

Network Density and Diene Conversion in Peroxide-Cured Gumstock EPDM Rubbers. A Solid-State NMR Study

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Summary: Peroxide-cross-linked EPM and EPDM rubbers have been investigated with magic-angle spinning ^1H NMR spectroscopy and static ^1H NMR relaxometry. The results yield a consistent nanoscale picture of the chemical and physical network properties in terms of chemical cross-links formed via macro-radical combination, chemical cross-links formed via addition to the double bonds, and physical cross-links resulting from chain entanglements.

Keywords: chain entanglement; cross-linking; ^1H NMR T_2 ; MAS ^1H NMR; nanoheterogeneity; rubbers

Introduction

Peroxide curing of elastomers is increasingly used instead of the traditional sulfur vulcanization. For EPDM terpolymers, synthesized from ethylene and propylene, as well as a small amount of a diene, like 5-ethylidene-2-norbornene (ENB), improved thermal stability and good properties of the networks over a large temperature range are obtained via peroxide cure. Since sulfur vulcanization requires double bonds, the only option for cross-linking of fully saturated polyolefins, such as polyethylene and poly(ethylene-co-propylene) (EPM) is peroxide curing. Although insight has been gained in the last decade in the chemistry of peroxide curing and progress has been made in the characterization of the resulting networks, there are still many questions. Figure 1 shows the generally accepted scheme for peroxide curing of EPDM.^[1]

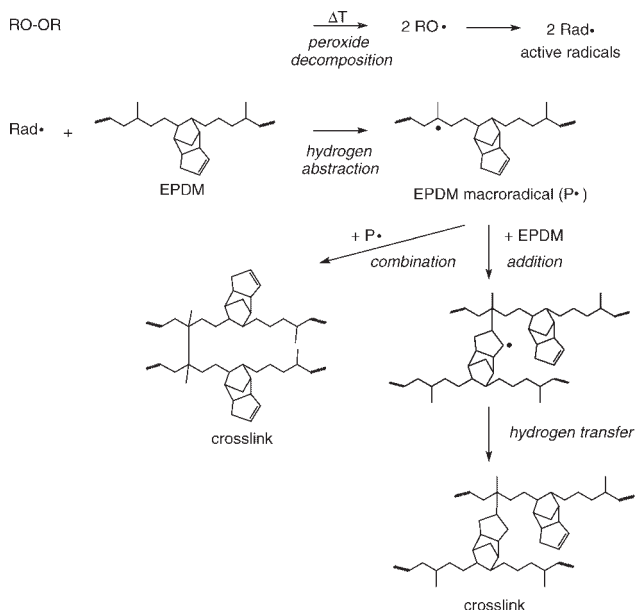
Peroxide cross-linking is initiated by temperature-induced decomposition of the peroxide into highly reactive radicals, which quickly abstract a hydrogen atom from the polymer forming EPDM macro-radicals. This step is kinetically determined and the relatively few diene comonomers in EPDM hardly play a role at this stage. The cross-linking may then proceed via two routes: (1) combination of two EPDM macro-radicals or (2) addition of a macro-radical to a diene comonomer followed by hydrogen transfer. The combination reaction actually terminates the free-radical reaction chain. The susceptibility of the residual diene unsaturation towards addition of the macro-radical determines its contribution to the final degree of cross-linking.

The aim of the study presented in this paper is to determine the contribution from the combination and addition route to the chemical cross-link density. This is not an easy task, since polymer networks generally have complex topologies. In addition to chemical cross-links, their mechanical properties are also influenced by physical cross-links which arise from trapped chain entanglements.^[2] Below we report results from a study on EPM and EPDM copolymers cross-linked with various amounts of

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**Figure 1.**

Scheme for peroxide curing of EPDM.

peroxide by means of high-field magic-angle spinning ^1H NMR spectroscopy and low-field ^1H NMR relaxometry. The obtained data permit a comparison of the degree of ENB conversion with the enhanced cross-link density attributed to ENB termonomers in EPDM.

Experimental

Materials

Two amorphous EPM and EPDM co- and terpolymers were obtained from DSM. The molar compositions and molecular weights are specified in Table 1.

For a systematic investigation of peroxide cross-linking, the two polymers were mixed in an open mill with various amounts

of bis(*t*-butylperoxy-*i*-propyl)benzene, commercially available as Perkadox 14–40 (AKZO Nobel): 1.25, 2.5, 5 and 10 parts per hundred rubber parts (phr). Samples were fully cross-linked in a hot press at 175 °C.

MAS ^1H NMR Spectroscopy

Magic-angle-spinning (MAS) ^1H NMR spectra were recorded on a Bruker DMX500 spectrometer with a ^1H resonance frequency of 500 MHz. A 4-mm MAS probe-head was used with a sample-rotation rate 12.5 kHz. The spectra were obtained by means of single-pulse excitation with a 90° pulse of 5 μs and recycling delay time of 5 s.

Static ^1H NMR Transverse-Relaxation Measurements

The proton transverse magnetization decays were measured on a Bruker Mini-spec MQ spectrometer at a proton frequency of 20 MHz. This spectrometer was equipped with a BVT-3000 variable temperature unit. The decay of the transverse magnetization was measured with the Hahn-echo pulse sequence, 90° – τ – 180° – τ – acquisition, where $\tau \geq 35 \mu\text{s}$. An echo

Table 1.

Composition and molecular weight of the EPM and EPDM co- and terpolymer.

	EPM	EPDM
Ethylene (wt-%)	49	54
Propylene (wt-%)	51	44
ENB (wt-%)	0	2
Molecular weight (kg mol^{-1})	150	250

signal is formed after the second pulse in the sequence with a maximum at time 2τ after the first pulse. By varying the pulse spacing in the sequence, the amplitude of the transverse magnetization, $A(2\tau)$, is measured as a function of time 2τ . The resulting decays were decomposed with a home-built software into two components with a Weibull and exponential shape, respectively.^[3,4]

Results and Discussion

The Conversion of ENB by MAS ^1H NMR Spectroscopy

MAS ^1H NMR spectra of EPDM are dominated by the signals of aliphatic protons around 1 ppm. At strong magnification of vinyl proton signals from ENB are visible between 4 and 6 ppm, as well as the aromatic protons of the bis(t-butylperoxy-isopropyl)benzene) between 7 and 9 ppm. Comparing the ^1H NMR spectra of e.g. EPDM with 2% ENB and 1.25 phr peroxide before and after cross-linking suggests that the peroxide has been largely converted, whereas only half of the residual ENB unsaturation has disappeared.

Determination of the Network Density by Static ^1H NMR Proton T_2 Measurements

^1H NMR transverse relaxation in polymers at temperatures well above T_g is a measure for large spatial scale motion of polymer chains, or more precisely the residual anisotropy of the polymer backbone at the millisecond timescale. Rigid polymers in the crystalline or glassy state have fast transverse relaxation with short characteristic times T_{2H} . In contrast, for highly mobile polymer chains in rubbers the relaxation is slow and the corresponding T_{2H} values long. At temperatures far above T_g the chain motion in cross-linked polymers is limited by network junctions causing a high-temperature plateau on the temperature dependence of T_{2H} . The smaller the chain length between cross-links, the more restricted the chain motions are, thus the larger the anisotropy of chain

motions and the shorter the T_{2H} value at the plateau, T_{2H}^P . The high-temperature limiting value T_{2H}^P is therefore a measure for the cross-link density. For ideal polymer networks, a direct relation exists between the cross-link density and T_{2H}^P value.^[3,5] In practice, however, one has to deal with network defects, such as dangling chain-ends, chain loops and sol. Careful analysis of the T_{2H} decay curves often allows separating the relaxation behavior of the network defects from that of network chains.^[3,4]

In order to determine the cross-link density we have recorded T_{2H} decays at 90 °C ($T_g \sim -55$ °C) for peroxide-cross-linked EPM and EPDM cured with various amounts of peroxide. The resulting relaxation curves were decomposed into a fast and a slow decaying component with a Weibull and exponential shape respectively. In general, a two component-like shape of the T_2 decay results from (1) the complex origin of the transverse relaxation for polymer chains and (2) network heterogeneity and network defects.^[4–6] The average relaxation time, T_2^{av} , can be related to volume-average cross-link density, where $T_2^{av} = f_{\text{short}}(T_2^{\text{short}})^{-1} + f_{\text{long}}(T_2^{\text{long}})^{-1}$ and the sum of fractional amplitudes of the relaxation components $f_{\text{short}} + f_{\text{long}} = 1$. The volume-average cross-link density, which is composed of chemical cross-links, temporary and trapped chain entanglements, is calculated for EPM and EPDM vulcanizates as described previously.^[2]

The resulting plot of the cross-link density for the EPM and EPDM copolymer at various initial peroxide contents is shown in Figure 3. Up to 10 phr, the cross-link density increases linearly with the amount of peroxide used. The trendlines do not pass through the origin, indicating that even without chemical cross-links the rubbers still behave as a cross-linked network at the time scale of the NMR method, i.e. in the order of milliseconds or longer. This is caused by temporary chain entanglements, which restrict the long spatial scale mobility of the polymer chains. Assuming that the overall density of chain entanglement is not

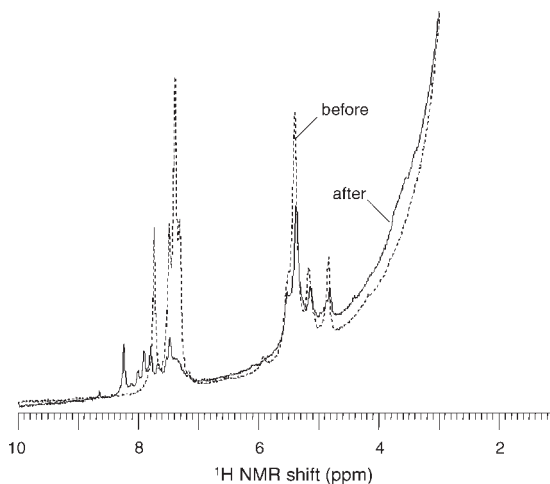


Figure 2.

12.5 kHz MAS ^1H NMR spectra of EPDM (2% ENB, 5 phr peroxide) before and after peroxide cross-linking, reflecting a ENB conversion of $\sim 50\%$.

significantly altered by the presence of ≤ 10 phr peroxide, the density of *chemical* cross-links can be estimated from the difference between the effective cross-link density with and without the peroxide.^[2] At e.g. 5 phr peroxide the respective chemical-cross-link density in EPM and EPDM is 0.08 and 0.17 mol/kg. Since in EPM no unsaturated termonomers are present, all peroxide cross-linking should proceed via

the combination of macro-radicals (cf. Figure 1). If by assumption the combination route in EPDM is equally efficient as in EPM, the twice higher chemical-cross-link density in EPDM with 2% ENB suggests that half of the peroxide cross-linking occurs via the addition route. At an initial peroxide level of 5 phr this would correspond to an ENB consumption of ca. 0.09 mol/kg. Compared to the initial ENB

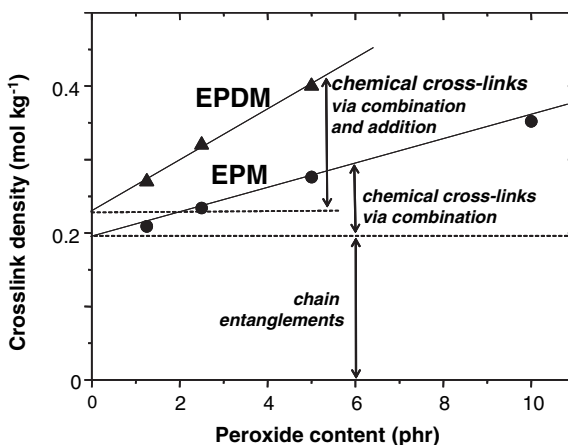


Figure 3.

The total effective network density for EPM (without ENB) and EPDM with 2% ENB versus peroxide content. Since no chemical cross-links are formed without peroxide, the intercept of the plot reflects the apparent entanglement density. The entanglement densities of EPM and EPDM are not the same, probably because they have different conformational states as a result of their different chemical composition.

content of 0.16 mol/kg, this represents a conversion degree of ca. 57%, which is consistent with the above discussed 50% decrease of the olefinic signals in the MAS ^1H NMR spectrum (Figure 2). This agreement between the two different NMR approaches provides strong evidence for the validity of our interpretation.

Along the same lines, we are currently investigating EPDM terpolymers with different ENB levels, and implementing novel ^1H Double-Quantum NMR techniques^[8,9] to further improve our analysis.

Conclusions

The use of ^1H NMR spectroscopy and T_2 relaxation analysis allows discrimination of three different contributions to the total cross-link density in peroxide cured EPM and EPDM vulcanizates, i.e. chain entanglements, and chemical cross-links originating from combination of macro-radicals and from addition of macro-radicals to the double bonds of the diene monomers. MAS ^1H NMR spectroscopy yields direct information about the ENB conversion as a result of peroxide cross-linking, whereas from ^1H NMR T_2 relaxation analysis the

total cross-link density can be determined and the contribution from chain entanglements evaluated. The ENB conversion estimated from the ^1H NMR spectra is consistent with the density of the cross-links formed via the addition route, as obtained from the proton T_2 analysis.

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