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Thermal degradation studies of poly(trimethylene carbonate) blends with either polylactide or polycaprolactone

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ABSTRACT

The thermal stability and degradation kinetics of poly(trimethylene carbonate) (PTMC) blends with different ratios of polylactide (PLA) and alternatively polycaprolactone (PCL) were investigated by thermogravimetric analysis under a nitrogen atmosphere. These studies were extended to the single components (i.e. PCL and PLA). In all cases, the derivative thermogravimetric curves indicated a complex decomposition process with at least two degradation steps. The kinetic parameters of the main step, including activation energy, reaction model and pre-exponential factor, were evaluated by the Kissinger, isoconversional (Friedman and KAS) and Coats–Redfern methods. Data of the main decomposition process were obtained by mathematical deconvolution of experimental DTG curves acquired at heating rates ranging from 2 to 40 °C/min.

It was demonstrated that degradation of blends did not correspond to a mere superposition of the characteristic decomposition processes of the two involved polymers. Furthermore, PCL and PLA influenced the decomposition of the less thermally stable PTMC component in a different way. Thus, PLA modified the degradation of PTMC, and specifically led to thermal stabilization and a new decomposition process characterized by a higher activation energy. On the other hand, PCL favored the degradation of PTMC by enhancing a typical minor decomposition process that occurred in the single component at a lower temperature.

The main decomposition step of PTMC, PLA, PCL and the studied blends always followed an Avrami model but with significant differences in their exponents (i.e. from 2 to 7).

1. Introduction

The use of biodegradable polyesters derived from lactones (e.g. polyglycolide (PGL), polylactide (PLA) and polycaprolactone (PCL)) in temporary biomedical applications has increased significantly over the past decade [1–4]. These materials can be used in various forms (films, fibers, foams, etc.) to cover a wide set of applications that range from bioabsorbable sutures, implantable medical devices or tissue engineering scaffolds to controlled drug delivery systems [5–9]. However, a constant effort to develop materials with improved properties is required due to the complex requirements of clinical applications.

In this way, poly(trimethylene carbonate) (PTMC) and its derivatives are currently receiving great attention due to their high flexibility [10] and potential applications as biomaterials, in particular in soft tissue engineering [11–13], and even as monofilament surgical sutures [14–16].

Evaluation of thermal stability and the degradation mechanism is crucial because materials are usually melt-processed. Hence, it is necessary to take precautions when polymers have high melting temperatures, as is the case of glycolide and lactide derivatives. Thermal degradation behavior of polymers can be modified by incorporation of different chemical units in the main chain and even by blending. For example, it has been reported that degradation behavior of copolymers constituted by glycolide and trimethylene carbonate units as well as blends of PTMC and PGL was significantly different from that determined for the corresponding homopolymers [17]. Specifically, the main degradation step of blends of PTMC and PGL had activation energies and frequency factors between those calculated for the homopolymers. Furthermore, degradation proceeded according to a well differentiated mechanism. The main goal of the present work is to provide insight into the thermal stability of physical mixtures based on PTMC and commercial polylactones such as PLA and PCL, complementing previous data obtained with PGL.

Degradation studies on PTMC indicated that two processes were involved in its decomposition: a non-radical ester interchange reaction leading to the corresponding cyclic monomer, and a random decarboxylation reaction (Fig. 1) [18]. The latter was the

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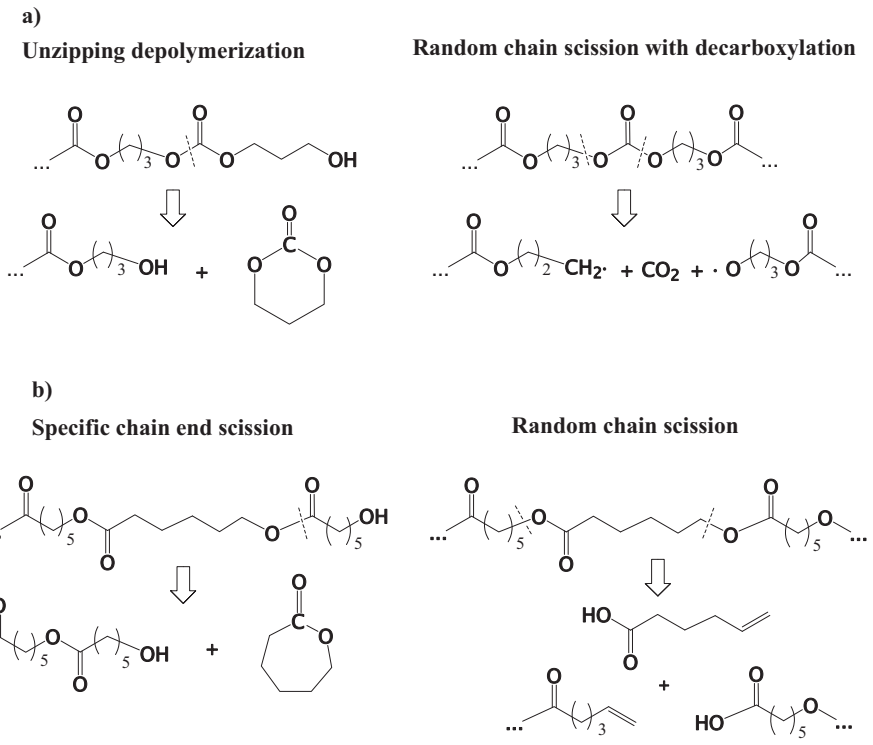

Fig. 1. (a) Unzipping depolymerization and decarboxylation reactions postulated for the degradation of poly(trimethylene carbonate) [18]. (b) Decarboxylation and backbiting reactions postulated for polycaprolactone [24].

main decomposition process and occurred at the highest temperature. The kinetics of this step was recently evaluated by the KAS, Friedman and Coats–Redfern methodologies [17], which gave an activation energy between 79 and 85 kJ/mol. An A_3 mechanism and a frequency factor $\ln(A/\text{min}^{-1})$ of 14.6 were also deduced.

Studies on the thermal degradation of PLA have provided different interpretations ranging between a first-order reaction model and a complex decomposition process [19,20]. Moreover, highly controversial results are still given in the most recent works. For example, it has been postulated a complex reaction process with the participation of at least two different mechanisms: an *n*th-order with an activation energy of 116–117 kJ/mol for the first process (F_n), and an *n*th-order with autocatalysis (C_n) and an activation energy of 161–162 kJ/mol for the second mechanism [21]. On the other hand, thermal degradation for conversion degrees between 0.2 and 0.7 has also been described by a nucleation model (A_2) [22] which suggests the presence of active zones (nuclei) favoring the formation and growth of gas bubbles in the polymer melt [23]. In this case, the activation energy calculated by the Friedman and Kissinger methods was close to 207 kJ/mol [22].

Thermal degradation studies concerning polycaprolactone have revealed the existence of two well differentiated steps through analysis of evolved products: chain cleavages randomly distributed along the chain with formation of H_2O, CO_2 and 5-hexenoic acid for the low temperature decomposition process and depolymerization via an unzipping polymerization process for the high temperature step (Fig. 1) [24]. The Friedman and Chang methods of analysis showed a 3-fold change (from 75 to 230–259 kJ/mol) in the activation energy from low to high temperatures during degradation [25].

2. Experimental

2.1. Materials

Trimethylene carbonate, initiator (diethylene glycol, DEG) and catalyst ($Sn(Oct)_2$) were purchased from Boehringer Ingelheim, Panreac and Sigma–Aldrich, respectively. Polymerization of trimethylene carbonate was performed under a nitrogen atmosphere in a stainless steel jacketed batch reactor at 0.2 MPa and 180 °C. PTMC was obtained with a weight average molecular weight of 83,000 g/mol. PTMC was amorphous with a glass transition temperature of −15 °C.

Polylactide, a product of Natureworks® (polymer 2002D), was kindly supplied by Nupik International (Polinyà, Spain). According to the manufacturer, this PLA has a D content of 4.25%, a residual monomer content of 0.3%, a density of 1.24 g/cm^3, a glass transition temperature (T_g) of 58 °C and a melting point of 153 °C. Polycaprolactone (M_w: 65,000 g/mol) was purchased from Sigma–Aldrich.

Blends of PTMC with either PLA or PCL were prepared by melting and mixing the appropriate amount of each homopolymer in the sample pan. Mixtures are named as PLA/PTMC-*x* and PCL/PTMC-*x* where *x* indicates the weight percentage of PLA or PCL in the blend.

2.2. Measurements

^{1}H NMR spectra were obtained with a Bruker AMX-300 spectrometer operating at 300.1 MHz. Chemical shifts were calibrated using tetramethylsilane as an internal standard and deuterated chloroform was used as the solvent.

Thermal degradation was determined at heating rates of 2, 5, 10, 20 and 40 °C/min with around 5 mg samples in a Q50 thermogravimetric analyzer of TA Instruments under a flow of dry nitrogen and in the temperature range from 50 to 600 °C. Deconvolution of the derivative thermogravimetric analysis (DTG) curve was performed with the PeakFit v4 program by Jandel Scientific Software using an asymmetric function known as “asymmetric double sigmoidal”.