Polymer Degradation and Stability 130 (2016) 348–355

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Predictive ageing of elastomers: Oxidation driven modulus changes for polychloroprene

Pierre Yves Le Gac [a], [*], Mathew Celina [b], Gérard Roux [c], Jacques Verdu [d], Peter Davies [a], Bruno Fayolle [d]

[a] IFREMER Centre de Bretagne, Marine Structures Laboratory, CS 10070, 29280 Plouzane, France
[b] Sandia National Laboratories, Organic Materials Science Dept. 1853, Albuquerque, NM 87185, USA
[c] Thales Underwater Systems, TUS, route des Dolines, BP 157, 06903 Sophia-Antipolis Cedex, France
[d] PIMM, Arts et Métiers ParisTech, CNRS, CNAM 151 Bd de l'Hôpital, 75013 Paris, France

ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form
13 June 2016
Accepted 14 June 2016
Available online 16 June 2016

Keywords:
Polychloroprene
Ageing
Sulfur vulcanization
Oxidation
Kinetic modeling
Modulus changes

ABSTRACT

The oxidative ageing in the range of 60 °C–140 °C of sulfur vulcanized polychloroprene has been studied by FTIR spectroscopy (double bond consumption), modulus changes and oxygen absorption measurements. Experiments were carried out on thin films and thick samples to investigate both homogeneous and inhomogeneous (diffusion controlled) oxidation with the goal of establishing the underlying correlation between oxidative degradation chemistry and mechanical property changes. A correlation between oxidatively driven degradation chemistry and modulus is possible using the established approaches of rubber elasticity where an effective crosslinking yield due to double bond reactions is of the order of 30% for this material (i.e. the loss of 3 double bonds results in one effective crosslink associated with material hardening). It is then possible to predict modulus changes induced by oxidation for vulcanized and unstabilized polychloroprene rubber. A kinetic model is introduced with two propagation reactions (hydrogen abstraction and radical addition to double bonds) and two stabilization processes involving sulfur containing moieties from the vulcanization process. The kinetic scheme was solved and the relevant rate constants determined. This model can adequately predict modulus changes in films and thick samples as a function of time and spatially resolved.

1. Introduction

Soon after the theory of rubber elasticity was established, its potential to characterize network structural changes during polymer degradation, especially oxidation was investigated [1]. In principle, the approach is simple: the material is subjected to constant elongation and the resulting stress is recorded during its exposure in the degradative environment under study. The stress σ for a stretching ratio λ varies with crosslink density (ν), and the ideal rubber theory in its simplest form establishes a link between both quantities:

$$\sigma = RT\rho\nu\left(\lambda^2 - \lambda^{-1}\right) \tag{1}$$

where R is the gas constant, T the temperature and ρ the polymer density.

From a practical point of view a lifetime is defined as the time to reach a limiting material property value for the application under consideration. Following Tobolsky's approach [1], we recognize that the rate of crosslink density change is the product of at least two terms (x, number of crosslinking events and s, number of chain scission events). For instance in the case of "pure" crosslinking (no chain scission), it is possible to state:

$$d\nu/dt = [d\nu/dx].[dx/dt] \tag{2}$$

where x is the number of crosslinking events and t the time.

The theory of rubber elasticity gives the first term, $d\nu/dx$, but the second term dx/dt (i.e. crosslinking per time) must be obtained from chemical kinetics. Tobolsky and his group used the concepts of free radical auto-oxidation kinetics [2] to build a kinetic model in which initiation is due to unimolecular or bimolecular hydroperoxide decomposition [3]. However, while this model explains the auto-accelerated behavior of oxidation and can predict oxygen consumption (in thin samples) or hydroperoxide concentration, it does not predict crosslink density, which is essential for a link

---

[*] Corresponding author.
E-mail address: pierre.yves.le.gac@ifremer.fr (P.Y. Le Gac).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.06.014

between mechanical properties and chemical parameters. Further, Tobolsky's initial model applied to saturated hydrocarbon polymers and does not take into account reactions of radical addition to existing double bonds, which play a key role in the oxidation of polydienic elastomers and other unsaturated polymers.

Surprisingly, Tobolsky's model was practically ignored during the last half century although it offers a significant level of complexity while still allowing for an analytical solution of the kinetic scheme.

More recently [4], the problem was reexamined and a numerical solution was proposed to avoid the numerous simplifying hypotheses used by Tobolsky and coworkers. Using numerical tools also allows kinetic schemes of a considerably higher degree of complexity to be studied, for instance for unsaturated elastomers with antioxidants [5,6].

In parallel, the research group at Sandia National Laboratories developed a simpler kinetic model with an analytical solution for a similar mechanistic scheme called the Basic Oxidation Scheme (also based on free radical auto-oxidation) [7]. With some assumptions, Gillen, Wise et al. proposed a kinetic model providing an analytical solution when coupling oxygen consumption rate and oxygen diffusion [8,9]. The main feature of this model is that the local oxidation rate is strongly dependent on the oxygen partial pressure. This aspect is fundamental to describe situations where oxidation is controlled by oxygen diffusion, i.e. a diffusion limited oxidation (DLO) regime for most materials at elevated temperatures. This approach was applied to nitrile and polychloroprene rubber oxidation [10,11].

In a previous paper, we applied a mechanistic approach to an unvulcanized unstabilized unfilled polychloroprene (CR) [12]. An oxidation mechanistic scheme involving oxygen alkyl and peroxyl additions to double bonds was investigated and solved numerically without any simplifying hypotheses. In that work the rate constants involved in the kinetic model derived from the mechanistic scheme were interpreted with double bond consumption kinetics. The present study expands this approach to model the oxidation of sulfur vulcanized polychoroprene and establishes the foundation for a quantitative relationship between molecular modifications and modulus changes during the oxidation process.

2. Material and methods

2.1. Material

The elastomer under study is based on polychloroprene with a predominantly trans 1–4 structure, which is vulcanized by a sulfur system in the presence of accelerators (MgO, ZnO and stearic acid) and where sulfur vulcanization consumes existing double bonds. In the current formulation the total amount of inorganic materials is about 20% and no additional stabilizer was added. Its initial characteristics are given in Table 1. Double bond concentration is calculated by assuming that each monomer contains one double bond (monomer molar mass being equal to 88 mol/g), whereas sulfur content is determined by elemental analysis. The concentration of crosslink sites (mol/kg) is calculated from the measured rubber modulus (E in equation (3)) by assuming that tetrafunctional crosslinks are predominant, where functionality (f) is then equal to 4 and density (ρ) is 1.245 kg/l:

$$[\text{crosslink sites}] = 2/f\ E/3RT\rho \tag{3}$$

The data shown in Table 1 require the following comments: Firstly, it is concluded that vulcanization has consumed only a small fraction of double bonds because the sulfur content is significantly lower than the total concentration of available double bonds. Therefore, the remaining double bond concentration in the elastomer is close to the theoretical value for unvulcanized polychloroprene.

Secondly, by comparing the concentration of sulfur content and crosslink sites, each crosslink site involves a maximum of 4 sulfur atoms. Usually, sulfur vulcanization is associated with disulfide (S_2) bridges [13], but may involve longer sulfide bridges. Further, some local sulfur reaction may not effectively contribute to the elastomer network. In fact, it is expected that more sulfur than the theoretically required amount to form an ideal S_2 crosslink based network is necessary for any practical vulcanization process. Based on modulus and the perceived number of crosslinks according to rubber elasticity, the average molecular weight between crosslinks is ~10 kg/mol.

Table 1
Initial characteristics of the polychloroprene material. Note: a) theoretical value calculated from the structure of the monomer unit; b) experimentally determined by elemental analysis; c) calculated from the rubber modulus.

Species	Concentration (mol/kg)	Concentration (mol/l)
Double bonds[a]	11.3	14
Sulfur[b]	0.36	0.45
Crosslink sites[c]	0.09	0.11

2.2. Exposure conditions and sample geometries

Thermal oxidation was performed in Memmert ovens with forced convection at temperatures from 60 to 140 °C ± 2 °C. Exposures were performed on both films (100 μm) and thick samples (4.8 mm). The films were cut from bulk material cooled by liquid nitrogen with a Leica microtome.

2.3. Chemical modifications

Chemical modifications in aged samples such as double bond consumption and carbonyl formation were monitored by FTIR spectroscopy in transmission mode using thin films (about 10 μm thickness). FTIR analyses were performed on a Perkin Elmer Spectrum 2 with a resolution of 4 cm^{-1}. Double bonds were carefully quantified as three peaks located between 1800 cm^{-1} and 1500 cm^{-1} and were fitted with Origin® software using a Gaussian peak for deconvolution purposes after baseline corrections. This deconvolution was explained in a previous study and yielded 3 peaks at 1790; 1725 and 1660 cm^{-1}, with the peak positions not changing as a function of ageing state [14]. The area for the 1660 cm^{-1} peak (double bond) was then calculated and normalized to the unaged material. This ratio was then multiplied by the initial double bond concentration ($[C{=}C]_0 = 14$ mol/l; see Table 1) in order to obtain a quantitative value of changes in double bonds. Therefore, for a specific ageing duration the double bond concentration $[C{=}C]_t$ is calculated as:

$$\left[C=C\right]t = A_{\text{aged sample}}/A_{\text{unaged sample}} * \left[C=C\right]_0 \tag{4}$$

2.4. Oxygen consumption

The consumption of oxygen during thermal ageing was determined using a commercial Oxzilla instrument with the previously described experimental approach [15]. The technique has been established as a routine analysis at Sandia National Laboratories with the instrumental response being calibrated using standard gas mixtures under a specific range setting. Total oxygen absorption in