



Property modelling

Mechanistic modeling of reversion phenomenon in sulphur cured natural rubber vulcanization kinetics

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ARTICLE INFO

Article history:

Received 16 April 2013

Accepted 7 June 2013

Keywords:

Rubber

Sulphur vulcanization

Reversion

Kinetics

Mechanistic model

ABSTRACT

A novel kinetic model of natural rubber sulphur vulcanization is proposed. The modeling approach takes into account current knowledge on the different polysulfidic structures present during vulcanization, and the associated individual reactions. A simplified scheme is proposed, giving a mechanistic view of the reversion phenomenon, which results in a decrease of the elastic modulus (related to the sulphur crosslink density) for long vulcanization times at high temperature. The resulting set of differential equations is solved by an appropriate numerical method to predict the evolution of the degree of vulcanization for isothermal cure conditions.

The vulcanization kinetics of a model natural rubber compound was characterized experimentally by rheological measurements, in order to test the proposed kinetic model. A remarkable agreement between model predictions and experimental data is observed. The identified kinetic parameters corresponding to the individual reactions taken into account by the mechanistic model are consistent with those of an existing, less refined, pseudo-mechanistic model. The proposed model thus allows bridging the gap between the prediction of macroscopic variations of the elastic modulus and the evolution of molecular scale structure during vulcanization when the reversion phenomenon is present.

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1. Introduction

The vulcanization of natural rubber (NR) with sulphur is particularly complex. Despite its practical application having been known for more than 150 years, its detailed reaction scheme is not still completely understood. Therefore, it remains difficult to model in order to develop efficient numerical simulation tools for the optimization of vulcanization processes.

From a macroscopic phenomenological point of view, the rubber vulcanization reaction results in evolution of the

elastic modulus of the rubber due to the formation of sulphur crosslinks between the polymer chains. Consequently, the practical interest of modeling of vulcanization kinetics is that it allows prediction of the mechanical performance of the material as a function of the thermal history during the curing process. For that reason, the experimental data used for modeling is generally obtained from dynamic rheological measurements of the evolution of the elastic modulus (related to the crosslink density) of rubber samples submitted to controlled cure temperature cycles. As is well known, the crosslink density can be detected by other techniques such as solvent swelling, but the most common and simple one is utilizing cure curves.

Contrary to many thermosetting polymers, the crosslink density of rubber compounds generally starts to increase

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very slowly during an “induction” period, after which the main vulcanization reaction takes place with a significantly faster increase of the crosslink density. Moreover, it can reach a maximum and start to decrease, resulting in weaker mechanical properties for longer curing times. This last phenomenon, called “reversion”, is well known for sulfur cured rubbers at high vulcanization temperatures (typically above 140 °C), and is generally attributed to the formation and subsequent degradation of some of the polysulfide crosslinks [1,2].

The available kinetic models able to predict these three steps of rubber vulcanization kinetics generally describe the induction period separately, assuming that the degree of vulcanization stays equal to zero, until an induction time following an Arrhenius type temperature dependence: This is the case for the mechanistic model of Coran [3], Ding and Leonov [4,5], as well as for the semi-mechanistic model of Han et al. [6]. A more recent semi-mechanistic differential model proposed by Leroy et al. [7] allows continuous prediction of the induction and vulcanization steps. This model is derived from the formalisms of Han et al. [6] and Colin et al. [8], and assumes that during the induction and vulcanization step the overall formation of sulphur crosslinks can be described by a Kamal & Sourour kinetic differential model [9].

Apart from these differences, all the above kinetic models [4–7] have in common the assumption that the reversion phenomenon is the consequence of the formation of two types of sulfur crosslinks during vulcanization: short mono- and disulfide crosslinks, which remain stable, and longer polysulfide crosslinks which can subsequently disappear due to thermal degradation. For example, the semi-mechanistic model of Han et al. [9] assumes the following simplified reaction scheme:



where:

- S represents the sulfur available for the formation of crosslinks;
- C_1 represents the stable sulfur crosslinks formed during vulcanization, with a rate constant K_1 .
- C_2 represents the unstable sulfur crosslinks, formed during vulcanization, with a rate constant K_2 .
- P represents the product of the reversion reaction, corresponding to the degradation of unstable crosslinks, with rate constant K_3 . It is assumed that this reaction is irreversible, the corresponding sulfur being unavailable for the formation of new crosslinks.

Despite these assumptions leading to a reasonable description of the reversion phenomenon, in terms of prediction of the decrease of elastic modulus using a reduced number of kinetic parameters, it is not satisfactory from a mechanistic point of view since it does not allow relating the global reaction kinetics to the current

knowledge of the different individual reactions involved in the reversion phenomenon. The aim of the present paper is to contribute to bridging this gap. We propose to develop a mechanistic model of reversion, taking into account the current knowledge about polysulfide structures formed during vulcanization.

Generally, in sulphur vulcanized rubber, it is commonly accepted that there are three types of sulfidic structures, namely C-S-C (monosulfidic structure), C-S₂-C (disulfidic structure) and C-S_x-C (polysulfidic structure). The primary reaction leading to polysulfidic structures involves the formation of reactive crosslinking precursors (which can typically contain between 2 and 8 S-S links) on a rubber chain by reaction with sulphurating agents. This precursor can then react either with another rubber chain, resulting in a crosslink, or with the same rubber chain by a backbiting reaction, resulting in a cyclic structure. In such a case, the polysulfidic structure does not contribute to the increase of crosslink density.

The evidence for these polysulfidic structures (both crosslinking and cyclic ones) is provided by important physical chemistry literature, obtained by IR, UV, ESR and Raman characterizations [10,11] or with chemical methods [12], or by means of solid state ¹³C nuclear magnetic resonance (NMR) studies [13], as done for instance in [14,15] for EPDM. In this last case, the polysulfidic structures are consistent with predictions based on model compounds and the presence of three different allylic positions in the repeating unit of natural rubber [13].

The percentages of each polysulfidic structure and the value of x depend on both rubber compound composition (sulphur curing system type and concentrations) and reaction conditions such as temperature and curing time [16]. It has been observed experimentally that, in the initial stage of the reaction, more crosslinking C-S_x-C (x = 4, 5 or more) bonds are found than in the later state. It is generally assumed that, when such long (C-S_x-C) polysulfidic crosslinks are formed, they can further react, leading either to shorter crosslinks (C-S-C), through a so called “maturation reaction”, or to cyclic polysulfidic structures by backbiting reactions. In such a case, the crosslink density decreases, which explains the reversion phenomenon if such a reaction becomes dominant.

Given the complexity of the above described reaction scheme which involves several reactions series and in parallel, the kinetic models found in literature generally either assume simplified schemes, such as the one given by Equation (1), or imply the use of simplified or empirical numerical implementation procedures [5,9,17] by practitioners. A rigorous theoretical approach seems still missing.

In particular, in order to propose a sound kinetic model, it is necessary to have in mind the difference of the energy bond between C-S-C and S-S that are respectively equal to 50.9 and 62.0 Kcal/mol. [18]. This indicates that in reality polysulfides crosslinks should not be considered as thermally less stable than mono and disulfides, as in the simplified pseudo-mechanistic model of Han et al. [9] shown in Equation (1).

Nevertheless, it seems reasonable to assume that, once a long polysulfidic crosslink is formed, the probability that the subsequent reactions that it will undergo lead to

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