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Optimization of extrusion production lines for EPDM rubber vulcanized with sulphur: A two-phase model based on Finite Elements and kinetic second order differential equation

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ABSTRACT

A numerical two-phase approach, based on experimental curometer charts and aimed at predicting the optimal production line parameters (exposition time and cure temperature) for extruded thick rubber items cured with accelerated sulphur is presented.

In the first phase, a simple kinetic model based on the actual reticulation reactions occurring during sulphur curing is utilized to fit experimental curometer data. The model is able to predict the degree of crosslinking at successive curing times and at different controlled temperatures and it requires the calibration of only three kinetic constants. The variation of such parameters with temperature is then evaluated by means of three experimental cure curves performed at three different temperatures. Both the case of indefinite increase of the torque and reversion can be handled.

In the second phase, considering the same rubber compound of step one, kinetic reaction parameters are implemented in a Finite Element (FE) software, specifically developed to perform thermal analyses on complex 2D geometries. As an example, an extruded cylindrical thick EPDM item is considered and meshed through four-noded isoparametric plane elements. Several FE simulations are repeated by changing exposition time t_c and external cure temperature T_n, to evaluate for each (t_c,T_n) couple the corresponding mechanical properties of the item at the end of the thermal treatment. An alternating tangent approach (AT) is used to drastically reduce the computational efforts required to converge to the optimal solution associated with the maximization of the average tensile strength.

1. Introduction

The optimization of the industrial vulcanization process of extruded EPDM items cured with accelerated sulphur is a topic of great technical relevance. As a matter of fact, producers are interested in the improvement of the final mechanical performance of polymers and polymer compounds, at the same time limiting the production costs. For instance, sulphur is normally preferred to peroxides merely for economic issues, despite the fact that the performance of rubber cured with peroxides – in terms of final mechanical properties – is much better with respect to that of rubber vulcanized with sulphur. Indeed, from a chemical point of view, sulphur vulcanization determines transversal chains constituted by more than one sulphur atom (link energy 270–272 kJ/mole) whereas for peroxides the link is much more stable, because it is created between two back-bone carbons belonging to contiguous chains (energy 346 kJ/mole).

Another important issue which makes the accelerated sulphur vulcanization rather intricate is that the associated chemical reactions are complex and involve only a few atoms in each polymer molecule. For this reason, to propose a quantitative macroscopic model predicting vulcanization in terms of rubber physical properties is a very difficult task.

In this field, among the others, historical contributions by Ding and Leonov (1996) and Ding, Leonov, and Coran (1996) are worth noting. Essentially, they are numerical approaches conceived for natural rubber, in which the models are enforced to follow simple partial equations similar to peroxide laws.

At present, it can be stated that, while the utilization of sulphur is quantitatively predominant, its chemistry of vulcanization remains an open issue, despite its discovery and utilization go back to Goodyear (Billmeier, 1984; Goodyear, 1844; Krejsa & Koenig, 1993a, 1993b).

Another important issue to consider is reversion, which occurs quite frequently in practice. From a macroscopic point of view, it

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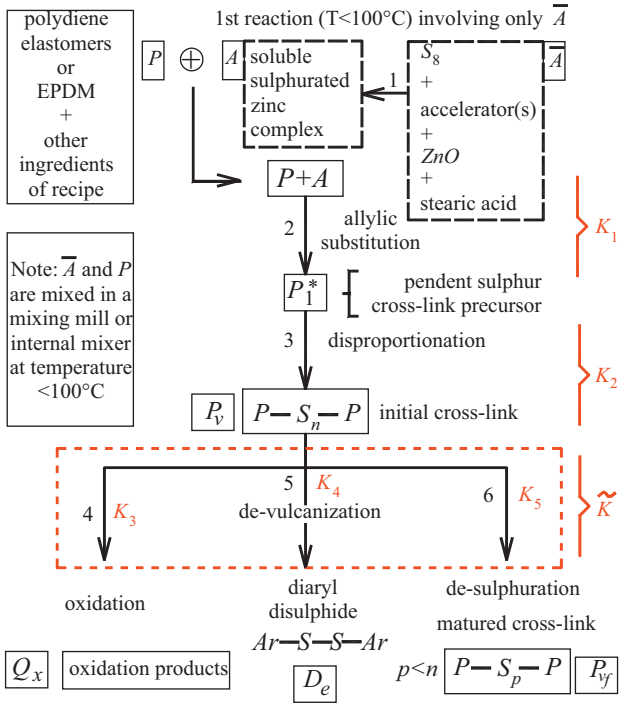

Fig. 1. Products and schematic reaction mechanisms of accelerated sulphur vulcanization of poly-diene and EPDM elastomers.

consists in a remarkable decrease of rubber vulcanized properties at the end of the curing process. Chen, Collins, Shelton, and Koenigs (1982) have shown that this phenomenon seems to appear when two reactions are competing during vulcanization. Reversion is often associated with high-temperature curing. For instance, Loo (1974) demonstrated that, when the cure temperature rises, the crosslink density drops, thus increasing the degree of reversion. Morrison and Porter (1984) confirmed that the observed reduction in vulcanizate properties is caused by two reactions proceeding in parallel, i.e. de-sulphuration and decomposition, see Fig. 1.

Focusing exclusively on EPDM rubber, the commonly accepted basic reactions involved – see also Krejsa and Koenig (1993a) – Fig. 1, are the following:

$$\begin{aligned}
&(a)\quad P + A \overset{K_1}{\rightarrow} P_1^* \\
&(b)\quad P_1^* \overset{K_2}{\rightarrow} P_v \\
&(c)\quad P_v \overset{K_3}{\rightarrow} Q_x \\
&(d)\quad P_v \overset{K_4}{\rightarrow} D_e \\
&(e)\quad P_v \overset{K_5}{\rightarrow} P_{v_f}
\end{aligned} \tag{1}$$

In Eq. (1), P and A are the polymer (EPDM) and soluble sulphureted zinc complex (S_8 + accelerators + ZnO + stearic acid) respectively, P_1^* is the pendent sulfur (crosslink precursor), P_v is the reticulated EPDM, P_{v_f} is the matured cross-link, Q_x is the oxidation product, D_e represents diaryl-disulphide and $K_{1,\ldots,5}$ are kinetic reaction constants. Here it is worth emphasizing that $K_{1,\ldots,5}$ are temperature dependent quantities, hence they rigorously should be indicated as $K_{1,\ldots,5}(T)$, where T is the absolute temperature. In what follows, for the sake of simplicity, the temperature dependence will be left out.

Reaction (a) in (1) represents the allylic substitution in Fig. 1, reaction (b) is the disproportionation, whereas reactions (c) (d) and (e) occurring in parallel are respectively the oxidation, the de-sulphuration and the de-vulcanization.

In this intricate framework, experimentation may represent a good starting point to collect macroscopic information on the degree of cross-linking. The standard test in this field is the so-called cure test, performed on a small rubber specimen maintained at fixed vulcanization temperature by means of traditional oscillating disc (ODR) or rotor-less (ASTM, 2007; Dick & Pawlowski, 1995) (RPA2000) curometers. Torque resistance of the curometer is evaluated at increasing exposition times and plotted in a cure curve, giving indirect macroscopic information on rubber reticulation kinetics at fixed temperature. The torque varies during the test, with a typical decrease in the initial stage, followed by a sudden increase at approximately 1/3 of time needed to complete the test (scorch time). In several cases, torque decreases near the end of the experimentation, exhibiting reversion. A single compound has its own characteristic cure curve at fixed temperature, which characterizes macroscopically the reticulation of the compound. A change in both accelerators molar ratios and temperature room changes the cure curve.

The aim of the present work is to propose a combined experimental and numerical model able to predict macroscopically the effect of accelerated sulphur curing, with particular emphasis on the numerical reproduction of reversion (Coran, 1978; Natta, Crespi, & Mazzanti, 1962; Natta, Crespi, & Mazzanti, 1963).

The approach is a two-phase one. In the first phase, for a given rubber compound, rheometer curves have to be experimentally evaluated at different vulcanization temperatures (at least three), ranging from low to high. Then, a kinetic model is developed, basing on reactions reported in Fig. 1. After some mathematical considerations on the reactions involved, a simple second order non-homogeneous differential equation is derived, representing the degree of reticulation (or conversely the torque resistance) of rubber. Parameters to set in the kinetic model are only three and a closed form solution is derived.

Once evaluated the kinetic constants involved in the reticulation process, the second phase relies on implementing kinetic model parameters within a non-standard FE software, for a thermal analysis of realistic thick rubber items. The software developed allows obtaining, element by element, temperature profiles at increasing curing times and the increase of output mechanical properties (tensile strength, tear resistance, elongation) as a function of curing time, passing through the numerical database collected in the first phase. As a matter of fact, each point of the item undergoes different temperatures, with considerable differences passing from the skin to the core. The corresponding crosslinking level for each point of the item is numerically evaluated (Morton, 1981) at fixed exposition time throughout the database collected in the first phase (reticulation kinetic model), allowing an estimation point by point of any output mechanical property.

In order to assess the capabilities of the two-phase approach proposed, in the paper an example of engineering interest is analyzed in detail, relying on a rubber thick cylinder (ray 18.8 mm) with a central circular hole of diameter equal to 16 mm. The compound used to realize the cylinder is an EPDM rubber with a medium amount of propylene content (about 40% in weight) and 4.5% in weight on ENB, vulcanized through accelerated sulphur, as described in detail next.

A recently presented bi-sectional procedure (alternating tangent approach AT; Milani & Milani, 2010, 2008) is utilized to determine, with a very limited computational effort, optimal input parameters (curing external temperature T_n and rubber exposition time t_c) for the example at hand. Output mechanical property (objective function) to optimize is represented by the average final tensile strength of the item.