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Polymer Degradation and Stability 90 (2005) 340–345

Polymer Degradation and Stability

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

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Received 21 October 2004; received in revised form 1 April 2005; accepted 4 April 2005

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

1. 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

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doi:10.1016/j.polymdegradstab.2005.04.050

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 polypropene (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 μm) 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 (~10%/year) of TPVs. PP/EPDM-based 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-2-norbornene (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 ethene-containing polyolefins (like plastomers), allowing an extension of this work in future studies.

2. Experimental

2.1. 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

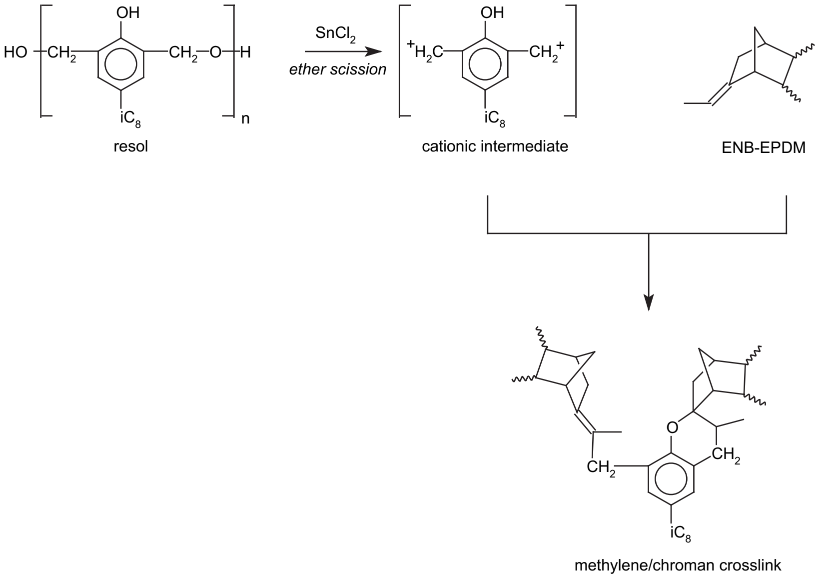

Fig. 1. Simplified mechanism of $SnCl_2$-activated resole crosslinking of ENB–EPDM [4–6].