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Experimental determination of the quantity and distribution of chemical crosslinks in unaged and aged natural rubber, part 1: Peroxide vulcanization

Samantha Howse, Christopher Porter, Tesfaldet Mengistu, Richard J. Pazur*

Department of National Defense, Quality Engineering Test Establishment, Polymer and Textile Science, Ottawa, ON, K1A 0K2, Canada

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ABSTRACT

A set of unfilled and stabilized natural rubber compounds containing different dicumyl peroxide concentrations were prepared and their chemical crosslink densities were determined using a variety of experimental techniques: stress-strain (Mooney-Rivlin), equilibrium solvent swell (Flory-Rhener) and low field time domain Nuclear Magnetic Resonance (NMR) by the Double Quantum (DQ) method. Testing was carried out on both the unaged and heat aged (96 h at 80 °C) samples. Increasing peroxide level caused a corresponding rise of crosslink density and a decrease in the chain entanglement density, while the relative crosslink distribution width remained unchanged. The molecular weight between entanglement points was in the expected range for natural rubber. Heterogeneous areas of high crosslinking (clusters) were low in concentration. Heat aging caused properties to deteriorate due to chain scission reactions that eliminated network chains creating a more heterogeneous system. Defect levels increased and more toluene soluble uncrosslinked chains were detected. The network chain and chain entanglement densities decreased with heat aging and the molar mass distribution between crosslinks substantially broadened independent of peroxide loading.

1. Introduction

The determination of the degree of crosslinking is critical in rubber materials given its direct effect on mechanical, dynamic and performance properties. Properties such as hardness, modulus, and elastic recovery increase with crosslink density while elongation at break, hysteresis, permanent set and friction decrease. Energy-to-break properties such as tear strength, fatigue life and toughness display a maximum at intermediate crosslink density values [1]. Knowledge of the crosslink density is not only fundamental in the molecular interpretation of rubberlike elasticity but it benefits in material design since certain properties can be targeted in order to create a wider range of rubber applications [2].

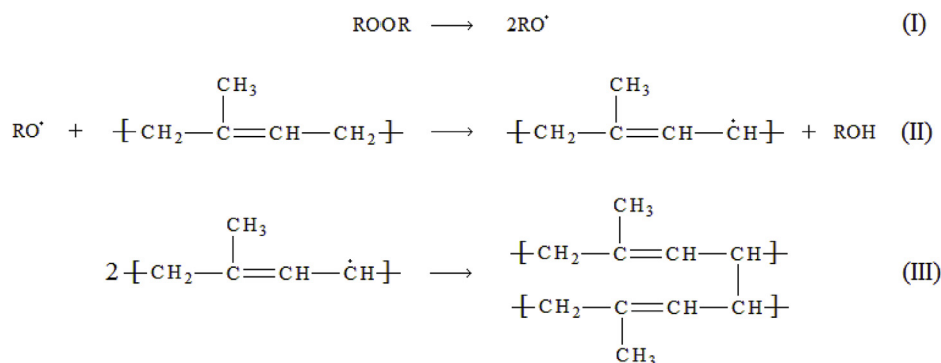
The most common experimental techniques to determine crosslinking level in rubber are uniaxial stress-strain analysis in extension or compression, and equilibrium volume swell measurements [2]. Low field proton NMR T_2 spin-spin relaxation measurements (Hahn-Echo) have also proven to be a practical and useful method for crosslink network structural determination in rubber systems [3–5]. The NMR relaxation process depends on the residual dipolar interactions which can be related to the polymer chain mobility. Local chain segment dynamics are restricted due to the presence of physical (chain entanglements) and chemical crosslinks. More direct and accurate

measurements of the residual dipole coupling are possible by employing multiple-quantum NMR techniques [6,7]. In a Double Quantum (DQ) experiment, a measurement of residual dipole couplings and their distribution can be related to local chain order and an effective crosslink density. The technique can provide the molecular weight distribution between crosslink points as well as the level of defects (dangling chain ends, loops, sol) in the rubber network. Furthermore, the residual dipole couplings and its distribution are not affected by the amount and type of filler.

Excellent reviews on the peroxide vulcanization of rubber are available in the literature [8–12]. The type and concentration of competing chemical reactions that take place during cure will depend on many parameters: polymer structure, peroxide type and concentration, cure temperature and the presence of additives such as co-agents and anti-degradants. The preferred route for the peroxide vulcanization of natural rubber is accomplished through the use of dicumyl peroxide (DCP) at active concentrations from 0.5 to 2.5 phr [13]. The accepted mechanistic pathway for the creation of carbon-carbon linkages in natural rubber (100% 1–4 *cis* –poly(isoprene)) is shown in [Schema 1](#). The application of heat induces peroxide decomposition through homolytic cleavage producing free radicals which attack the α -methylene of the poly(isoprene) chain through hydrogen abstraction. The most reactive position for hydrogen abstraction has been illustrated in

* Corresponding author.

E-mail address: richard.pazur@forces.gc.ca (R.J. Pazur).<https://doi.org/10.1016/j.polymeresting.2018.07.002>Received 7 May 2018; Received in revised form 4 July 2018; Accepted 5 July 2018
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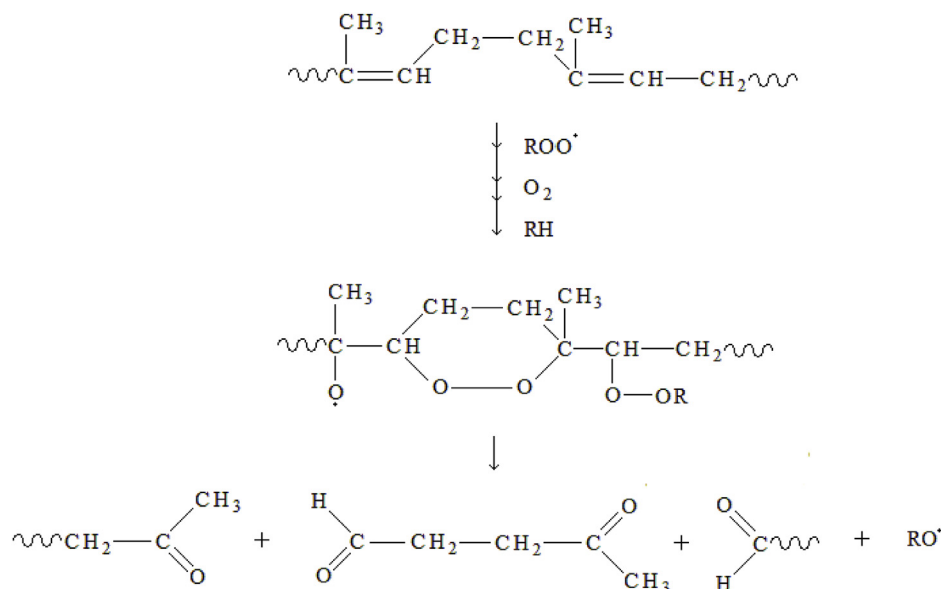
Scheme 1. The formation of C-C crosslinks through use of peroxide as vulcanizing agent for natural rubber.

Scheme 1, II. The methyl group is able to protect the double bond by sterically hindering free radical addition. The coupling of two polymeric radicals generates a crosslink through a termination reaction. Other side reactions such as addition of the peroxy radicals to the isoprene double bond or chain scission reactions due to polymer radical decomposition may occur, however, the methyl group effectively protects the double bond by sterically hindering free radical addition. Furthermore, the resonance structure of the polymeric radical contains a tertiary allyl radical protected by the methyl group which forces crosslinking to take place between the polymeric radicals. The abstraction reaction is the preferred route in using DCP in natural rubber at usual concentrations. In fact, DCP is considered as a quantitative crosslinking agent for natural rubber as 1 mol of peroxide generates approximately 1 mol of crosslinks.

Oxidation of elastomers causes a deterioration in physical properties brought about by the net effect of stiffening through crosslinking and softening due to chain scission reactions [9]. The major pathway of network destruction of peroxide cured natural rubber possessing the structure of **Scheme 1, III** during thermo-oxidation is the chain scission reaction which is more prevalent at higher temperatures. In **Scheme 2**, a summary including the primary intermediate and final end products has been drawn [9,11,14]. During thermo-oxidation, hydroperoxides are generated which then decompose to form oxy and peroxy radicals. The reaction of oxygen with the radical of the tertiary carbon produces an alkylperoxy radical which adds to the neighbouring double bond

forming a stable cycloperoxide and transferring the radical to the adjacent tertiary carbon. Addition of oxygen to this displaced radical can generate another cycloperoxide (and so-called peroxide clusters), or it may form a hydroperoxide. Decomposition of the clustered peroxides causes cleavage of the polyisoprene backbone and the formation of levulinolaldehyde. The chain cleavage and resulting formation of levulinolaldehyde which acts as a solvent, both cause softening of the polymer matrix.

The structural analysis of a DCP cured NR system by using DQ-NMR has been thoroughly examined by Valentin et al. [15]. In contrast to a sulfur vulcanized system, the networks were composed of a higher amount of non-elastic defects (loops, dangling chain ends), a heterogeneous crosslink distribution and possessed slower local segmental dynamics. The crosslink distribution showed evidence of bimodality and broadening at higher DCP concentrations. Highly reticulated zones or clusters were attributed to macro-radical addition reactions onto adjacent double bonds. Such heterogeneous areas have been identified in previous works and were considered responsible for the low tensile, modulus and tear strength behavior due to localized stress accumulation and chain breakage during deformation [16–18]. Higher peroxide levels can lead to an excess amount of residual (unreacted) peroxide causing side reactions which can disrupt chain regularity [19]. In addition, the higher crosslink densities restrict mobility of the chain backbone inhibiting stress-induced crystallization and thus lowering ultimate properties [15,20]. Lower peroxide levels and vulcanization



Scheme 2. The major accepted pathway to describe the oxidation process of natural rubber causing chain scission, levulinolaldehyde formation and compound softening.

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