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Degradation of styrene butadiene rubber (SBR) in anaerobic conditions

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ABSTRACT

In this work, the degradation kinetics of styrene butadiene rubber (SBR) in solution was studied in anaerobic conditions. Degradation reactions in the presence of cumene hydroperoxide at different concentrations (0.20, 0.28, 0.32, 0.50, 0.60% in weight), temperatures (60, 75, 85, 100 and 120 °C) and aromatic solvent (10 and 20%) were performed. The fragmentation rates of polymer chains, which define the degradation kinetics, were calculated from the change in molecular weight distribution with time. The degradation was performed in a reactor with anaerobic conditions and the characterization was performed by multiangle light scattering coupled to size exclusion chromatography (SEC-MALS). Using population balance equations, it was possible to calculate the kinetic constants for thermal and thermooxidative degradation. Analysis of the results led to the conclusion that random scission of polymer chains produced by macroradicals formed by hydrogen abstraction constituted the predominant SBR degradation mechanism. Adding alkylbenzene as a transfer agent significantly reduced the degradation.

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1. Introduction

Physical properties of polymers depend to a large degree on molar mass, its distribution and molecular architecture, therefore, chain scission and crosslinking play an important role in polymer performance. For this reason, it is important not only to evaluate the chemical changes in a polymer reaction, but also the changes in molar mass distribution [1].

Polydienes degradation occurs at specific sites because double bonds in the main chain act as reactive points. A series of hydrogen transfer reactions may occur in polydienes when they are heated in the absence of oxygen. Transfer of allylic hydrogen can lead to chain scission. Pendant vinylene groups promote the lability of allylic hydrogen, producing stable radicals, leading to β scission processes or chain recombination [1,2]. The scheme of the β scission for polybutadiene (PB) is shown in Fig. 1a and b.

In the presence of peroxides, degradation of these polymers occurs throughout a mechanism of abstraction of the allylic hydrogen in the main chain, which may result in either a β scission or a crosslinking reaction from the recombination or termination reaction at high concentration. Thermal degradation of PB has been described with the reaction scheme shown in Fig. 1b [2].

Likewise, for polystyrene (PS) degradation, a free radical mechanism has been proposed where the radical generated from the hydrogen abstraction of the tertiary carbon can be stabilized by induction effects of aromatic rings and can then undergo chain scission as shown in Fig. 1c [3].

These scission reactions do not imply the termination of the macro-radicals, therefore, they can be considered as chain reactions that increase the number of chains in the system and lead to low molecular weight products.

Peroxides and hydroperoxide homolitic decomposition with temperature lead to reactive primary alcoxy radicals, which are stabilized by abstracting labile hydrogen from the polymer chains to form more stable tertiary or allylic radicals [4,5].

Polymer degradation processes may be described by population balance equations (PBE), which can model the changes in molar

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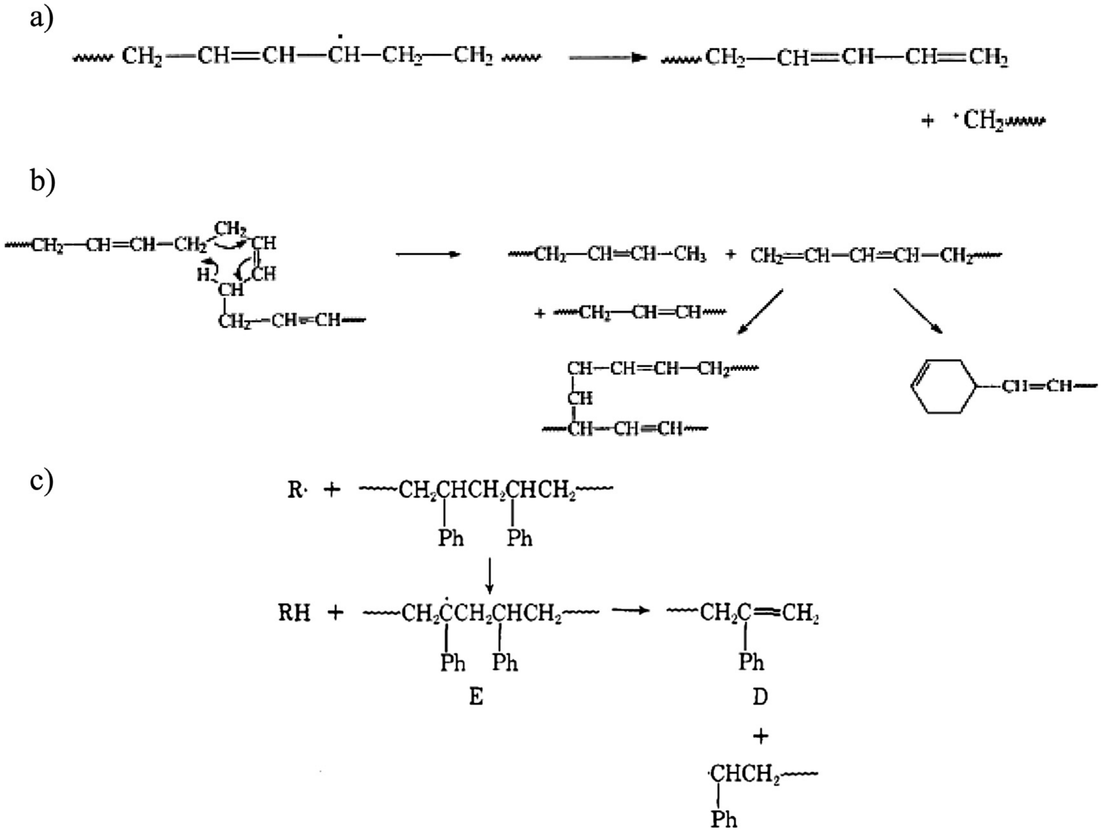

Fig. 1. a) β Scission of PB from allylic radical [2] b) Reaction scheme proposed for thermal decomposition of PB [2] c) Mechanism for free radical degradation of Polystyrene [3].

mass distribution as a consequence of polymer chain fragmentation.

In this work, the kinetics aspects of the anaerobic degradation of a styrene butadiene rubber (SBR) dissolved in a paraffinic mineral oil as a function of time is evaluated. The parameters studied are: temperature, concentration of an organic hydroperoxide, and concentration of a radical transfer agent.

The molar mass distribution is obtained by gel permeation chromatography (GPC) coupled with multiangle light scattering (SEC-MALS). The fragmentation kinetic is analyzed by population balance equation (PBE) theory.

2. Model description

One of the advantages of using PBE is the possibility of including phenomenological parameters that affect the kinetics of degradation reactions. It is also a way to handle continuous mixtures of particles of the same chemical features, and analyzing continuous reactions in one single integro-differential equation.

If x is the molar mass of a polymer chain, the weight molar mass distribution is given by $xf_1(\mathbf{x}, t)$, while the number molar mass distribution is $f_1(\mathbf{x}, t)$. The molar concentration of the polymer in a molar mass range of $(x,x + dx)$ is $f_1(\mathbf{x}, t)dx$.

Thus, the total number of particles in a specific time t, can be calculated as:

$$N(t) = \int f_1(x,t)\mathrm{d}x \tag{1}$$

Fig. 2 shows two density functions, one at time $t = t_0$ and the other at time t. Considering a subset of the x domain, $[a,b]$, the change in number of molecules in time $t–t_0$ is given by the shaded region, defined as [6]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_a^b f_1(x,t)\mathrm{d}x = \frac{\mathrm{d}N}{\mathrm{d}t} \tag{2}$$

The n-th moments of the distribution can be also defined as:

$$\mu_n = \int_0^\infty x^n f_1(x,t)\mathrm{d}x \tag{3}$$

Then, the zero moment is given by the area below the curve defined by the number molar mass distribution, and represents the total molar concentration, or number of moles of polymer chains.

The first moment is the total mass of the polymer or mass concentration, and may be represented by Equation (4):

$$\mu_1 = \int_0^\infty x f_1(x,t)\mathrm{d}x \tag{4}$$

Assuming mass conservation during the reaction, the first moment should be constant in time.

From distributions moments it is possible to determine other important characterization parameters, such as the number average molecular weight $M_n = \mu_1/\mu_0$, the weight average molecular weight $M_w = \mu_2/\mu_1$; and the polydispersity index $M_w/M_n = \mu_2\mu_0/\mu_1^2$.

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