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Determining rubber composition of waste tyres using devolatilisation kinetics

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ABSTRACT

The rubber composition of three different waste tyre crumbs has been predicted using a kinetics model for tyre devolatilisation. The kinetics are based on a sophisticated mechanism which includes two consecutive devolatilisation reactions for the rubbers and a single intermediate condensed product. Activation energies are obtained using model-free kinetics and are subsequently incorporated as fixed values in model-based kinetics. The model has been validated with binary and ternary mixtures of three predominant tyre rubbers (natural polyisoprene, butadiene and styrene-butadiene rubber) and subsequently applied for three waste tyre crumbs consisting of different ratios of passenger car and truck tyres. It turned out that the model is capable of predicting the natural polyisoprene content very accurately. Due to the similarity of butadiene and styrene-butadiene rubber, discriminating quantitatively between these two rubbers is notoriously difficult. The present model is however capable of correctly indicating increasing styrene contents in tyre crumbs.

1. Introduction

There are many different types and brands of tyres, which typically also have different rubber compositions. Once tyres reach their end-of-life they will be, if intended for recycling, accumulated irrespective of their particular rubber composition. At present the main selection criterion is tyre type, separating mainly between truck tyres (TT) and passenger car tyres (PCT). In order to efficiently use these mixtures of waste tyres for recycling purposes, their actual rubber composition is an inconvenient unknown.

There have been several previous attempts to determine the rubber composition of waste tyres using various analytical methods. These methods include Py-GCMS [1,2], TGA-MS [3], TGA-DSC [1,4–6], TGA-FTIR [1,7], and TGA in combination with devolatilisation kinetics [8,9]. All these studies indicate that it is not a straightforward exercise to obtain an accurate prediction of the rubber composition, and especially to make a distinction between the butadiene and styrene-butadiene rubber contents. Lee and coworkers concluded from their comparative study that Py-GCMS was the most accurate method [1]. However, both studies using devolatilisation kinetics assumed that all rubbers devolatilise fully independently and therefore use simple superimposition of the devolatilisation of the pseudocomponents [8,9], a methodology that can be improved.

The devolatilisation kinetics of waste tyres has been extensively investigated over the last decades [10,11]. Generally, a mechanism with three independently reacting pseudocomponents has been assumed [12,13], while some studies included consecutive reactions [14], parallel reactions of single pseudocomponents [12], or elastomer-simulation as the pseudocomponents [15]. Although the results of the application of these more advanced devolatilisation mechanisms were promising, they have not yet been applied for the prediction of rubber contents in waste tyres.

Next, model-based kinetics, with a power-law function as the conversion function, are most widely employed for the modelling of waste tyre devolatilisation kinetics [12–15]. Model-free isoconversional methods have been implemented more sparingly [16,17].

The objective of this study is to obtain the rubber composition of waste tyre crumbs using combined model-free and model-based kinetics employing a sophisticated devolatilisation mechanism. This paper consists of three parts. First the devolatilisation mechanism and kinetics modelling approach is presented. Subsequently, the model is validated with experimental results of binary and ternary mixtures with known compositions of natural polyisoprene rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR). Finally, the model is applied to three waste tyre crumbs with different TT to PCT ratios.

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2. Experimental

Natural rubber (SMR 20) was sourced from Continental Tyre SA, while 97% *cis*-polybutadiene rubber (Neodene 40) and a styrene-butadiene random copolymer (Afpol 1500, 23.5% styrene) were both procured from Karbochem, a local rubber manufacturer. The rubbers have been cryogenically milled in order to obtain a particle size below 1 mm, but other than that were used as received. Three different tyre crumbs (all with mesh size 40) were obtained from three different local tyre recycling companies (Dawhi Rubber Recycling, SA Tyre Recyclers and Goswell Developments) and used as received.

A Mettler Toledo TGA/DCS 1 analyser was used for the kinetics experiments. For the binary and ternary validation experiments samples were prepared to be 12 mg, while for the experiments with the crumbs a sample size of 10 mg was used. Experiments have been performed in duplicates to verify reproducibility. The average values of the relative standard deviation between the duplicates of the rubbers and tyre crumb experiments are 4.5% and 2.5%, respectively. The former value is higher due to additional variations in the exact masses of the individually weighed rubbers. The kinetics experiment consisted of a drying period of 5 min at 110 °C, followed by a ramp up to 600 °C at constant heating rate (5, 10 and 20 °C min^{-1}) and a nitrogen flow of 100 mL min^{-1}. It is assumed that at these particle sizes and heating rates mass and heat transfer limitations are negligible [18].

3. Kinetics model

A waste tyre crumb particle consists of four main constituents, i.e., a filler, ash, chemical additives and the rubber mixture. Firstly, it is assumed that the filler (generally carbon black) and ash are inert and not influencing the rubber devolatilisation [19]. Next, the chemical additives evaporate separately from the rubbers to volatiles at lower temperatures. Finally, the devolatilisation of the rubbers proceed via two consecutive devolatilisation reactions, i.e., primary depolymerisation and crosslinking (condensation) of the polymers and consecutive secondary degradation of the intermediate condensed product (ICP). This rubber devolatilisation mechanism is summarised in Fig. 1 and has been discussed in more detail previously [20,21].

While it is assumed that the rubbers depolymerise independently and similarly as they would separately, they all contribute to a single ICP. This results in the tyre devolatilisation mechanism as presented in Fig. 2. The weight ratios involved in either primary or secondary devolatilisation for each rubber were taken from experiments with the individual rubbers [20]. The other weight fractions, i.e., those of the additives and the three rubbers in the tyre matrix, are estimated in the present model.

For the evaporation reaction of the additives (R1) and the rubber depolymerisation reactions (R2–R4) previously determined kinetics parameters are used [20]. Furthermore, the ICP, which originates from crosslinking (condensation) of the polymer radicals during depolymerisation, is a mixed product of all the three rubbers, since these reactions cannot be assumed to be selective for any type of rubber. Therefore, a single ICP is formed for every tyre crumb, and one set of kinetics parameters (E, A and n) has to be estimated for its degradation reaction (R5). Accordingly, although a sophisticated devolatilisation mechanism is employed, only six parameters have to be estimated, i.e., the E, A and n of the degradation reaction and the weight fraction (γ) of the additives and of two of the three rubbers (the last is calculated by difference).

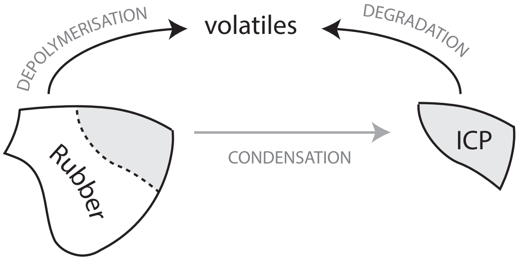

Fig. 1. Devolatilisation mechanism of a tyre rubber. ICP = intermediate condensed product.

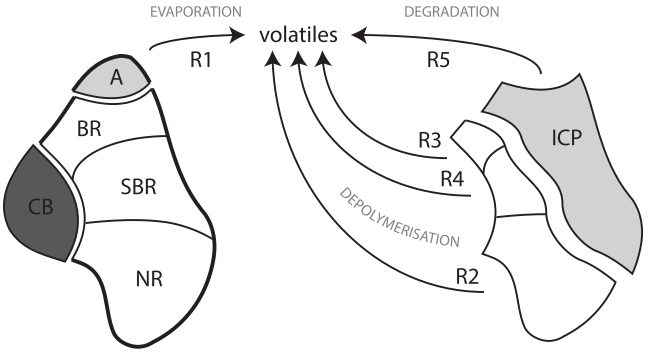

Fig. 2. Devolatilisation mechanism of a waste tyre crumb particle. A = additives; CB = carbon black; NR = natural rubber; BR = butadiene rubber; SBR = styrene-butadiene rubber; ICP = intermediate condensed product.

The activation energy E of the degradation reaction is determined separately using the Friedman method, a differential model-free isoconversional technique [22]. Values of E are calculated for constant values of the conversion between 0.01 and 0.99 with intervals of 0.01. Next, for every heating rate the conversion corresponding to maximum weight loss during degradation was determined (these values typically differ only 2–4% between the different heating rates). Finally, the average of all values of E between the maximum and minimum conversion corresponding to the peak of degradation for the different heating rates was taken as the final value of E. This value is then implemented in the model-based kinetics.

The applied model-based kinetics are similar to those used for the separate tyre rubbers [20]. This model entails a multivariate non-linear regression method of the solid-state Arrhenius rate of change of the conversion,

$$\frac{d\alpha_j}{dt} = A\,exp\left[-\frac{E}{RT}\right](1-\alpha_j)^n \tag{1}$$

where α_j represents the conversion of pseudocomponent j (–), t time (s), A the pre-exponential factor (s^{-1}), E is the activation energy (J mol^{-1}), R the universal gas constant (8.314 $\text{J mol}^{-1}\,\text{K}^{-1}$), T the temperature (K) and $(1-\alpha)^n$ is the conversion function, with n as the reaction order (–). The total change in conversion for the tyre crumb is then,

$$\begin{aligned}\frac{d\alpha}{dt} &= \gamma_A\frac{d\alpha_A}{dt}\\ &\quad+(1-\gamma_A)\sum_{i=1}^{N}\left[\gamma_i\gamma_{i,1}\frac{d\alpha_{i,1}}{dt}\right]\\ &\quad+(1-\gamma_A)\sum_{i=1}^{N}[\gamma_i\alpha_{i,1}]\sum_{i=1}^{N}[\gamma_i\gamma_{i,2}]\frac{d\alpha_2}{dt}\end{aligned} \tag{2}$$

where i represents the ith rubber of a total of $N = 3$ rubbers and the subscript A, 1 and 2 indicate the additives or the fraction of the rubbers that devolatilise via primary and secondary devolatilisation, respectively. Note that the three main terms in Eq. (2) (from top to bottom) correlate with the evaporation, depolymerisation and degradation reactions as indicated in Fig. 2, respectively.