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Material Behaviour

Degradation during processing in poly(butylene adipate-*co*-terephthalate)/vegetable fiber compounds estimated by torque rheometry

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ABSTRACT

The effect of filler type and concentration on the rate of degradation of poly(butylene adipate-*co*-terephthalate)/vegetable fiber compounds was studied using a convenient and sensitive procedure based on torque rheometry, which was used for the quantitative estimate in real time of incipient degradation during melt processing in polymer systems. It was found that the presence and level of two filler types, taken from two different layers of the fruit of the babassu palm tree, greatly enhance the slight degradation tendency of the matrix when processed in a laboratory internal mixer. The qualitative trends and quantitative estimates may be explained by the chemical and morphological characteristics of the two fillers, as observed by optical microscopy.

1. Introduction

The economic and social importance of biodegradable and environmental-friendly materials – among them polymer matrix compounds – is so well known by specialists and lay people alike, as to dispense further comment [1,2]. The compounds studied in the present work are based on the synthetic semicrystalline thermoplastic polyester poly(butylene adipate-*co*-terephthalate) (PBAT), which is fully biodegradable, with reasonable mechanical and barrier properties, coupled with a thermal stability better than most natural polymers [3,4]. The filler, vegetable fibers derived from the fruit of the babassu palm tree, is a low-cost fully renewable resource [5]. Consequently – if the incorporation of this kind of filler enhances or lowers the properties to a tolerable extent – PBAT/babassu compounds could be an economically significant development. This is one of the motivations of the present contribution.

Among the characteristics that may be affected by filler content and processing conditions is degradation under processing. Degradation is an insidious phenomenon that affects practically all polymers. Biodegradable thermoplastic blends and compounds are particularly prone do thermal and thermo-oxidative degradation during processing, manifested through diminishing molar mass, which may significantly affect the final properties of the product [6–9].

Melt viscosity is very sensitive to slight changes in molar mass. Consequently, rheological methods are widely used to study changes in molar mass attributed to degradation [10,11]. Torque rheometry is a fairly simple method that has not been fully exploited in polymer degradation studies. Although it has been proposed to study the melt processing of temperature sensitive thermoplastics [12], to date no systematic use has been reported of the use of rate of torque drop as a measure of the rate of degradation. Torque rheometry provides a fast and simple way to study the initial stages of polymer degradation under simulated processing conditions [13].

In an internal mixer operated at constant rotor speed, torque is proportional to viscosity during the last stages of processing – the processing of a filled or unfilled melts. At the moderate rates of mostly shear deformation prevalent in the processing chamber of internal mixers, viscosity depends on a 3.4 power of the weight average molar mass, if in the newtonian plateau, with a slightly

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lower exponent in the transition region [13–15]. For this reason, melt viscosity – as opposed to intrinsic viscosity – is the property of choice to study small variations of molar mass.

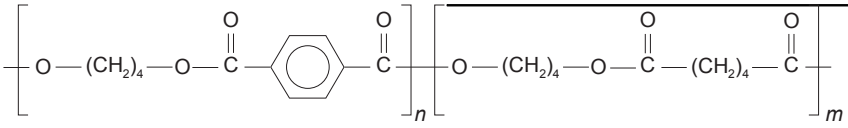
While torque rheometry cannot provide very precise values of the absolute viscosity, the technique is well suited for comparative studies: to investigate the effect of composition and processing condition on melt viscosity, hence in molar mass. It has been successfully applied to investigate the efficiency of chain extender additives that compensate viscosity drop caused by incipient degradation and "recover" the rheology of the melt [16], or even significantly increase it [17]. In this contribution, we extend the methodology to plain degradation.

Two different types of vegetable filler will be tested: a fine flour derived from the mesocarp (middle layer) of the babassu fruit, and a coarse fibrous material obtained from the epicarp (external layer) of the fruit. Optical microscopy is used to reveal the degree of dispersion, while torque rheometry is applied to study the effect of filler type and loading level on the increase or decrease of viscosity and rate of degradation, compared with neat matrix.

2. Experimental

2.1. Materials

The polymeric matrix tested is the poly(butylene adipate-*co*-terephthalate) (PBAT), commercially available as BASF Ecoflex® F Blend C1200, simply PBAT according to the manufacturer.



PBAT has a density of 1.26 g/cm^3 at ambient temperature, melt flow rate between 3 and 5 dg/min (ISO 1133, 190°C/2.16 kg), glass transition temperature of −30 °C, and crystalline melting temperature at 110–115 °C [2]. A slightly higher melting point of 135 °C and a low degree of crystallinity (10–15%) was observed in our laboratory [18].

The vegetable fillers used are the mesocarp and epicarp obtained from the babassu fruit (*Orrbignya speciosa*), coming from Florestas Brasileiras S.A., Itapecuru-MIrim-MA. The babassu mesocarp is given in micronized form (codded: meso) and the epicarp as short fibers (codded: epi). The fillers are used as received and show heterogeneous natural products without pre-processing.

Babassu mesocarp is composed of cellulose (45%), hemicellulose (34%), and lignin (18%) with 3% of mineral ashes; epicarp has less cellulose (30%) and more lignin (33%) with only 1% ashes [19]. Density of the raw fillers were measured pycnometry, obtaining values of 1.49 ± 0.02 and 1.17 ± 0.01 g/cm^3 for mesocarp and epicarp, respectively.

2.2. Methodology

Samples of neat PBAT and composites containing 10, 20 and 30% mesocarp and epicarp were processed in a Haake Rheomix 3000 laboratory internal mixer, fitted with high intensity ("roller" type) rotors, operated at a nominal speed $N = 120$ rpm. The processing chamber was 70% full in all cases, estimated at room temperature, and its walls were kept at 170 °C, during all tests. The processing time was 20 min. In composites, the matrix was fed at the beginning of the test, followed by incorporation of the filler 1–2 min later, without interrupting the process. The software of the instrument supplied numerical values of time t, internal temperature T (taken as the mean temperature of the material inside the processing chamber during the melt processing stage), and total torque Z.

2.2.1. Torque rheometry analysis

In tests performed in an internal mixer operated at constant rotor speed, during the last processing stage (melt processing) torque Z is directly proportional to melt viscosity η:

$$Z = k_1 \eta \tag{1}$$

and viscosity is proportional to a high power of the weight-average molar mass of the polymer matrix M_w [10]; for a pseudoplastic melt of index n, approximately:

$$\eta = k_2 M_w^{2,5+n} \tag{2}$$

Constants k_1 and k_2 depend on mixer geometry, material properties, processing conditions, and temperature [14,15]. For PBAT under processing conditions at 120 rpm $n \approx 0{,}8$ [17].

Viscosity, hence torque, depends on temperature and molar mass; variations of torque during the terminal stage of processing could be attributed to the combined effect of melt temperature and matrix molar mass changes. The effect of temperature may be eliminated using a temperature-adjusted torque Z*:

$$Z^* = Z \exp\{\beta(T - T^*)\} \tag{3}$$

where T^* is an arbitrary (constant) temperature, and β is the exponential temperature coefficient of the viscosity [15]. For PBAT, $\beta \approx 0{,}020$ °C^{-1} has been determined experimentally in previous work [17].

Once a terminal time interval Δt is chosen (between 15 and 20 min in this work) the relative rate of change of adjusted torque is, approximately:

$$R_Z = \frac{1}{\overline{Z^*}} \frac{\Delta Z^*}{\Delta t} \tag{4}$$

where $\overline{Z^*}$ is the mean value over the selected time interval, may be taken as a measure of the rate of degradation; $100R_Z$ is just the percent variation of adjusted torque per unit processing time. Because the high-power dependence of torque on molar mass, Eqs. (1) and (2), R_Z is a very sensitive – albeit comparative – way to measure the rate of degradation under processing.

A similar measure, more direct but less sensitive, may be the relative rate of change of the weight-average molar mass, approximately:

$$R_M = \frac{1}{\overline{M_w}} \frac{\Delta M_w}{\Delta t} = \frac{1}{\Delta t} \left(\frac{\Delta Z^*}{\overline{Z^*}} \right)^{1/(2,5+n)} \tag{5}$$

derived from Eqs. (1), (2) and (4); $100R_M$ is the percent variation of