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Oxidation of unvulcanized, unstabilized polychloroprene: A kinetic study

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ABSTRACT

Thermal oxidation in air at atmospheric pressure, in the 80–140 °C temperature range and in oxygen at 100 °C in the 0.02–3 MPa pressure range, of unvulcanized, unstabilized, unfilled polychloroprene (CR) has been characterized using FTIR and chlorine concentration measurement. The kinetic analysis was focused on double bond consumption. A mechanistic scheme involving unimolecular and bimolecular hydroperoxide decomposition, oxygen addition to alkyl radicals, hydrogen abstraction on allylic methylenes, alkyl and peroxyl additions to double bonds and terminations involving alkyl and peroxy radicals was elaborated. The corresponding rate constants were partly extracted from the literature and partly determined from experimental data using the kinetic model derived from the mechanistic scheme in an inverse approach. Among the specificities of polychloroprene, the following were revealed: The rate of double bond consumption is a hyperbolic function of oxygen pressure that allows a law previously established for the oxidation of saturated substrates to be generalized. CR oxidation is characterized by the absence of an induction period that reveals the instability of hydroperoxides. The kinetic analysis also reveals that peroxyl addition is faster than hydrogen abstraction but slower in CR than in common hydrocarbon polydienes.

1. Introduction

Elastomers derived from vulcanized poly 2 chloro butadiene (polychloroprene) have been known for almost 80 years. They show better resistance to ozone and oil than common hydrocarbon polydienic elastomers and are particularly appreciated for their good properties in aqueous media (gloves, joints, etc.). It is now well recognized that radical chain oxidation is one of the most important modes of thermal ageing for this polymer, that has led to a non-negligible amount of literature in the past half century. Despite that, certain aspects of their degradation mechanisms remain obscure and the available quantitative data remain largely insufficient to envisage non-empirical lifetime prediction based on an indisputable kinetic model. The aim of this work is to try to contribute to the elaboration of such model. It has been chosen to decompose the investigation into several steps, corresponding to material structure and composition of increasing complexity. The first step corresponds to the starting polychloroprene (lCR) linear polymer. In the industrial samples under study, all the other material components (crosslinks, fillers) are in relatively low concentration or unreactive and are thus expected to have an influence of second order on oxidation behaviour. This latter will be thus described as the oxidation of lCR monomer units (and/or structural irregularities) eventually perturbed by crosslinking agents and additives. The second step of the investigation will focus on additive-free vulcanisates (vCR) in order to appreciate the effect of crosslinking agents (here sulphur, of which the effect on oxidation has already been the object of many studies for other elastomers). The third step consists of studying the effect of stabilizers on the oxidation of industrial vulcanisates (iCR).

Concerning the relatively recent literature on polychloroprene thermal ageing, we dispose first of data relative to thermal degradation in neutral atmosphere at 150 °C [1]. NMR and IR data indicate the important role of 1–2/1–4 sequences (Fig. 1). Commercial grades of lCR are essentially composed of 1–4 sequences but some 1–2 isomers are present, and are characterized by the presence of a labile chlorine atom destabilized by its tertiary placement and by the presence of a double bond in an α position. The homolytic splitting of the C—Cl bond is favoured by the resonance stabilization of the resulting allyl radical. Cl° radicals can add to double bonds or

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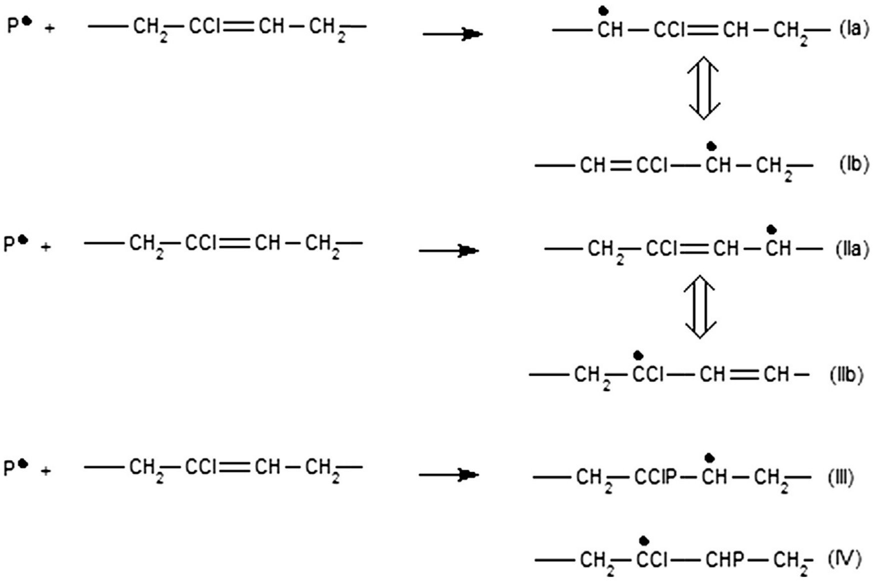

Fig. 1. Possible reactions of the 1–4 monomer unit with a radical.

abstract hydrogens to give hydrogen chloride and thus propagate oxidation. Miyata and Atsumi [1] show a correlation between the yields of 1–2 isomerizations and HCl evolution indicating that the 1–2 isomer is the precursor of both species. How to exploit these results in the frame of a study of thermal oxidation? The first approach is to suppose that oxidation radical chains could be initiated by the thermolysis of a labile polymer bond. The dissociation energy of C–Cl bonds attached to double bonds, as in the monomer unit, is very high; these bonds cannot participate in initiation events. Secondary C–Cl bonds in regular monomer units of PVC for instance have dissociation energy of 320 ± 10 kJ/mol, lower than that of C–H bonds in saturated compounds but stable at least at temperatures lower than 80 °C. Tertiary C–Cl bonds or allylic C–Cl bonds are destabilized by respectively inductive and mesomeric effects; they are often cited as "weak points" in the thermal degradation of PVC. Indeed tertiary C–Cl bonds in allylic placement, combining both destabilizing effects, must be especially unstable. Their dissociation energy is expected to be of the order of 250 kJ/mol. They can therefore play a role in initial steps of lCR or CR thermal oxidation. However, it must be recalled that oxidation leads to the formation of peroxides (including hydroperoxides) of which the dissociation energy is of the order of 180 kJ/mol in hydrocarbon peroxides and significantly lower in α chloro peroxides of which the explosive behaviour at temperatures close to ambient temperature has been the cause of major catastrophes, in PVC polymerization plants for instance.

Let us now consider thermal oxidation. A significant difficulty in the study of polydiene oxidation is the occurrence of two kinds of radical propagation processes: hydrogen abstraction on allylic carbons and addition reactions on double bonds. In the case of a dissymmetric monomer unit such as the polychloroprene one, this opens the way to at least four reaction pathways, even six if isomerizations of allyl radicals are taken into account, Fig. 1.

Let us first note that radicals Ia and Ib are identical, they will be called I here. In the following, only radical Ia will be considered. The existence of intermediary allyl radicals has been recognized for a long time [2]. According to Shelton et al. path II is favoured relative to path I [3] owing to the stabilizing effect of the chlorine atom in the β position of the reacted methylene. Concerning addition reactions, we dispose of the example of PVC polymerization [4] to appreciate the relative probability of the formation of radicals III or IV. It is clear that the "anti Markovnikov" process - in which it is the less substituted carbon which is attacked - is favoured. Additions are thus expected to give predominantly radical IV. To summarize, we expect the presence of essentially three "primary radicals": IIa, IIb and IV.

These radicals react very fast with oxygen to give considerably less reactive peroxy radicals. The latter can abstract hydrogens on allylic methylenes or add to double bonds. As in the case of polyisoprene [5], additions can be inter or intramolecular; in the first case they give crosslinks, in the second they give cycles. In the case of α chloroperoxyls, an interesting peculiarity is the possibility, for the cyclization, to propagate as a zip reaction along the chain. It is noteworthy that, except for hydroperoxides coming from radical IIa, all the other peroxides or hydroperoxides have a chlorine atom in α position. The high instability of α chloro peroxides is well known; it is presumably responsible for the absence of an induction period in lPCR oxidation. Finally, we expect for each primary radical three kinds of products: hydroperoxides, intermolecular peroxide bridges and cyclic peroxides, which may form sequences.

Highly sensitive methods for measuring oxygen absorption allowed interesting quantitative results to be obtained: values of the order of $1.3 \cdot 10^{-9}$ [6] or 3–4 10^{-9} mol kg^{-1} s^{-1} [7] have been observed at 50 °C. The measurements reveal that a steady state is established rapidly after the beginning of exposure. As frequently found, the apparent activation energy for global oxidation is higher at high temperature (typically above 80 °C) than at low temperature [6,7]. This behaviour has been explained by the fact that termination processes, which are the most dependent on segmental mobility among all the other elementary steps of oxidation radical chains, are less and less efficient when the temperature decreases [8].

The nature of stable oxidation products has been investigated by Delor et al. [9] essentially on the basis of IR measurements. As expected the spectra reveal the disappearance of double bonds and the appearance of a variety of oxygen containing structures, among which acid chlorides absorbing at 1790 cm^{-1} of which the presence has been confirmed by derivatization (transformation into primary amine by reaction with ammonia). Delor et al. proposed a mechanistic scheme for processes starting from a hydrogen abstraction event; addition processes were neglected, probably because