Modelling of the Grafting of Maleic Anhydride Onto Polyethylene in an Extruder

A. V. Machado, A. Gaspar-Cunha*, J. A. Covas

Department of Polymer Engineering, University of Minho, 4800-058 Guimarães, Portugal

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Abstract

Grafting of maleic anhydride onto polyethylene is studied both computationally and experimentally. The mathematical model involves coupling the reaction kinetics to the description of flow in a twin-screw extruder. The predictions match the experimental observations satisfactorily.

Introduction

Grafting monomers onto thermoplastics using twin-screw extrusion is an important chemical modification technology, since this is a relatively inexpensive and rapid way of producing materials with desirable properties. Most of the attention on grafting of monomers onto polyolefins has focused on maleic anhydride, because of its high reactivity with most polymers containing reactive groups [1]. A good physical understanding of the chemical reactions occurring in compounding extruders is currently available [2, 3]. The kinetic model of the reaction has also been developed [4], but is still necessary to couple it to a modeling routine of twin-screw extrusion. This work performs this coupling, by modifying the LUDOVIC software (which is a commercial code developed to predict co-rotating twin screw extrusion) in order to include the reaction kinetics and thus to predict properties of the modified polyethylene (grafted MA content, molecular weight distribution and rheological behaviour). The predictions are compared with experimental data.

Kinetic model

The radical reactions between a vinyl monomer and polyethylene encompass the following steps:
a) Thermal decomposition of the initiator (usually, organic peroxide):

$$I \rightarrow 2R \cdot (k_d) \tag{1}$$

b) Radical attack onto polymer:

$$R\cdot + P \rightarrow RH + P\cdot (k_{tr}) \tag{2}$$

c) Initiation of grafting onto polymer:

$$P\cdot + M \rightarrow PM\cdot \left(k_g\right) \tag{3}$$

d) Termination:

$$P\cdot + P\cdot \rightarrow P - P(k_t) \tag{4}$$

$$PM\cdot + P \rightarrow PMH + P\cdot (k_{tr}) \tag{5}$$

The thermal decomposition of the initiator provides the primary free radicals (Re) that attack the polymer backbone. Abstraction of hydrogen from the latter provides a macroradical initiating the desired grafting reaction. The proposed kinetic scheme is completed by various terminations. Fukuoka [4] developed a kinetic model based on the above scheme, which yields the reaction rate (equations 6 and 7), molecular weight distribution (equations 8 to 10) and rheological properties (equations 11 to 14) of the modified material.

$$\frac{dq}{dt} = K(1-q)\sqrt{[I]} \tag{6}$$

where q is the reaction conversion defined as:

$$q \equiv \frac{[M]_0 - [M]}{[M]_0} \tag{7}$$

and K is an apparent rate constant.

$$[P_n]_k = \frac{\lambda_2}{n} + \left([P_n]_{k-1} - \frac{\lambda_2}{n}\right)\exp\left(-n\lambda_1 \Delta t\right. \tag{8}$$

where:

$$\lambda_1 \equiv \frac{2fk_d[I]}{[P]} \tag{9}$$

$$\lambda_2 \equiv \frac{\sum_{r=1}^{n}\ r[P_r](n-r)[P_{n-r}]}{[P]} \tag{10}$$

$$\eta_{\dot{\gamma}} = \frac{\eta_0}{1 + C(\eta_0\dot{\gamma})^{1-m}} \tag{11}$$

$$\eta_0 = B\exp\left[\frac{\Delta E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{12}$$

$$B = \alpha_1 \bar{M}_w^{3.4} + \alpha_0 \tag{13}$$

$$C = \beta_1 \frac{\bar{M}_z}{\bar{M}_w} + \beta_0 \tag{14}$$

Flow in co-rotating twin screw extruders. The flow conditions inside an intermeshing conjugated co-rotating twin-screw extruder were determined using the LUDOVIC [0]software. In this program, the screws are sub-divided into the conveying, left handed and kneading blocks elementary units, local one-dimensional approaches being used to describe the flow. Since this type of extruders operates with external gravimetric/volumetric feeding, i.e., under starve fed conditions, the channelfilling ratio is unknown a priori. Hence, computations are carried out at the die and proceed backwards, up to the melting location, which is known. However, since the temperature at the die exit is also unknown, an iterative procedure is required. The software yields the main flow parameters, such as melt temperature, melt pressure, shear rate, viscosity, residence time, specific mechanical energy and filling ratio, all along the screws.

Coupling flow with reaction kinetics. Fig. 1 illustrates the structure of the program developed. Initially, the process flow parameters are computed using the LUDOVIC software. These comprise the pressure, the residence time distribution and the temperature axial profiles, as well as the velocities along the extruder. Then, the evolution of the maleic anhydride, peroxide and molecular weight distribution along the extruder of the modified polyethylene can be predicted considering the local melt temperatures and residence times.

An iterative procedure is then initiated, involving the calculation of new flow parameters, which depend on the molecular weight distribution calculated initially. The program ends when the MWD difference between two consecutive iterations is lower than a predefined error.

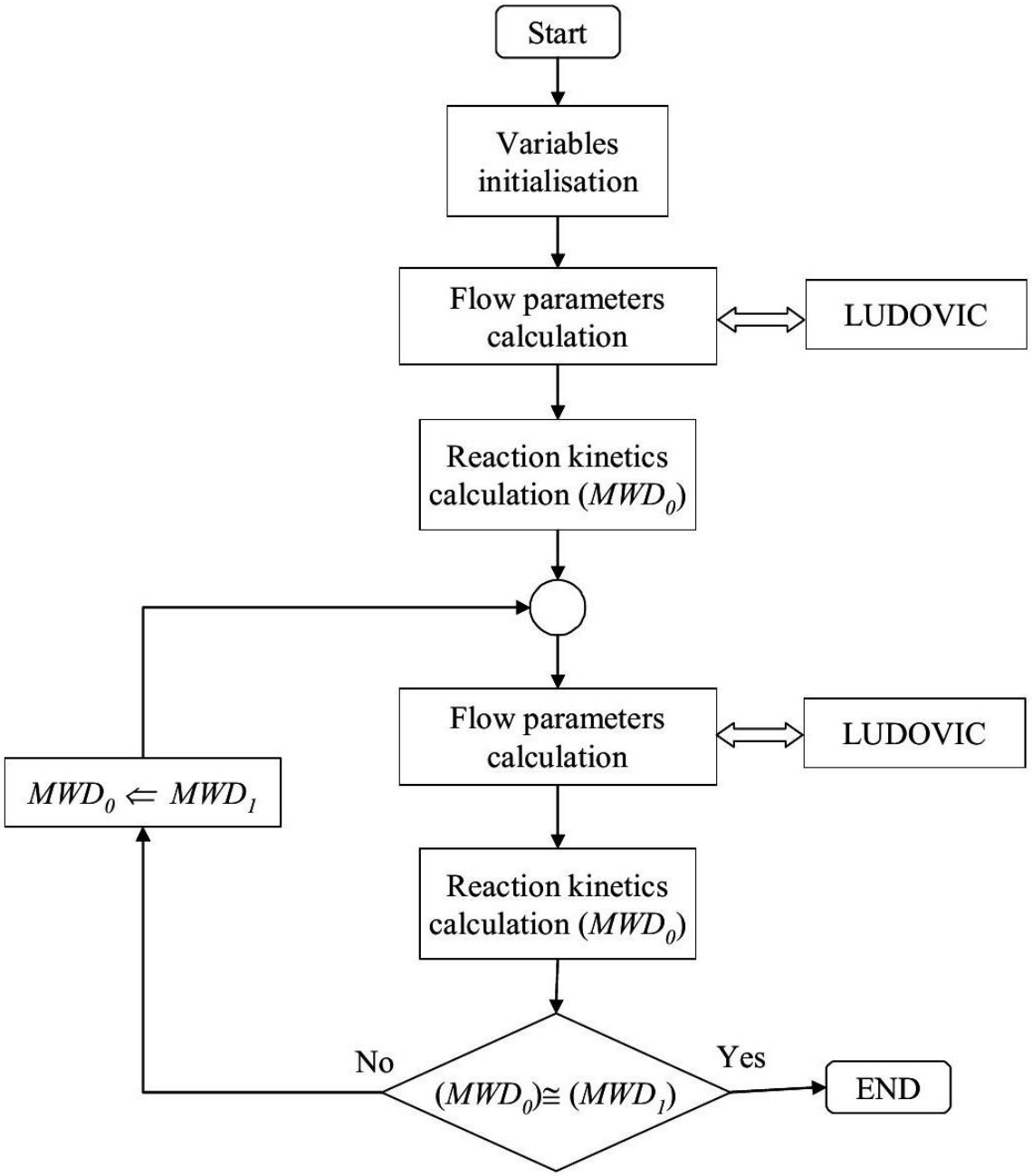

Fig. 1. Flowchart of the calculation of the reaction kinetics in the extruder.

Modeling versus experiments

Polyethylene was modified with 5 phr maleic anhydride and 1 phr peroxide (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane) in a Leistritz LSM30.34 co-rotating twin screw extruder operating with a flow rate of 10 kg/h (via a K-TRON gravimetric feeder), the screws rotating at 150

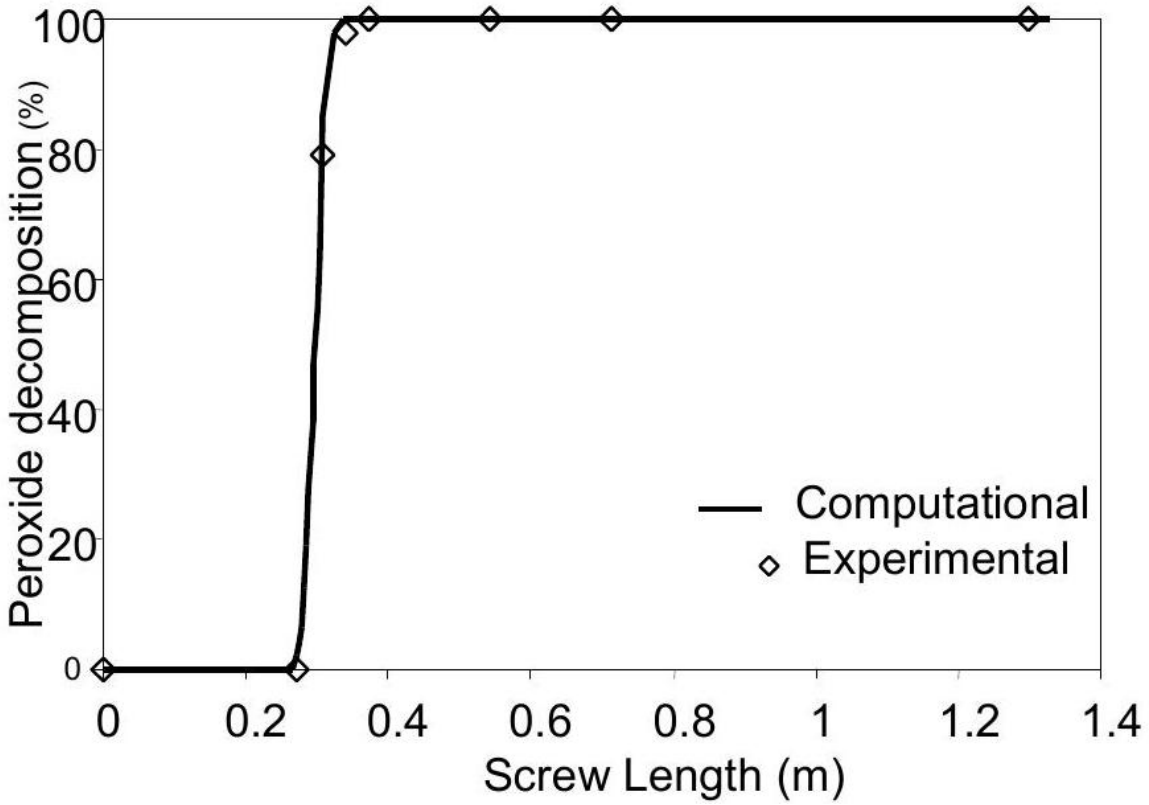

Fig. 2. Peroxide decomposition along the screw axis. Computational versus experimental data. rpm and the barrel/die set uniformly at 150°C. Samples were collected along the barrel at specific locations using available sampling devices. The residual peroxide was determined by Gas Chromatography, whereas the MA content was quantified by FTIR (see detailed description at [5]). Fig. 2 compares the resulting computational and experimental results. The good correlation between both is evident. The reaction takes place in the first part of the extruder, i.e., upon melting of the polymer, which is consistent with previous work [3]. This can be explained by the local temperature, residence time and the low half-life of the peroxide under these conditions.

Conclusions

Mathematical modeling of a grafting reaction occurring in a twin-screw extruder was implemented and validated experimentally, despite the need of further evidence to support this conclusion. This tool can now be used for optimization purposes, i.e., to determine the best operating conditions or screw geometry inducing the highest conversions.

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