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Mechanism of Peroxide Cross-Linking of EPDM Rubber

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Summary: The results of three experimental studies, i.e. GC-MS of peroxide-cross-linked alkene/alkane mixtures, ^{13}C NMR of peroxide-cured, ^{13}C-labeled 2-ethylidene-5-norbornene - ethylene-propylene-diene-monomer (EPDM) and EPR of peroxide curing of EPDM, are combined, yielding a more accurate description of the mechanism of peroxide cure of EPDM. Both alkyl and allyl macro-radicals are formed via H-abstraction from the EPM main chain and the residual diene unsaturation, respectively. Combination of these macro-radicals yields alkyl/alkyl, alkyl/allyl and allyl/allyl cross-links and addition of these macro-radicals to the residual diene unsaturation yields alkyl/alkene and allyl/alkene cross-links.

Keywords: cross-linking; EPDM; mechanism; peroxide; structure

Introduction

Terpolymerization of ethylene, propylene and a non-conjugated diene yields ethylene-propylene-diene-monomer (EPDM) rubber with a saturated polymer backbone and residual unsaturation in the side groups (Figure 1, top). As a result, EPDM rubber (or EPDM, for short) has a superior resistance against oxygen, ozone, heat and irradiation over polydiene rubbers, such as natural rubber (NR), butyl rubber (BR) and styrene-butyl rubber (SBR).[1,2] This makes EP(D)M the elastomer of choice for outdoor and elevated-temperature applications, such as automotive profiles, window gaskets, roof sheeting, waste-water seals, electrical cable & wires and V belts, and explains the growth of EPDM into the largest non-tyre rubber of today with a total volume amounting to 1100 kton/year. As other elastomers, EPDM has to be cross-linked to achieve its optimum performance in terms of elasticity, tensile and tear strength and solvent resistance. Introduction of unsaturation via incorporation of the diene monomer enables sulfur vulcanization (~80% of EPDM applications) and enhances the peroxide curing efficiency (~15%). The obvious advantage of peroxide cure over sulfur vulcanization is the formation of thermo-stable C–C bonds instead of thermo-labile S–S bonds. Peroxide cure, therefore, allows the full exploitation of the excellent heat resistance of EPDM. The peroxide curing efficiency of EPDM is determined by the structure of the diene.[3,4] 2-Vinyl-5-norbornene (VNB) provides a substantially higher efficiency for peroxide cure than 2-ethylidene-5-norbornene (ENB) and dicyclopentadiene (DCPD), which explains the growing interest in recently developed VNB-EPDM polymers.[5,6]

Both the mechanism of peroxide cross-linking of EPDM rubber[7,8] and the subsequent practical consequences[9,10] have been reviewed. The basic steps in the generally accepted mechanism of peroxide cure of EPDM are presented in Figure 2. The chain of free-radical reactions is initiated by thermal decomposition of the peroxide, yielding primary alkoxy (RO•) or secondary alkyl radicals (R•). Subsequent abstraction of H-atoms from the EPDM polymer results in the formation of EPDM

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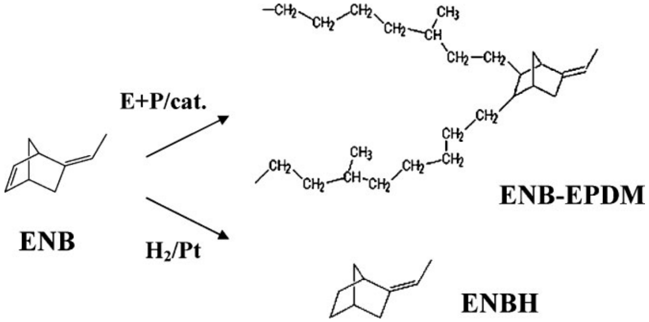

Figure 1.
Conversion of 2-ethylidene-5-norbornene (ENB) via (top) ter-polymerization with ethylene and propylene into ENB-EPDM rubber and (bottom) hydrogenation to the 2-ethylidene norbornane (ENBH) model compound.

macro-radicals (EPDM•). Calculations based on kinetic data for H-abstraction indicate that H-abstraction mainly occurs along the saturated EPM polymer backbone,[11] whereas several electron paramagnetic resonance (EPR) spectroscopy studies have shown the selective formation of allyl radicals derived from the diene monomer. The actual cross-linking proceeds via two pathways, which have been shown to be additive.[12] Two EPDM macro-radicals either combine or, alternatively, a macro-radical adds to an EPDM unsaturation. Visible spectroscopy has confirmed the conversion of the EPDM unsaturation upon peroxide cure.[13] The high reactivity of VNB-EPDM towards peroxide cure is explained by the low steric hindrance of the terminal VNB unsaturation.[4] It is noted that in practical EPDM/peroxide compounds usually co-agents, such as triallyl (iso)cyanurate, trimethylolpropane trimethacrylate or *m*-phenylenebis(maleimide), are included to increase the peroxide curing efficiency,[14] which obviously affects the mechanism of peroxide cure.

More details on the mechanism of peroxide cure of EPDM and the structures formed are lacking, mainly due to the complexity of the system (large number of structures formed at low concentrations) combined with the relatively difficult, analytical accessibility of cross-linked polymer networks. Recently, several studies were performed to obtain further insight in the chemical mechanism of peroxide cure of EPDM. First, a study on peroxide cross-linking of low-molecular-weight model compounds for EPDM was performed.[15] The use of gas chromatography (GC) and especially GC × GC allowed the separation of a wide variety of ‘‘cross-linked’’ products. The precise structure of the various products could be obtained by careful interpretation of the mass spectrometry (MS) data. Secondly, a solid state ^{13}C nuclear magnetic resonance (NMR) study was performed on peroxide-cured ^{13}C-labeled EPDM.[16] ^{13}C labeling results in a dramatic increase in sensitivity when studying the new structures formed upon peroxide cure. Finally, an EPR study was performed on the decomposition of peroxide in EPDMs with various diene monomers.[17] Although this third study was initiated to investigate the free-radical

½ ROOR → RO• → R'•	initiation
EPDM-H + RO•/R'• → EPDM• + ROH/R'H	H-abstraction
2 EPDM• → EPDM-EPDM	combination
EPDM• + EPDM → EPDM-EPDM• → EPDM-EPDM-H	addition

Figure 2.
Generally accepted mechanism for peroxide cure of EPDM.[7–10]

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species formed in the course of peroxide cure, it eventually provided information on the structure of some of the cross-links. In this review, the results of these three studies will be combined, providing a more accurate mechanism for peroxide cure of EPDM.

Experimental Part

For full experimental details on the GC-MS, ^{13}C NMR and EPR studies on peroxide cross-linking of EPDM (models), the reader is referred to the original papers.[15–17]

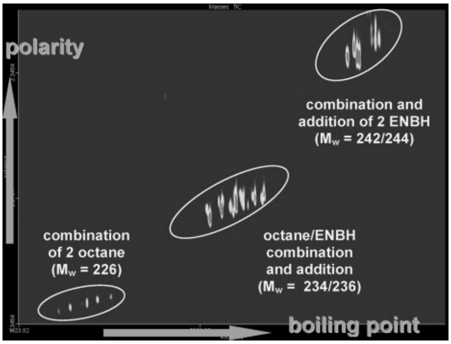

Figure 3.
GC-GC-MS chromatogram of reaction product of *n*-octane with ENBH (10 wt%) and DCP (5 wt%) (30 minutes at 433 K).

Results and Discussion

GC-MS Study of Model Compound Cross-Linking[15]

Mixtures of an alkene (5–20 wt%), viz. hydrogenated ENB (Figure 1), DCPD and VNB (ENBH, DCPDH and VNBH, respectively), with an alkane, viz. *n*-octane or *n*-decane, were ‘‘cross-linked’’ with 5 wt% dicumyl peroxide (DCP) for 30 minutes at 433 K. The products were analyzed with GC-MS and GC-GC-MS. In the following discussion, the results for an ENBH/*n*-octane/DCP mixture will be explained in detail as an illustration for the whole series of alkene/alkane model experiments performed. In addition to the expected DCP decomposition products (cumyl alcohol and acetophenone), several clusters of reaction products were observed (Figure 3). Cluster I consists of *n*-octane dimers with a molecular weight (MW) of 226 Da, i.e. equal to the sum of MW of two *n*-octane molecules minus 2 Da, but varying in branching structure. These dimers were formed as a result of combination of two octyl radicals, formed in turn via H-abstraction from *n*-octane by the peroxide radicals. In a more in-depth study, a series of linear and branched alkanes was cross-linked with DCP.[18] Detailed interpretation of the MS spectra allowed the identification of the precise structure of the various dimers, which consequently provided information on the selectivity for H-abstraction from the various C positions: $CH > CH_2 > CH_3$. Cluster II consists of coupling products of one *n*-octane and one ENBH molecule. MS showed species with MW of 234 Da, i.e. equal to the sum of MW of *n*-octane and ENBH, and 236 Da, i.e. equal to the MW sum minus 2 Da. The first series of products were formed via addition of an octyl radical to the ENBH unsaturation, followed by H-transfer. The second series of products were formed via combination of an octyl and an ENBH allyl radical, both formed in turn by H-abstraction from *n*-octane and ENBH, respectively. As for cluster I, a variety of coupling products with different branching structures were observed. Detailed interpretation of the MS spectra showed that H-abstraction from ENBH preferably occurred at the allylic C3 and C9 positions. Cluster III consists of ENBH dimers with MW of 242 Da, i.e. equal to the sum of MW of two ENBH molecules, and 244 Da, i.e. equal to the MW sum minus 2 Da. The ENBH dimers with MW 242 Da were formed via addition of an ENBH allyl radical to the ENBH unsaturation, followed by H-transfer, and the ENBH dimers with MW 244 Da were formed via combination of two ENBH allyl radicals, in analogy to the structures from cluster II.

GC-MS did not only enable the identification of the various species, but also allowed the quantification of their respective concentrations (Figure 4). It was shown that increasing the alkene content in the alkene/alkane mixture resulted in a linear increase of the alkene conversion and in a linear decrease of the alkane conversion. The conversions increased in the order ENBH ~ DCPDH < VNBH (1:1:2). This agreed fairly well with experimental data on peroxide curing efficiencies determined by rheometry of peroxide cure of EPDMs with various diene monomers[3,12] and demonstrated again the higher reactivity of the VNB(H) terminal unsaturation. It was also shown that the total amount of combination products in clusters I, II and III was constant, i.e. independent of the alkane and alkene structures and concentrations, suggesting that it was simply determined by the peroxide content. However, the total amount of addition products from clusters II and III did depend on the diene structure, following again the sequence ENBH ~ DCPDH < VNBH, and the concentration of the alkene. It was finally calculated that in a 10 wt% alkene solution H-abstraction on a molar basis from the alkane and alkene was approximately 1:1 and subsequent formation of dimers via combination followed simple statistics, viz. alkyl/alkyl: alkyl/allyl: allyl/allyl ~ 1:2:1.

^{13}C NMR Study of Peroxide-Cured, ^{13}C-Labeled ENB-EPDM[16]

The development of high-temperature magic-angle-spinning (MAS) solid-state NMR spectroscopy has enabled a breakthrough in the chemical characterization of cross-linked rubbers.[19] Unfortunately, the diene monomer content of EPDM is rather low, the conversion of the diene upon cross-linking is low, and, finally, a large number of new cross-link structures are formed. As a result, MAS ^{13}C NMR of cross-linked EPDM does not provide any insight in the cross-linking mechanism. Actually, Figure 5 (top) shows that the diene unsaturation (ENB: C2 and C8) was hardly visible for cross-linked commercial EPDM. Thus, EPDM with ^{13}C labels at the olefinic C2 and C8 positions was prepared,[20] peroxide was added via a solution route and step-wise cross-linking at 433 K as a function of time was performed. Figures 5 (center) and (bottom) show the very intense olefinic signals, both for the starting and the peroxide-cured, ^{13}C-labeled EPDM. Figures 5 (center) and (bottom) clearly show that the intensities of the olefinic C2 and C8 signals decreased upon peroxide curing, as a result of the addition reactions.

Figure 6 shows a magnification of the solid-state ^{13}C NMR spectrum of

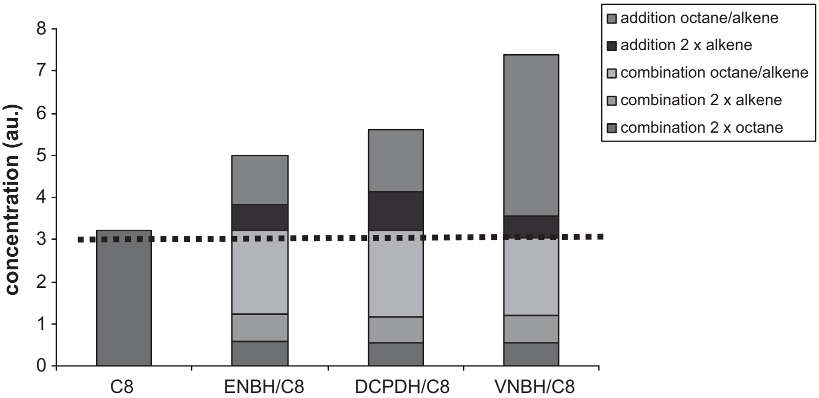

Figure 4.
Concentration (in arbitrary units) of reaction products of 10 wt% ENBH, DCPDH and VNBH in *n*-octane with 5 wt% DCP (30 minutes at 433 K) (dark grey shades indicate various combination and addition cross-link structures, respectively; dashed line indicates total concentration of combination cross-links).

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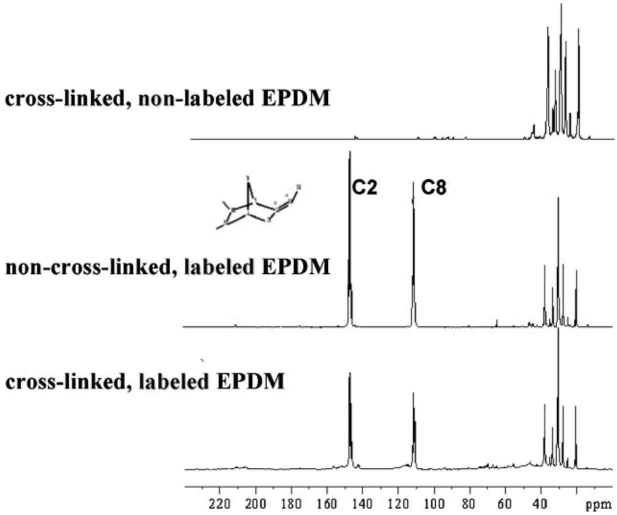

Figure 5.
Effect of selective ^{13}C-labeling of ENB unsaturation on MAS solid-state ^{13}C NMR spectra of (cross-linked) EPDM.

peroxide-cured ^{13}C-labeled EPDM. New aliphatic signals between 45 and 60 ppm were observed, which were assigned to saturated C2 and C8 atoms formed upon addition reactions. Next to the non-reacted olefinic C2 and C8 atoms at 147 and 110 ppm, respectively, a large number of new olefinic signals were observed, which were assigned to cross-link structures with intact unsaturation, resulting from combination reactions of allylic ENB-EPDM macro-radicals. Combination at the C3 and C9 allylic positions was most probable. Finally, new peaks were observed between 60 and 100 ppm and between 160 and 220 ppm. These were

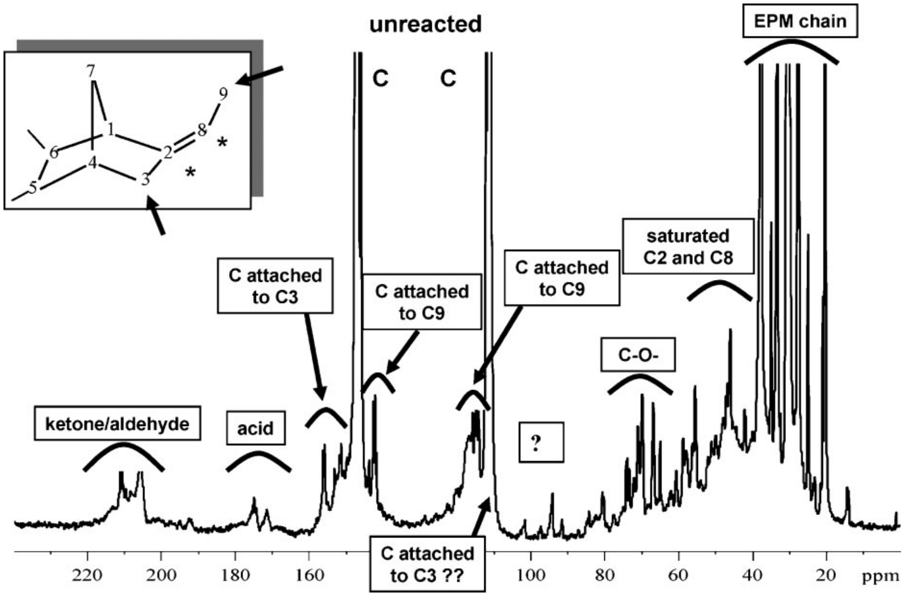

Figure 6.
Assignment of solid state ^{13}C NMR spectrum of step-wise peroxide-cured ^{13}C-labeld ENB-EPDM.

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assigned to a variety of oxidation products with C–O (ether, alcohol and/or [hydro]peroxide) and C=O (acid, ketone and aldehyde) units, respectively. The intensity of these oxidation-related signals was rather high relatively to the new aliphatic and olefinic cross-link-related signals. This was probably due to the fact that the peroxide cure experiment was carried out stepwise with a small amount of labeled EPDM, resulting in repeated exposure to air. Indeed, by performing a second peroxide curing experiment with labeled EPDM in one step, the NMR signals of the oxidized species strongly decreased in intensity.

EPR Study of Peroxide Decomposition in EPDM[17]

A variety of EPDMs with different diene structures and contents was mixed with 5 wt% of DCP via a solution route. EPR spectra were recorded at 440 K as a function of time. In the following discussion, the results for a 1.2 wt% DCPD-EPDM (Figure 7) will be explained in detail as an illustration for the whole series of EPDMs studied. The EPR spectra consisted of a superposition of two sub-spectra, both at the same field position. The first sub-spectrum showed a clear hyperfine coupling with sharp spectral features, whereas the second sub-spectrum was just a broad (~15 G wide) Gaussian line contribution. The first spectrum fully agreed with a simulated spectrum of the allyl radical of DCPD-EPDM (compare first and second spectra in Figure 7; hyperfine coupling constants are also given). It is noted that radicals were not formed at the allylic DCPD bridgehead position as this would violate Bredt's rule. The broad line feature was tentatively assigned to a second allyl radical, which had the same structure as the allyl radical of DCPD-EPDM, but was positioned in a cross-link. The low mobility of this structure explained the lack of sharp EPR features.

In most spectra, the double integral intensity of the broad line component was significantly larger than that of the sharp line component. The intensity of the sharp line component increased steeply at short times and then decreased slowly to zero at longer times. The intensity of the broad line component usually increased more slowly and also decayed more slowly to zero at even longer reaction times. It is surprising to note that rheometry indicated that peroxide curing of EPDM was more or less completed after 10 to 15 minutes at 440 K, which agreed with 6 to 9 times the half-life of DCP (440 K: ~100 s), i.e. >98% conversion of DCP. However, strong EPR signals of both sharp and broad line features were still observed after one hour or even longer. In addition, it was noted that no signals related to peroxide-derived

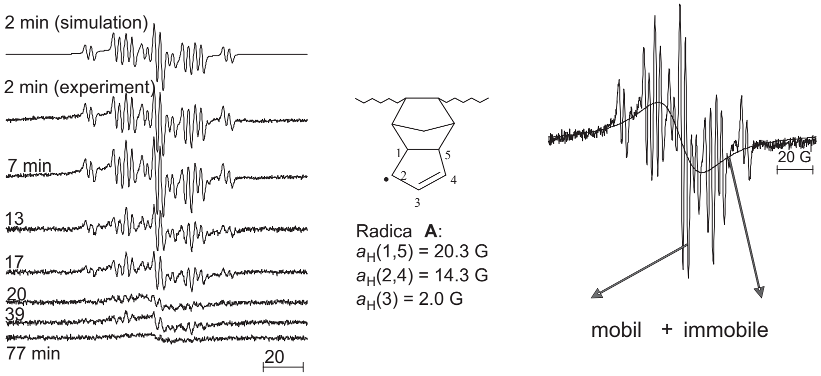

Figure 7.
Evolution of the EPR spectra upon heating of 1.2 wt% DCPD-EPDM with 5 wt% DCP at 440 K and assignment of structure of the sharp line component.

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radicals or radicals formed via H-abstraction from the EPM backbone were observed. This was most probably due to the high reactivity of these alkoxy and alkyl radicals, resulting in concentrations which were too low to be detected by EPR. The latter results indicated that it was not possible to study the complete sequence of free-radical reactions during peroxide cure of EPDM. Actually, the observation of just the two allyl radicals of unreacted DCPD-EPDM and of DCPD-EPDM cross-links, showed that EPR in this case was merely a technique to probe the network structure as a function of time. The observation of the broad line feature and its assignment to the allyl radical of a DCPD unit in a cross-link was fully in accordance with the results of the model and ^{13}C NMR studies, discussed above, and was evidence for the participation of allyl EPDM radicals in cross-link formation.

Further Discussion

Based on the three experimental studies, discussed above in some detail, a more accurate chemical mechanism for the peroxide cross-linking of EPDM is proposed (Figure 8). Thermal decomposition of the peroxide yields primary alkoxy radicals, which may convert to alkyl radicals via β-scission. These radicals abstract H-atoms from the EPDM polymer, both at the CH_2 and CH units in the EPM main chain and at the allylic positions of the diene unit,

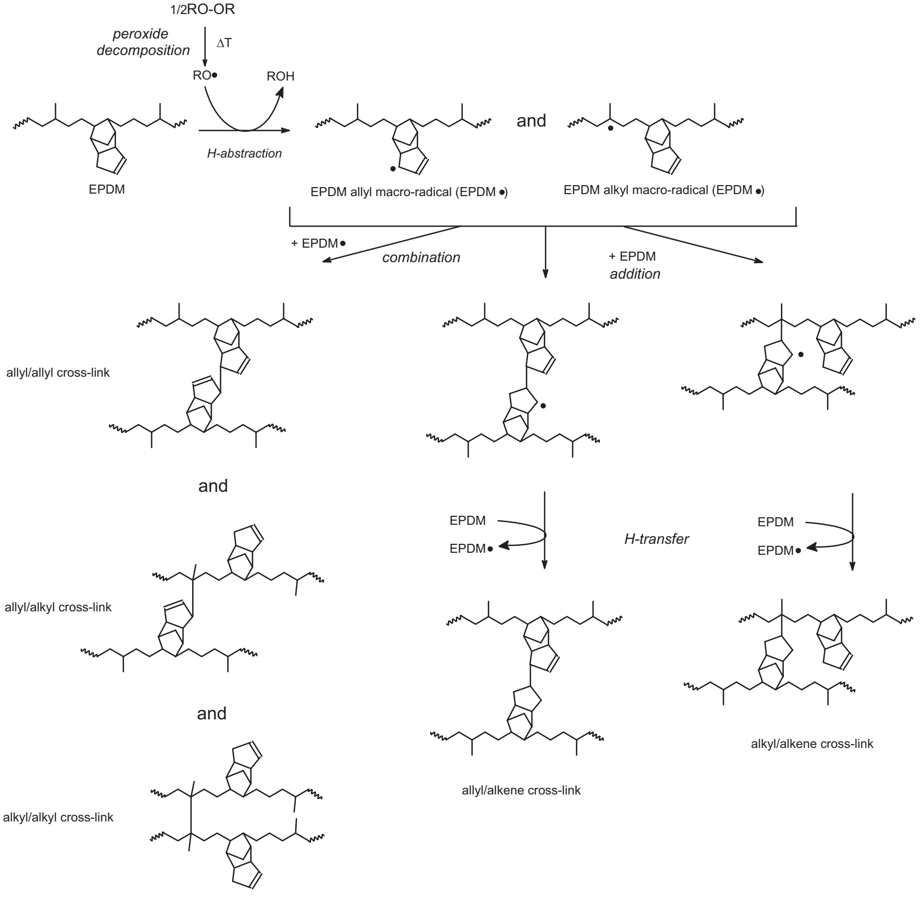

Figure 8.
Mechanism of peroxide cross-linking of DCPD-EPDM rubber.

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yielding EPDM alkyl and allyl macro-radicals, respectively, in a ~1:1 ratio. The allylic H-atoms of the diene monomer have a higher intrinsic reactivity for H-abstraction than the aliphatic H-atoms of the EPM chain. However, H-abstraction also occurs from the polymer backbone as a result of the large molar excess of aliphatic versus allylic H-atoms in EPDM. Cross-linking is achieved via two routes. First, termination of two EPDM macro-radicals via combination yields alkyl/alkyl, alkyl/allyl and allyl/allyl cross-links with 0, 1 and 2 diene units, respectively, and with 0, 1 and 2 unsaturations, respectively, in the actual cross-link between the two rubber chains. Secondly, an EPDM macro-radical adds to a residual EPDM unsaturation. For steric reasons the macro-radical thus formed will probably not propagate with a second diene unsaturation. It will more likely terminate via H-transfer, yielding allyl/alkene and alkyl/alkene cross-links with 2 and 1 diene units, respectively, and with 1 and 0 unsaturation, respectively, in the actual cross-link. Note that in the case of peroxide cure of EPM without diene, only saturated alkyl/alkyl combination cross-links are formed. Next, the macro-radical addition path does not terminate the radical species. Therefore, the contributions of macro-radical combination and addition are additive. The total amount of combination cross-links is constant and independent of the EP(D)M composition. The total amount of addition cross-links increases with increasing diene content and in the order ENB ~ DCPD < VNB. Typical diene conversions were ~25% for ENB and DCPD and ~50% for VNB.

Conclusion

Based on these studies a more accurate chemical mechanism for the peroxide cross-linking of EPDM is proposed. In agreement with the commonly accepted scheme for peroxide cure,[7–10] a distinction is made between cross-links formed via combination of two EPDM macro-radicals and via addition of a macro-radical to an EPDM unsaturation. Conclusive evidence is now provided showing that the free radicals participating in these reactions originate both from the EPM polymer backbone and the residual diene unsaturation, yielding a complicated mixture of cross-link structures with varying number of diene units and unsaturations in the actual cross-links.

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