Chapter 13

Chain Mobility in Crosslinked EPDM Rubbers. Comparison of \(^1\)H NMR \(T_2\) Relaxometry and Double-Quantum \(^1\)H NMR

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\(^1\)H NMR transverse relaxation and double-quantum (DQ) build up have been compared for a series of EPDM grades crosslinked with different amounts of sulfur or peroxide. The modulus at 100% elongation of the same EPDM samples correlates linearly to the effective transverse-relaxation and DQ build-up rate, suggesting that both rates are proportional to the total network density caused by chain entanglements and crosslinks. For none of the rates, however, the linear trends of sulfur- and peroxide-crosslinked EPDM coincide. This suggests that sulfur- and peroxide-crosslinked EPDM networks are qualitatively different, which is confirmed by different distributions of residual dipolar coupling constants.

Introduction

Elastomers, like ethylene-propylene copolymers (EPM) or ethylene-propylene-diene terpolymers (EPDM), are crosslinked to improve their
performance, such as elasticity, tensile strength and resistance to solvents. Traditionally, sulfur vulcanization is applied, which, however, suffers from S-S bond cleavage at elevated temperatures. Peroxide cure results in more thermally stable networks (1). The mechanical properties of the rubber networks are not only determined by the chemical crosslinks but also by the physical entanglements between the polymer chains. Macroscopic characterization techniques, like mechanical measurements, yield overall information of the crosslink density. Solid-state $^1$H NMR gives a more detailed picture of the network density and the heterogeneity thereof in different parts of the rubber network. The higher the density of crosslinks and entanglements, the more restricted the polymer-chain mobility and thus the higher the residual proton dipole coupling, as reflected in the $^1$H NMR lineshape, transverse ($T_2$) relaxation (2, 3) and the build up of double-quantum coherence (4, 5) For rigid non-oriented polymers the orientation dependence of the dipolar $^1$H-$^1$H coupling leads to broad $^1$H NMR lineshapes. In mobile polymers the dipole coupling is partly averaged by chain motions, which are fast compared to the static dipole coupling constant $D_0$ ($\sim 10^4$ Hz). Since in a real mobile polymer the cumulative rotational effect of chain motions is not isotropic, a residual dipole coupling (RDC) with reduced coupling constant $D$ remains. This is reflected in the NMR spectrum by a narrower lineshape. The less restricted the chain motion, the narrower the lineshape.

Although, in principle, the linewidth in a $^1$H NMR spectrum can be used as a source of information about chain mobility, it tends to be polluted by other linebroadening mechanisms, like chemical-shift heterogeneity and magnetic susceptibility. For mobile polymers with narrow $^1$H NMR lines, such as weakly crosslinked elastomers above $T_g$, this inhomogeneous broadening can significantly spoil the interpretation. Therefore as an improved approach, $^1$H NMR transverse relaxation, reflected in Hahn-echo decays, is often investigated for characterization of chain mobility in polymer networks (2, 6–8). By reflecting the overall anisotropy of sub-millisecond polymer motions, the $T_2$ relaxation time for elastomer networks is sensitive to the conformational mean position of the network chains, which is affected by the presence of chemical and physical network junctions. Long network chains undergo less restricted motions, resulting in strongly averaged dipole couplings and thus long $T_2$ values. Short network chains have short $T_2$ relaxation times.

For ideal polymer networks, a direct relation exists between the crosslink density and proton transverse relaxation far above the glass transition $T_g$, where chain mobility is fast and only restricted by the network junctions (6, 7, 9, 10). In practice, however, one has to deal with network defects, such as dangling chain-ends, chain loops and sol. Careful analysis of the $T_2$ decay curves often allows separating the relaxation behavior of the network defects from that of network chains. The theory of the transverse relaxation in crosslinked rubbers is based on the submolecule concept of network chains with both ends fixed in a laboratory system of coordinates regardless of the origin of the junctions. By assumption, the network chain consists of a number of statistical segments between the network junctions. The Kuhn and Grün model of freely jointed chains is used to calculate the conformational mean of the chain function in elastomers with low crosslink density (network chains obeying the Gaussian
chain statistics). The weight average molar mass of polymer chains between neighboring network junctions in crosslinked elastomers can be calculated from the transverse relaxation rate at the high temperature plateau.

$^1$H NMR $T_2$ relaxation of a polymer reflects the overall anisotropy of chain motions that are fast on the sub-millisecond timescale. It is also particularly sensitive to intermediate motions at the millisecond timescale. If intermediate motions are significantly present in the broad range of timescales governing polymer dynamics, the validity of standard theories relating network density via the anisotropy of sub-millisecond motions to $T_2$ relaxation can be questioned (11). As further improvement, Double-Quantum (DQ) NMR has therefore been advocated (5). The same residual dipolar coupling that underlie $T_2$ relaxation can also be used to generate double-quantum coherences in hydrogen spin pairs. By a strategic combination of NMR signals, the DQ NMR technique is able to distinguish between a coherent build-up of double-quantum coherence, and incoherent loss of transverse magnetization. The DQ build-up rate measured in this way only reflects the residual dipole coupling averaged by the fast chain motions. The effect of intermediate motions ends up in the incoherent part and is not included in analysis in terms of network density. The advantage is that the technique zooms in on the anisotropy of fast motions, which is more correctly analyzed by use of the submolecule theories for rubber networks. In the previous investigation (12–14) of chemical structures and density of crosslinks in peroxide-cured EPDM the main focus was on MAS $^1$H and $^{13}$C NMR spectroscopy and static $^1$H NMR $T_2$ relaxometry. In the present paper we want to compare the outcome of $T_2$ relaxometry and DQ build-up measurements for a series of sulfur- and peroxide-crosslinked EPDM grades, and get a more detailed picture of different network distributions caused by the different crosslinking method.

**Experimental Section**

**Materials**

Amorphous EPM and EPDM co- and terpolymers with 0, 2, 4.5 and 9 wt.% ethylidene norbonene (ENB) and respective ethylene content of 49, 54, 52, 48 wt.% were obtained from DSM Elastomers (K3200, V2727, K4802 and K4703). For the systematic $T_2$ relaxometry study of peroxide crosslinking illustrated in Fig. 1, the EP(D)M grades were cured with 1.25, 2.5, and 5 parts per hundred rubber parts (phr) of bis (t-butylperoxy-i-propyl)benzene), commercially available as Perkadox Px-14-40 (AKZO). The combined $T_2$ relaxometry and double-quantum build-up study described in this chapter was applied to five sulfur-vulcanized EPDM systems with 9 wt.% ENB and varied sulfur levels of 0.7, 0.8, 1.2, 5 and 4.5 phr (as well as accelerating additives), and three peroxide-cured EPDM systems with peroxide levels of 1.25, 2.5 and 5 phr and co-varying ENB content of 0, 2 and 9 wt.% ENB, respectively. Further sample-preparation details can be found elsewhere (2, 13).

\(^1\)H NMR

\(^1\)H NMR Transverse Relaxometry

\(^1\)H NMR transverse relaxation was measured by use of the Hahn-echo pulse sequence on a Bruker Minispec MQ spectrometer at a proton frequency of 20 MHz. All decays of the transverse magnetization were obtained and analyzed as described previously (6, 7). Briefly, the Hahn-echo decays were decomposed into three relaxation components with in total 6 fit parameters. To avoid overfitting artefacts only the weight-average relaxation rate \(R_2 = 1/T_2\) of the three components was used for the analysis. According to submolecule model of crosslinked rubbers, the effective relaxation rate \(R_2\) in a polymer network is proportional to the average density of network junctions resulting from quasi-permanent chain entanglements and chemical crosslinks. For EPDM the proportionality constant, which depends on the molecular structure and the flexibility of the polymer chains, equals 0.285 mmol s kg\(^{-1}\).

Multiple-Quantum \(^1\)H NMR

\(^1\)H multiple-quantum NMR measurements were performed on a Bruker Minispec mp20 at 90 °C. The adjustment procedures and pulse sequences applied are specified in references (5) and (15).

Results and Discussion

\(^1\)H NMR Transverse Relaxometry

Fig. 1a shows the effective transverse relaxation rate \(R_2 = 1/T_2\) of ethylene-propylene copolymer (EPM) and three ethylene-propylene-diene terpolymer (EPDM) grades, respectively, containing 2, 4.5 and 9 wt% of 5-ethylidene-2-norbonene (ENB) as the third monomer, crosslinked with a varied amount of peroxide. The transverse relaxation rate is proportional to the underlying total rubber network density, i.e. the sum of physical entanglements and chemical crosslinks. Thus, for the given proportionality constant determined by the molecular structure and flexibility of the polymer chains, the relaxation rates can be directly translated into network densities (Fig. 1a, vertical axis righthand side). Up to 5 phr peroxide the network density of the crosslinked EP(D)M grades depend linearly on the peroxide level. Extrapolation to zero peroxide yields similar chain entanglement densities in the range 0.20 - 0.24 mol/kg. This is consistent with the outcome of previous NMR and other studies (2, 16). The higher network density after peroxide crosslinking is caused by the formation of chemical crosslinks. The presence of ENB monomers in the EPDM chain leads to enhanced crosslink formation. These ENB monomers are involved in crosslinking reactions via addition of macro-radicals to the pendant ENB unsaturation and via combination of ENB-derived allyl radicals (14).
Figure 1. (a) $^1$H NMR transverse relaxation rates $R_2 = 1/T_2$ and network density of EP(D)M grades with 0, 2, 4.5 and 9 wt.% ENB crosslinked with varied initial peroxide content. The three peroxide-cured EP(D)M systems that have also been studied with DQ NMR are encircled. (b) Correlation of rheometer torque difference of the EPM and EPDM grades with total network crosslink density derived from $^1$H NMR relaxometry.

Figure 1b shows the excellent correlation between separately measured rheometer torque difference for the complete set of peroxide-cured EPM and EPDM grades and the total network density determined from NMR. Apparently, the network density calculated from $T_2$ relaxometry has a real physical meaning and is relevant for the macroscopic properties of the crosslinked EPDM rubbers.

Multiple-Quantum $^1$H NMR

The left side of Fig. 2 shows DQ build-up curves of EPDM with 9 wt.% ENB and crosslinked with sulfur amounts of 0.7, 1.5 and 4.5 phr. The results are compared with the DQ build-up curves of three peroxide-cured EP(D)M systems with 0, 2 and 9 wt.% ENB and respective peroxide levels of 1.25, 2.5 and 5 phr (Fig. 2, right). The three peroxide-cured systems represent a typical selection across the set of EP(D)Ms already characterized with $T_2$ relaxometry (encircled points in Fig. 1a). Both the DQ build up $S_{DQ}$ and the reference decay $S_{ref}$ were recorded. Fig. 2 shows the $S_{DQ}$, $S_{ref}$ and the sum $S_\Sigma = S_{DQ} + S_{ref}$ as a function of evolution time $t_{DQ}$ (sum of excitation and reconversion time). For comparison the curve fits to the Hahn-echo decays of the same samples are also shown. $S_{ref}$ and $S_{DQ}$ show the typical decay - and build-up behavior, respectively. For an isotropic ensemble of isolated spin pairs without relaxation and spin diffusion, $S_{ref}$ and $S_{DQ}$ should approach each other at sufficient long evolution time. This is indeed observed for the sulfur-vulcanized systems, but not for peroxide-cured EPDM, where $S_{ref}$ is always bigger than $S_{DQ}$. Apparently the latter contains a comparably large fraction (~10% monomer units, *vide infra*) of mobile chain fragments, such as long network chains or “dangling ends”. The DQ build-up rate of these fragments is low compared to the overall loss of coherence due to $T_2$ relaxation. As a result, these mobile chain fragments will only contribute to $S_{ref}$ and hardly to $S_{DQ}$, which causes $S_{ref}$ to be systematically larger than $S_{DQ}$ even at
long DQ evolution time. The loss of overall coherence is reflected by the decay of $S_\Sigma$. The observed sum-intensity decays (~5 ms) are always slower than the corresponding Hahn-echo decays (~1 ms).

The difference between $S_{\text{ref}}$ and $S_{\text{DQ}}$ at long time is a signature of “incoherent” components, of which the loss of overall coherence is faster than the build-up of DQ coherence. To remove these components from the NMR data we have therefore fitted a bi-exponential model to the difference intensity $S_{\text{ref}} - S_{\text{DQ}}$ over the range 5 – 18 ms, and used this to normalize the DQ build up according to:

$$S_{\text{DQ}}^N(\tau_{\text{ex}}) = \frac{S_{\text{DQ}}(\tau_{\text{ex}})}{S_{\text{ref}}(\tau_{\text{ex}}) + S_{\text{DQ}}(\tau_{\text{ex}}) - a \exp(-\tau_{\text{ex}}/T_{2a}) + b \exp(-\tau_{\text{ex}}/T_{2b})}$$  \[1\]

![Graph showing DQ build-up intensity $S_{\text{DQ}}$, reference intensity $S_{\text{ref}}$ (magnetization not converted into DQ coherence) and their sum $S_\Sigma$ versus the evolution time $\tau_{\text{DQ}}$, as compared to Hahn-echo decay curves, and bi-exponential curves fitted to the tail of $S_{\text{ref}}$ between 5 and 18 ms.](image)

Figure 2. $DQ$ build-up intensity $S_{\text{DQ}}$, reference intensity $S_{\text{ref}}$ (magnetization not converted into DQ coherence) and their sum $S_\Sigma$ versus the evolution time $\tau_{\text{DQ}}$, as compared to Hahn-echo decay curves, and bi-exponential curves fitted to the tail of $S_{\text{ref}}$ between 5 and 18 ms. The results shown here are (left) for EPDM with 9 wt.% ENB vulcanized with 0.7, 1.5 and 4.5 phr sulfur and (right) for EP(D)M with 0, 2 and 9 wt.% ENB cured with 1.25, 2.5 and 5 phr peroxide, respectively.
The bi-exponential correction is negligible for the sulfur-vulcanized EPDM (Fig. 2, left), and corresponds to the removal of ~10% of the initial intensity for the peroxide-cured EPDM, with a tendency to decrease at increasing peroxide-level (Fig. 2, right).

The normalized DQ build-up curves for the same sulfur- and peroxide-crosslinked EPDM rubbers are depicted up to 5 ms in Fig. 3. As expected, the DQ build-up becomes faster at higher sulfur and peroxide/ENB levels. The respective shapes reflect the underlying distribution of residual dipole coupling constants. Before giving a detailed analysis in terms of specific distribution models, we note an interesting shape similarity among the build-up curves of the sulfur-vulcanized EPDM systems when plotted along a logarithmic time axis (Fig. 4a). Up to 1.5-phr sulfur the curves coincide upon scaling the evolution time (Fig. 4c). The same is true for peroxide-cured EPDM up to peroxide levels of 2.5 phr (Fig. 4b and 4d).

![Normalized DQ build-up curves with curve fits based on a Gaussian and bi-Gaussian distribution of residual dipole coupling (RDC) constants for the same sulfur- and peroxide-crosslinked EP(D)M systems as in Fig. 2. Simulated curves for a bi-Gaussian distribution of RDC constants fit better to the observed DQ build ups than those for a Gaussian RDC distribution.](image)

The faster the DQ build-up, the bigger the required scaling factor, which thus represents a model-free “relative build-up rate” $R_{DQ}$. Arbitrarily taking the curve of 1.25-phr peroxide-cured EPM as the reference, we have determined the time-scaling factors of the other curves with respect to this curve. There is a systematic
shape difference between sulfur- and peroxide-cured EP(D)M, which cannot be removed by time scaling (Fig. 5). This makes comparison of the relative build-up rates between sulfur- and peroxide-cured EPDM slightly ambiguous, but a rough comparison is still possible.

$R_{DQ}$ depends similarly on the sulfur and peroxide levels as the (weighted-average) Hahn-echo decay rate $R_2 = 1/T_2$ (Fig. 6a and 6b). As shown in Fig. 1a, the effective relaxation rate $R_2$ of peroxide-cured EP(D)M varies linearly with the peroxide level below 5 phr. In contrast, for sulfur-cured EPDM $R_2$ and $R_{DQ}$ follow a kind of saturation curve. This indicates that at sulfur levels > 4 phr the content of third monomers becomes limiting for the crosslink density, which agrees with earlier observations (2).

Since $R_2$ and $R_{DQ}$ appear to follow different slopes for sulfur- and peroxide-cured EPDM, one could wonder which of the two, $R_2$ or $R_{DQ}$, correlates best with the macroscopic mechanical properties. The ideal behavior would be an NMR parameter predicting, e.g., the modulus, independent of the applied curing method. Fig. 6c and 6d shows plots of the modulus at 100 % elongation ($M_{100}$) versus either $R_2$ or $R_{DQ}$. For each of the two crosslinking types there is a linear correlation between the modulus and $R_2$ and $R_{DQ}$, respectively. However, for neither $R_2$ nor $R_{DQ}$ the crosslinking-type dependence disappears. This confirms that the $R_2$ and $R_{DQ}$ difference between sulfur- and peroxide-crosslinked networks is not so much caused by NMR artifacts related to the selected NMR parameter, but may actually be related to the even qualitatively different types of networks formed.

![Figure 4](image-url). Normalized quantum build-up curves of (a,c) sulfur-vulcanized and (b,d) peroxide-cured EPDM crosslinked at varied levels of sulfur and peroxide, respectively, versus (a,b) evolution time and (c,d) scaled evolution time. The five sulfur-vulcanized EPDM rubbers all contained 9 wt.% ENB. The three peroxide-cured EPDM systems are the same as in Fig. 2.
**Figure 5.** Normalized quantum build-up curves of EPDM vulcanized with 0.7 phr sulfur and EPM cured with 1.25 phr peroxide versus the scaled DQ evolution time.

**Figure 6.** (a) Effective relaxation rates $R_2$ and (b) relative DQ build-up rates $R_{DQ}$ for the same sulfur- and peroxide-crosslinked EP(D)M rubbers as in Fig. 4. (c,d) correlation between the modulus at 100% elongation $M_{100}$ and (c) $R_2$ and (d) $R_{DQ}$. For clarity the data are labeled with the ENB content of the specific EP(D)M grade, i.e. 9 wt.% for the five sulfur-vulcanized systems, and 0, 2 and 9 wt.% for the three peroxide-cured systems. The curved lines connecting the data for the sulfur-vulcanized systems in (a) and (b) are guides for the eye only.

The similar dependence of $R_2$ and $R_{DQ}$ on the sulfur- or peroxide levels is also clear from the linear correlations between the two (Fig. 7). Sulfur- and peroxide-crosslinked EPDM samples show different slopes, which may
reflect the difference in the underlying network topology. Peroxide can generate radicals anywhere along the EPDM chains, whereas sulfur requires the residual unsaturation of the third monomer to generate crosslinks. Interestingly, the linear correlations between $R_2$ and $R_{DQ}$ for sulfur-vulcanized and peroxide-cured EPDM cross each other at $R_{DQ} = 0$ and a positive value $R_2^* \sim 300 \text{ s}^{-1}$. This may indicate that the entanglements, which determine $R_2$ and $R_{DQ}$ in the absence of chemical crosslinks, may be different. Alternatively, $R_2^* = 1/T_2^{BWR}$ may represent Bloch-Wangness-Redfield type of relaxation contributions (17, 18) associated with incoherent loss of transverse magnetization:

$$\frac{1}{T_2^{eff}} = \frac{1}{T_2^{BWR}} + \frac{1}{T_2^{coh}}$$

where $1/T_2^{coh}$ denotes the decay rate of the Hahn echo under the influence of the coherent dipolar dephasing.

![Figure 7. Correlation between effective relaxation rate $R_2$ and $R_{DQ}$ for the same sulfur- and peroxide-cured EP(D)M samples as in Fig. 4.](image)

After this essentially model-free analysis we have also analyzed the DQ build-up curves in terms of mono- and bi-modal Gaussian distributions:

$$g^{(n)}(D) = \sum_{k=1}^{n} \frac{f_k}{\sigma_k \sqrt{\pi}} \exp\left(-\frac{(D - D_c^{(k)})^2}{\sigma_k^2}\right)$$

with $n = 1$ or $2$, respectively, and in the latter case $f_1 + f_2 = 1$, $D_c^{(1)}$, $D_c^{(2)}$, $\sigma_1$ and $\sigma_2$ the center values and widths of the two Gaussian components describing the distribution of residual dipolar coupling (RDC) constants. This distribution can be convoluted with the Gaussian initial behavior of the DQ build-up curves for an isotropic ensemble of isolated spin pairs with identical residual couplings $D$:

$$S_{DQ}^N(D, \tau_{DQ}) \approx 0.5 \left\{ 1 - \exp\left(-0.4D^2\tau_{DQ}^2\right) \right\}$$
The resulting analytical expression for the DQ build-up curve is (15):

\[ S_{DQ}^N(D_{av}, \sigma, \tau_{DQ}) = \]

\[ = 0.5 \sum_{k=1}^{n} f_k \left\{ \exp \left( -\frac{0.4 \left( D_{av}^{(k)} \right)^2 \tau_{DQ}}{1 + 0.8 \sigma_k^2 \tau_{DQ}^2} \right) \right\} \frac{1}{\sqrt{1 + 0.8 \sigma_k^2 \tau_{DQ}^2}} \]

Curves based on a single Gaussian distribution of RDC constants with the maximum at 0 fit well to the initial part of the DQ build-up curves of the peroxide-cured EPDM (Fig. 3, right hand side). At increasing peroxide content the width of the half-Gaussian RDC distribution increases (Fig. 8b), but the maximum stays at 0. This indicates that the chains between the network junctions become shorter at increasing peroxide content, but there is always a significant fraction with long chain segments \((D_{res}=0)\) even at high peroxide content. Such network structure could indicate a tendency of peroxide to form heterogeneous networks with parts of the EPDM chains non-crosslinked. One of the chemical pathways in the peroxide crosslinking of EPDM is the addition of EPDM macro-radicals to the residual unsaturation of ENB monomers in the polymer chain. This is followed by a hydrogen transfer, generating a new EPDM macro-radical which can add to the unsaturation of another ENB monomer, or combine with another EPDM macro-radical (13). The net result is a cluster of two or four crosslinks. In addition, a side reaction of peroxide curing is main chain degradation yielding a rubber network with dangling ends. Other types of chain reactions, such as formation of multifunctional crosslinks by double-bond polymerization, may also play a role during peroxide curing. These various reactions lead to a broad distribution of chain mobility, and thus to a broad RDC distribution. Similar observations were in fact previously reported for peroxide cross-linked natural and butadiene rubbers (19).

In contrast to the peroxide-cured samples, mono-modal curves based on Eq. 5 do not fit well to the DQ build-up curves of sulfur-crosslinked EPDM (Fig. 3, left). Bi-modal distributions consisting of a broad Gaussian centered at 0 and a narrow Gaussian with variable center and width fit better. In this case both the center and the width of the dominant narrow Gaussian component increases at increasing sulfur content (Fig. 8c). The good fit with the bimodal model should not be interpreted as indication of pronounced inhomogeneity, as the RDC distribution is in fact dominated by the narrower component. (Note the logarithmic scale in Fig. 8.) As support for this argument, sulfur vulcanization of natural rubber, i.e., poly(isoprene), also yields homogeneous networks (19). Sulfur vulcanization requires the residual unsaturation of the ENB monomer which is known to be
incorporated randomly into the EPDM chains. Sulfur vulcanization thus produces crosslinks more homogeneously distributed along the chain.

![Graphs showing probability density against (2/5)D/2π (kHz) for Sulfur vulcanized and Peroxide cured EPDM grades.](image)

**Figure 8.** (a,b) (single-)Gaussian and (c,d) bi-Gaussian RDC distributions yielding DQ build-up curves which fit best to the experimental data of the (a,c) sulfur- and (b,d) peroxide-crosslinked EPDM grades.

**Conclusion**

We have compared $^1$H NMR transverse relaxation and double-quantum (DQ) build up for sulfur- and peroxide-crosslinked EPDM grades with varied sulfur- and peroxide content. The network density derived from transverse relaxation correlates well with macroscopic properties such as the rheometer torque difference and the modulus at 100% elongation. For peroxide-cured EPDM DQ NMR indicates a heterogeneous network with a significant amount of dangling ends, whereas sulfur-vulcanized EPDM shows the features of a more homogeneous polymer network. For both types of crosslinking, the DQ build up is faster at increasing curative content, which is consistent with an increased immobilization of the polymer chains. The DQ build-up curves of the sulfur-crosslinked EPDM samples have similar shapes, and can be made to coincide by time scaling. The DQ build-up curves of the peroxide-cured EPDM
grades have a different shape. Whereas the peroxide-crosslinked EPDM grades show a linear increase of the effective relaxation rates \( R_2 \) and relative DQ build-up rates up to 4.5 phr peroxide, the corresponding rates for sulfur-vulcanized EPDM grades level off already at initial sulfur content > 1.5 phr. Mechanical properties, like the modulus at 100% elongation, correlate linearly with both the effective relaxation rate \( R_2 \) and the relative DQ build-up rate \( R_{DQ} \), but for neither of the two rates the linear trends for sulfur- and peroxide EPDM grades coincide. This is probably a consequence of the underlying different types of rubber networks. A difference between sulfur- and peroxide-crosslinking is that the first requires the unsaturation of the ENB monomers which are randomly distributed along the EPDM chain, whereas peroxide radicals create combination crosslinks anywhere along the chain, as well as addition crosslinks and other possible chain reactions.

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**References**