially in the case of soft TPVs with high rubber levels and their characteristic, irregularly shaped domains, and iv) TPVs are usually quite heterogeneous (large variation of domain shape and size throughout a sample) (Figure 3). Recently, a series

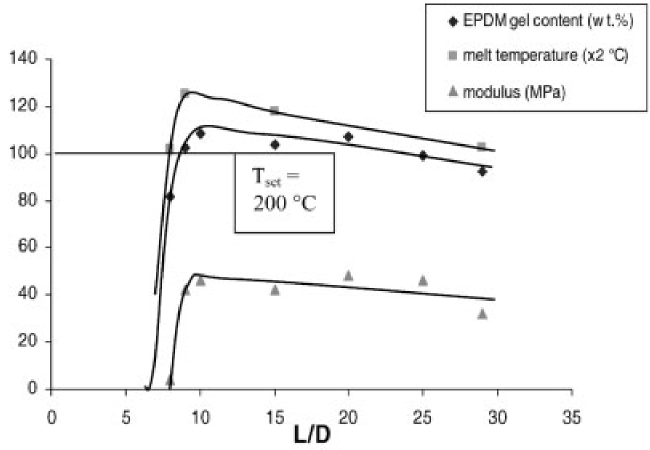

Figure 2.
Evolution of melt temperature, modulus (at 25 °C) and EPDM gel content as a function of screw length for EPDM/HDPE/oil (33/33/33; w/w/w) TPV.

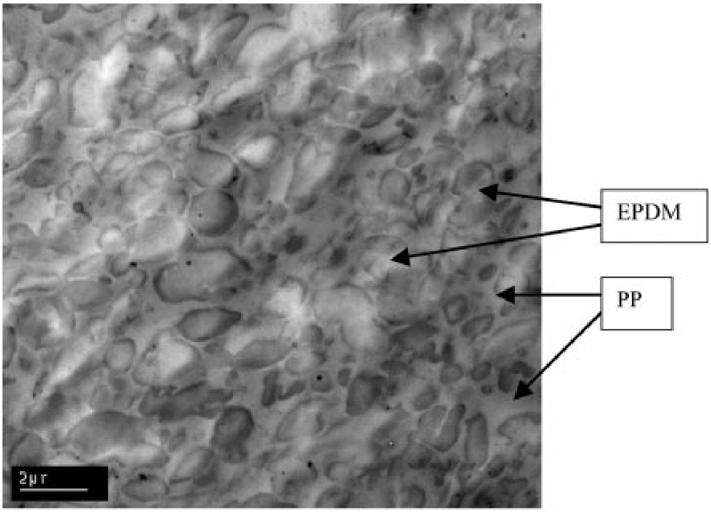

Figure 3.
Typical TEM image of EPDM/PP/oil-based TPV.

of TEM images has been obtained by varying the angle of view, which was subsequently converted into 3D images using image analysis software. It was shown that most rubber particles were separated in 3D space, whereas the traditional 2D images showed co-continuous morphologies.[10]

Oil Distribution

Processing oil is used in large amounts in TPVs and their presence and distribution in the EPDM and PP phases will affect the properties both in the solid state and the melt. An extensive study using dynamic rheology and dielectric spectroscopy has been quite informative.[11,12] In solid TPVs the oil resides in the EPDM dispersion, but also in the amorphous PP phase with a PP/EPDM distribution coefficient that is independent of the composition and somewhat below unity ($\sim$0.8). In the melt the oil distribution coefficient is mainly below unity, but increases upon increasing the oil and/or decreasing PP contents, probably because the cross-linked EPDM phase is limited in its oil uptake. The processing oils which are usually used are hydrocarbons with an EPM-like structure,[13] explaining the slight preference for the EPDM phase.

Elasticity Model

In a way, the elasticity of TPVs has always been something of a mystery: how to explain the elasticity of a TPV when the cross-linked rubber phase is dispersed ? 2D Fourier Transform -Infrared studies have shown that especially the EPDM domains, but also the PP crystallites and the PP amorphous phase orient upon elongation.[14,15] Upon relaxation the EPDM domains relax to some extent only, which is consistent with the permanent macroscopic deformation of the TPV during the same experiment. Atomic Force Microscopy studies have shown that upon TPV elongation the thin thermoplastic layers at the equator of the rubber particles are subject to plastic yielding and that upon TPV relaxation they are drawn back by the elastic rubber domains and fold back to a harmonica-like structure (‘‘buckling’’) (Figure 4).[16,17] This behaviour has been validated with some finite-element analyses[18] and also explains why TPVs behave fully elastic, i.e. no permanent set, during subsequent cycles.

Rheology

The melt processability of TPVs is ‘‘easily’’ understood, because the thermoplastic

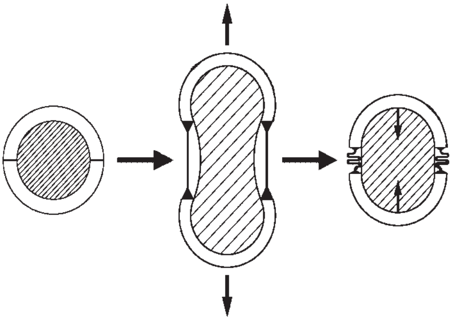

Figure 4.
TPV elasticity model showing yielding of PP layers upon TPV deformation and "buckling" upon TPV relaxation, explaining permanent deformation in the first cycle.

phase forms the matrix. However, using dynamic mechanical analysis, creep experiments and capillary rheology it was shown that this is a too simplified picture (Figure 5). At low shear stress the system behaves like an elastic network of rubbery particles having a yield stress.[19] At intermediate stress TPVs behave like a PP melt filled with rubber particles. At high stress the rheological properties of the PP matrix become dominant. During melt processing deformation occurs only in those regions, where the local shear stress is higher than the yield stress of the rubbery network, and the rubber particles will "roll" over each other. Plug flow will occur if the local shear stress is below the yield stress.

Issues to be Addressed

Both the process of TPV production and the structure-properties relationships of the TPVs thus formed are still not fully understood. As a result, TPV products have been developed in a somewhat empirical fashion. More insight is required to optimise the dynamic vulcanisation process, to exploit the TPVs to their maximum extent and to expand their field of applications. The following scientific and technical issues should be addressed:

- dynamic vulcanisation: the thermodynamics and kinetics of melting, dispersion, cross-linking and morphology development should be studied as a function of time in batch mixers and along the screw axis in industrial extruders; in addition, models should be developed combining all these phenomena;
- morphology: more understanding of the parameters affecting the final TPV morphology in the melt is required; in addition, the morphological changes that

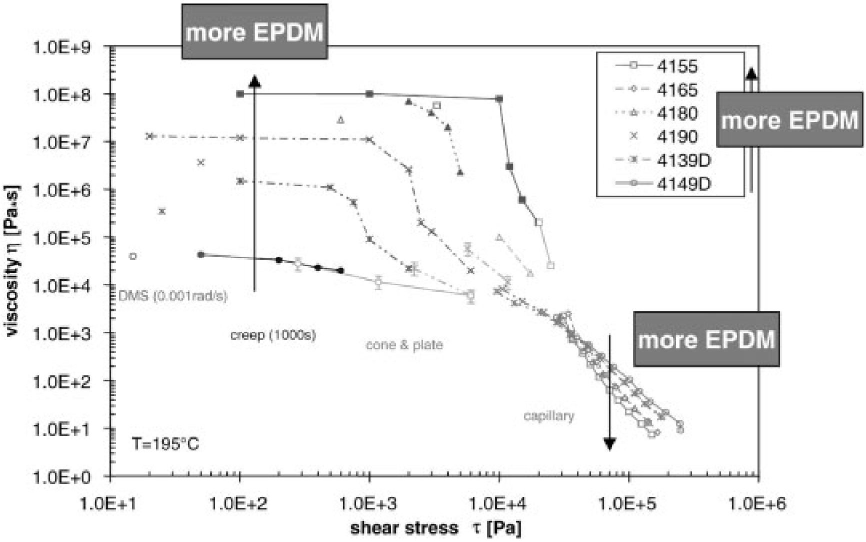

Figure 5.
Melt viscosity versus shear stress at 195 °C for TPVs with decreasing hardness, i.e. increasing EPDM/PP ratio.

occur upon cooling down (PP crystallisation, redistribution of oil and swelling of rubber domains) should be investigated; an intriguing question is why TPVs are characterised by such irregular rubber domains;
- rheology: more detailed studies are needed to understand the fundamentals of the rheology of the EPDM-rich PP blends; for example: how to explain the unexpected processability of TPVs with a co-continuous rubber phase ?
- elasticity: increasing the cross-link density results in enhanced TPV elasticity, but only to a certain level; how can the elasticity be further improved to the level of thermoset elastomers ? in addition, how can the hardness of TPVs significantly be reduced below 40 ShA without sacrificing on melt processability ?

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