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Improvement of the thermal stability of branched poly(lactic acid) obtained by reactive extrusion

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ABSTRACT

One-step reactive extrusion-calendering process (REX-calendering) has been used in order to obtain sheets of 1 mm from poly(lactic acid) modified with a styrene-acrylic multifunctional oligomeric agent. In a preliminary internal mixer study, torque versus time has been monitored in order to ascertain chain extender ratios and reaction time. Once all the parameters were optimized, reactive extrusion experiments have been performed. An enhanced general analytical equation has been developed in order to evaluate the kinetic parameters of the thermal degradation of PLA sheets manufactured by reactive extrusion. This improvement has consisted of replacing the n-order conversion function by a modified form of the Sestak–Berggren equation $f(\alpha) = c\,(1-\alpha)^n\alpha^m$ that led to a better adjustment of experimental data and also adequately represented the conventional mechanisms for solid-state processes. The kinetic parameters so obtained have been compared to those determined by conventional differential methods and n-order reaction kinetics. Given that the thermal degradation of PLA has been argued to be caused by random chain scission reactions of ester groups, the conversion function $f(\alpha) = 2\,(\alpha^{1/2} - \alpha)$, corresponding to a random scission mechanism for $L = 2$ (as well as other functions for L values up to 8), has been tested. Once optimized the kinetic model, the thermal degradation kinetics of sheets obtained by REX-calendering process was compared to that of conventional sheets and polymer matrix.

1. Introduction

In the 21st century, due to the increasing environmental consciousness renewable resource based and inherently biodegradable polymers gain more and more role. One of the most promising renewable resources to produce biopolymers is starch. Its fermentation allows the production of poly(lactic acid) (PLA). In the beginning, poly(lactic acid) was mainly used for medical applications due to its high fabrication costs but now PLA polymers have finally found a commercial application in single use disposal items due to its low price compared with other biodegradable polymers. However, proportions as little as 4% mol of the D-lactic enantiomer (typical in commercial grades) reduce the rate of crystallization to such levels that, in standard processing conditions, the product is practically amorphous and has brittle behavior [1]. As well as many aliphatic polyesters, PLA is subject to some thermal degradations and instabilities above its melting temperature, especially during processing. Radical and non-radical reactions were proposed to explain the various and complex mechanisms that could occur during processing, leading to a reduction of the molecular weight and viscosity. As a result, a general decrease in the material properties is expected [2]. Several authors [3,4] reported that the residual water or moisture content inside the polymer matrix activates hydrolysis reactions implying the split-up of the ester linkage into alcohol and acid carboxylic groups. Doi et al. (1990) [5] as well as Yu et al. (2003) [6] argued that thermal and hydrolysis reactions for biocopolymers could be generated by random chain scission reactions of the ester groups. Coupled with these two last mechanisms, intra- and intermolecular transesterification reactions could also cause a drop in molecular weight at longer reaction times [7,8]. In fact, backbiting effect (zip-like depolymerization) leads to the formation of cyclic oligomers (lactide) and lactic acid which is catalyzed by the presence of monomers, oligomers or hydroxyl groups. Pyrolysis mechanisms should also be considered but at high temperatures (>300 °C) where cis-elimination gives rise to the formation of carboxylic acid groups and a polymer chain containing acryloyl groups [9].

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The extrusion process can take advantage of these degradation reaction products when combined with reactive agents, this promoting different types of chemical reactions [10]: (a) Free radical, anionic, cationic, condensation and coordination polymerization of monomers or oligomers to high molecular weight polymers; (b) Controlled degradation and cross-linking of polymers by means of a free radical initiator for preparing a product with controlled molecular weight distribution; (c) Functionalization of commodity polymers for producing materials to be used in grafting applications; (d) Polymer modification by grafting of monomers or mixture of monomers onto the backbone of existing polymers for improving various properties of the starting materials. Free radical initiators and ionizing radiation can be used to initiate the grafting reactions; (e) Interchain copolymer formation. Usually, this type of reaction involves combination of reactive groups from several polymers to form a graft copolymer; (f) Coupling reactions that involve reaction of a homopolymer with a polyfunctional coupling agent/filler in the preparation of high-performance products. On one side, reactive extrusion is an attractive way to minimize the degradation effects during processing and to enlarge its processing window. On the other side, Corre et al. [11] as well as Pilla et al. [12] reported that chain architecture modification by chain branching enhances PLA melt properties. Chain branching degree depends on the functionality of the reactive agent and generally leads to an increase in molecular weight.

A new aspect that arises in this communication, in comparison with previous works [11,12] on this subject, was the production of structural modified PLA sheets through one-step reactive extrusion-calendering process (REX-calendering) in a pilot plant. The main goal is to obtain sheets that could be used directly in the manufacturing of thermoformed packaging and other applications.

The ever increasing commercial importance of polymeric materials has entailed a continuous interest in their thermal stability. As a consequence, a huge number of papers dealing with this topic have been published in the last years [13–23]. The kinetic modeling of the decomposition process plays a central role in many of those studies, being crucial for an accurate prediction of the materials behavior under different working conditions [2,24–36]. A precise prediction requires the knowledge of the so called kinetic triplet, namely, the activation energy, the pre-exponential factor and the kinetic model, $f(\alpha)$. This latter parameter, also known as conversion function, is an algebraic expression that is associated with the physical model that describes the kinetics of a solid state reaction. Therefore, the kinetic analysis also provides some understanding of the mechanism of the reaction under study. Knowledge of the mechanism of thermal degradation of available macromolecules is very helpful in the field of the thermal stability of polymers [19].

Although the temperatures of the TGA experiments (up to 390 °C at a heating rate of 10 K/min) are higher than those of the processing operating conditions (up to 175 °C), the experiments carried out under linear heating rate are used to determine the thermal stability and the kinetic parameters driving the thermal degradation process. It should be noted that when proper kinetic parameters are obtained for the decomposition processes, those processes could be modeled and predicted under conditions different from those used in the conventional TGA experiments (including assays at lower temperatures such as those used during the polymer processing). Moreover, when the polymer is processed, its chemical structure changes. This modification in its molecular architecture can be assessed by means of TGA. When polymer fragments are created as a consequence of processing, they will be more readily volatilized during high temperature TGA conditions. On the contrary, when chain length increases by using a chain extender, the macromolecular branched structure will be less readily volatilized. Moreover, the results obtained by TGA (α vs t, $d\alpha/dt$ vs t and $d^2\alpha/dt^2$ vs t) represent the “thermal fingerprints” of the polymer, which is an excellent way to identify its molecular architecture after its processing. On the other hand, pieces manufactured with this polymer can undergo degradation at temperatures higher than those present during its processing due to service conditions (i.e. material exposed to heat and accidents, among others).

The analysis was performed by means of the differential kinetic equation and the general analytical equation (GAE), developed by Carrasco (1993) [37], by using two different conversion functions: the n-order kinetic model and a modified form of the Sestak–Berggren equation (1971) [38]. The introduction of the conversion function developed by Sestak–Berggren into the general analytical equation has allowed the GAE to be enhanced. The kinetic parameters thus obtained were used to construct the experimental master plots $f(\alpha)/f(0.5)$ in order to ascertain the best reaction mechanism(s) representing the thermal degradation of sheets obtained by REX-calendering (*i.e.* nucleation and growth, geometrical, reaction order, diffusion and random scission).

2. Theoretical background

The reaction rate of a solid state reaction can be described by the following differential equation:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where A is the Arrhenius pre-exponential factor, R is the gas constant, E the activation energy, α the reacted fraction, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α. Equation (1) is a general expression that describes the relationship among the reaction rate, reacted fraction and temperature independently of the thermal pathway used for recording the experimental data. In the case that the experimental data were recorded at a constant heating rate $\beta = dT/dt$, Equation (1) can be written as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

2.1. Analysis based on parameters at the maximum reaction rate

The most known method which is based on parameters at the maximum reaction rate was proposed by Kissinger (1957) [39]. Its equation can be formulated as follows:

$$\ln\frac{\beta}{T_m^2} = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_m} \tag{3}$$

2.2. Isoconversional analysis

Isoconversional methods (*i.e.* model-free methods) are used for determining the activation energy as a function of the reacted fraction without any previous assumption on the kinetic model fitted by the reaction. The main used methods are those proposed by Friedman (1964) [40] and Flynn-Wall–Ozawa (1966, 1970) [41,42]. These methods provide accurate values of activation energies even if the activation energy was a function of the reacted fraction. The Friedman method is a differential method which calculates kinetic parameters at a given α. The Flynn-Wall–Ozawa method is an integral method which also determines parameters at