Thermal degradation kinetics and decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and low molecular weight aliphatic diols

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ABSTRACT

In the present work three novel alipharomatic polyesters, namely poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), and poly(butylene 2,5-furandicarboxylate) (PBF) have been prepared by applying the two-stage melt polycondensation method. The interest for polyesters prepared from renewable resources has increased recently, since they can be synthesized using monomers, like furfural or hydroxymethylfurfural and aliphatic diols. A systematic investigation of the thermal stability and decomposition kinetics of furanoate polyesters was performed using thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectroscopy (Py–GC/MS). From TGA curves and activation energies it was found that PBF is less stable thermally, than the other two polyesters. The thorough studies of evolving decomposition compounds along with the isoconversional and model-fitting analysis of mass loss data led to the proposal of a decomposition mechanism for every polyester. The decomposition mechanism of 2,5-furandicarboxylate polyesters was evaluated with Py–GC/MS and from the identified decomposition products it was found that the decomposition of these polyesters is taking place mainly via β-hydrogen bond scission and in lower extent with α-hydrogen scission. 2,5-Furandicarboxylic acid, furoic acid, allyl- and diallyl-compounds are produced in the first case while aldehydes in the second. Radical decomposition also takes place producing carbonyl compounds.

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1. Introduction

The worldwide concern on the shortage of non-renewable petroleum resources over the last decades, has lead the interest of the academic and industrial community towards the development of novel chemicals and materials based on renewable resources [1–5]. Towards this scope, several biobased polymers and polymer nanocomposites have been prepared and are already well-established in commercial uses [6–8]. One of the major problems of such materials is that the prices of the monomers and oligomers which are used as building blocks for those biobased materials is still high, however the continuously growing research efforts, are expected to contribute to the lowering of those costs.

Among these efforts, polyesters based on furan monomers, constitute a unique family of polymers prepared from vegetable renewable resources. 5-Hydroxymethylfurfural (HMF) is already widely available and it is synthesized from sugars and polysaccharides. HMF can be used to synthesize with its turn, 2,5-furandicarboxylic acid (FDCA), which is a member of the furan family, is a biomass-derived product [9,10] and it is considered one of the most promising monomers for the synthesis of polyesters, polyamides, and polyurethanes. The key structural feature associated with FDCA is the close resemblance to its aromatic counterparts, which enables it to synthesize polymers via step-growth mechanisms [11]. FDCA can be produced from cellulose or semicellulose through a multistep process [12], its structure is similar to that of terephthalic acid (TA) and in the near future, it is expected to replace the petrochemical-based terephthalic acid on several occasions. Besides their similar structure, some differences in their ring size and their polarity can attribute different characteristics to FDCA and TA-based polyesters. TA exhibits an

interatomic distance of 5.731 Å between carboxylic acid groups, while FDCA is shorter, the distance being 4.830 Å. Furthermore, the linear *p*-phenyl connection in TA results in an angle of 180° between carboxylic acid carbons, while the nonlinear structure of FDCA presents an angle of 129.4° [13].

The emerging developments on the synthesis of FDCA [13–15], have led to the preparation of several FDCA based polyesters, such as poly(ethylene 2,5-furandicarboxylate), poly(butylene 2,5-furandicarboxylate), poly(propylene 2,5-furandicarboxylate), and others, along with some FDCA-based copolyesters. Most of the literature reports which present the synthesis procedure, also perform a comparison between the FDCA-based polyesters and the respective TA-based polyesters [12,16–19]. However, there is no published work concerning the comparative study of the thermal degradation of these polyesters and the evaluation of their decomposition mechanism. As a matter of fact, the temperature window for processing as well as for applications of a polymer is strongly dependent on its thermal stability and for this reason several reports look into the decomposition of the materials by using thermogravimetric analysis [1–5,10,13,20–23]. To avoid a gradual deterioration of the physical properties of a polymeric product, thermal degradation reactions must be inhibited or retarded. In turn, successful stabilization must be based on an understanding of the precise mechanism by which each type of degradation occurs.

In the current manuscript, a set of furan based polyesters [poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), and poly(butylene 2,5-furandicarboxylate) (PBF)] has been synthesized by melt polycondensation under mild conditions using 2,5-furandicarboxylic acid and aliphatic diols with 2–4 methylene groups (ethylene glycol, 1,3-propanediol, and 1,4-butanediol). The aim of the present work is to study the thermal degradation of these polyesters along with a decomposition kinetics study, which was implemented on the experimental data from thermogravimetric analysis (TGA), in order to reveal similarities and differences on their decomposition mechanism. Furthermore, pyrolysis-gas chromatography/mass spectroscopy (Py–GC/MS) was employed on the polyesters in order to identify the individual fragments from each sample and obtain structural information concerning the decomposition mechanism of these polyesters.

2. Experimental

2.1. Materials

2,5-Furandicarboxylic acid (purum 97%), 1,2-ethyleneglycol (EG, anhydrous 99.8%), 1,3-propanediol (PD, ≥99.6%), 1,4-butanediol (BD, 99%), and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. All other materials and solvents used were of analytical grade.

2.2. Synthesis of 2,5-dimethylfuran-dicarboxylate (DMFD)

15.6 g of 2,5-furandicarboxylic acid, 200 mL of anhydrous methanol and 2 mL of concentrated sulfuric acid were transferred into a random flask (500 mL) and the mixture was refluxed for 5 h. The excess of the methanol was distilled and the solution was filtered through a disposable Teflon membrane filter. During filtration, dimethylester was precipitated as white powder and after cooling 100 mL of distilled water was added. The dispersion was partially neutralized by adding Na_2CO_3 5% w/v during stirring, while pH was measured continuously. The white powder was filtered and the solid was washed several times with distilled water and dried. The isolated white methylester was recrystallized with a mixture of 50/50 v/v methanol/water. After cooling
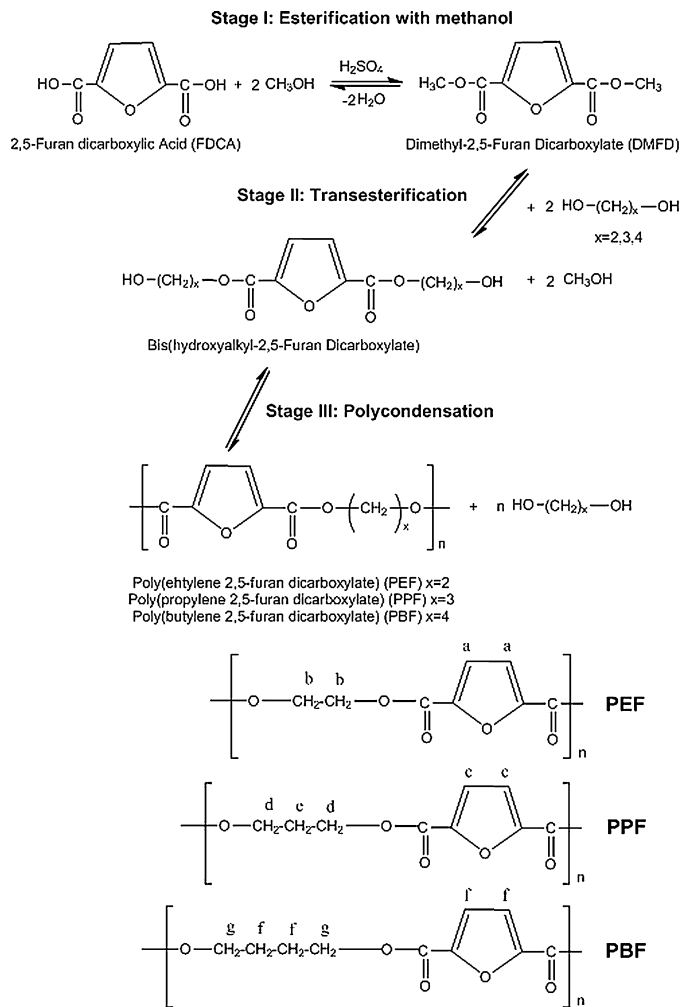
Scheme 1. Synthetic route for 2,5-furandicarboxylate polyesters.

2,5-dimethylfuran-dicarboxylate (DMFD) was precipitated in the form of white needles. The reaction yield was calculated at 83%.

2.3. Polyester synthesis

The polyesters were prepared by the melt polycondensation method as shown in Scheme 1 in a glass batch reactor [24,25] using the proper amounts of DMFD/diols = 1/2.2, which were charged into the reaction tube of the polyesterification apparatus. TBT (400 ppm) was added as catalyst.

2.4. Polyester characterization

2.4.1. Intrinsic viscosity measurement

Intrinsic viscosity [η] measurements were performed using an Ubbelohde viscometer at 30 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). The sample was maintained in the above mixture of solvents at 90 °C for some time to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter made from Teflon.

2.4.2. Nuclear magnetic resonance (NMR)

^{1}H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. A mixture of deuterated trifluoroacetic acid (DTFA) and chloroform in a ratio 3/1 w/w (DTFA/CDCl₃) was used as solvent in order to