



Standard methods for characterizations of structure and hydrolytic degradation of aliphatic/aromatic copolyesters

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ABSTRACT

Aliphatic/aromatic copolyesters, which possess good mechanical property and degradability, are of immense interest. Standard characterization techniques for the copolymer structure and degradation behaviors have been developed. The techniques are applied to examine hydrolytic degradation of poly(ethylene terephthalate-co-lactic acid) in a phosphate buffer solution (pH 7.2) at 60 °C. The weight loss of the copolymer and pH of the medium as a function of time are examined. ¹H NMR spectra provide information on microstructure and molecular weight of the samples, where deviations of the results from the actual values are observed, due to low solubility of the copolymer. More accurate results are obtained from TGA and FTIR experiments, as the samples are characterized in bulk. Insight into degradation mechanisms of the copolymer is derived from FTIR spectra. The content of aromatic esters in the soluble degraded species is determined from UV–Vis spectroscopy. These standard methods can be applied to various types of degradable aliphatic/aromatic copolyesters, which are essential in property assessment and determination of their potential applications.

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1. Introduction

The demand for plastic use has rapidly increased, due to the material versatility and durability. This, in turn, adversely generates large amounts of wastes, which causes serious environmental problems. Decomposition of petroleum-based plastic wastes requires long time periods, because the material is highly resistant to environment influences such as humidity or microbial attack. One of the current mass-produced synthetic polymers that is highly resistant to biological and hydrolytic degradation is poly(ethylene terephthalate) (PET), a thermoplastic aromatic polyester that has excellent material properties. PET is commercially used in various applications, such as textile fibers, soft-drink bottles, and packaging films. Owing to the increased awareness of environmental issues, recycling of PET has been practiced [1,2]. However, this is difficult or inexpedient due to technical and economic considerations.

A promising alternative to replace conventional plastics in mass use is (bio)degradable polymers, in which various types of aliphatic polyesters play a major role with respect to industrial relevance

[3,4]. Polylactic acid (PLA) offers the advantage of being not only degradable, but also renewable since its monomer, lactic acid (LA), is produced from microbial fermentation of agricultural raw materials [4–6]. PLA possesses physical and mechanical properties comparable to commodity plastics, and can be processed like most thermoplastics. In addition, its degradability can be incorporated into other polymers to produce materials with desired properties for specific applications [7–13]. As a result, PLA and its derivatives have gained popularity for use in agricultural, biomedical, and packaging applications.

Given their respective advantages, copolymerization of PET and PLA produces an aliphatic/aromatic copolyester with excellent mechanical properties but still retains its degradability. Many studies have focused on the synthesis, characterizations, and processability of these copolymers [7–9,14–17]. Olewnik et al. reported that the synthesis and characterizations of poly(ethylene terephthalate-co-lactic acid) (PET-co-PLA) by a melt reaction of LA and bis-(2-hydroxyethyl terephthalate) (BHET) in the presence of tin(II)chloride [8]. Acar et al. synthesized a similar copolymer, but from a different process, where recycled PET bottles and LA monomer were employed as starting materials [7].

In our recent work, copolymers of terephthalate and lactic acid were synthesized from LA, dimethyl terephthalate (DMT) and

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various diols as monomers. The resulting aliphatic/aromatic copolymers showed appreciable hydrolytic degradability in phosphate buffer solutions at room temperature and at 60 °C [16], which is in good agreement with other reports [4,7,9,16,18]. Characterization of chemical structures and degradation mechanisms of the resulting copolymers are essential for assessment of the materials properties. ^1H NMR is commonly employed in the structure characterization of the copolymers. Measurement of percentage weight loss of sample as a function of degradation time is a simple technique that is widely employed [4,7,11,18]. However, the results from this experiment cannot provide insight into mechanisms of degradation and structure of the degraded species. The low solubility of the copolymers also limits the use of NMR measurement in some samples, especially for those with high aromatic contents.

In this work, standard characterization techniques utilizing FTIR, TGA, and UV–Vis spectroscopy have been developed to assess the chemical structure and degradation behaviors of aliphatic/aromatic copolyesters. These are applicable to copolymer samples with various aromatic contents, as dissolution is not required in the sample preparation. Advantages and disadvantages of individual characterization techniques are compared and discussed.

2. Experimental

2.1. Materials

Lactic acid (LA) (88 wt aqueous solution), ethylene glycol (EG), and potassium dihydrogen phosphate (KH_2PO_4) were purchased from Carlo Erba. DMT and BHET were supplied by Acros. Antimony trioxide (Sb_2O_3) was provided by Sigma–Aldrich. All chemicals were used without further purification.

2.2. Synthesis of PET-co-PLA copolymer

PET-co-PLA copolymer was synthesized by polycondensation of LA, DMT and EG, using a Sb_2O_3 catalyst, as described earlier [16,19,20]. Properties of the copolymer before and as a function of degradation times were characterized by ^1H NMR, FTIR, XRD, TGA, and DSC experiments. An overview of properties characterizations and examinations of degradation behaviors is summarized in Fig. 1. Chemical structure and properties of the original copolymer were characterized. The copolymer was then subject to hydrolytic degradation, where degree of degradation and mechanisms were examined by following the weight loss and changes in chemical structure of the remaining solid sample. The nature and content of the soluble degraded species were also characterized by examining UV–Vis spectra and pH of the medium.

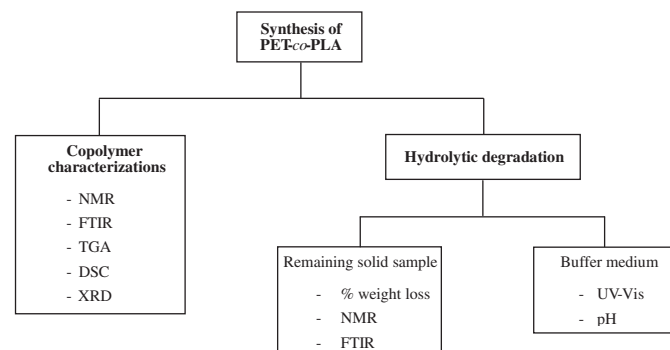


Fig. 1. Overview of experimental procedures.

2.3. Hydrolytic degradation tests

Hydrolytic degradation tests were performed in a 0.1 M phosphate buffer solution at pH 7.2 by using accelerated conditions, *i.e.* low-MW copolymer in powder form at high temperature. The copolymer powder was placed in vials containing the buffer solution at 60 °C. After certain times of incubation, the remaining solid was removed from the buffer medium, and dried in a vacuum oven at 60 °C for 3 days. The dried sample was weighed and its weight loss was calculated. Chemical structure and thermal stability of the remaining sample were characterized by ^1H NMR, FTIR, and TGA experiments. The buffer medium was not renewed during the degradation period, and its pH was measured as a function of hydrolysis time using a pH meter (Ecoscan pH5). The content of the degraded species dissolved in the buffer medium was analyzed by a UV–Vis spectroscopy.

2.4. Characterizations

^1H NMR spectra of the original copolymer and its degraded products were recorded on a 500 MHz spectrometer (a Bruker ZHO48201 AV500D). A 7% v/v trifluoroacetic acid/ CDCl_3 mixed solvent was used. The spectrum was recorded immediately after the preparation of solutions to avoid end-group esterification of copolymer [8,21]. FTIR spectra were recorded on a Thermo Nicolet 6700 spectrometer. Solid samples were mixed with KBr powder and pressed into a pellet form. The concentration of sample in KBr powder was carefully determined to obtain spectra that obey the Beer–Lambert’s Law, which is essential for quantitative analysis. Each spectrum was recorded in a transmission mode with a total of 16 scans at a 2 cm^{-1} resolution. Quantitative analysis was performed by employing the “Peak resolve” module integrated in the OMNIC program.

DSC analysis was performed in N_2 atmosphere on a Mettler Toledo DSC 822. Transition temperatures were measured on the second heating curves. Samples were scanned from 0 to 240 °C at a heating/cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere from 20 to 1000 °C using a Mettler Toledo TGA/SDTA851⁶ at a heating rate of 20 °C/min. Differential TGA thermogram (DTGA) was generated and used in the determination of thermal degradation of the samples. Crystal-line characteristics of the copolymer samples were characterized by X-Ray Diffractometer (XRD, JEOL JDX-3530) using $\text{Cu K}_{\alpha 1}$ radiation, scanning from 2θ of 5–50° with a 0.02° step size.

UV–Vis spectroscopic analysis (Spectronic Genesys 10 UV Scanning) was performed to determine hydrolysis mechanisms. The buffer medium before and after specific hydrolysis time was transferred into a quartz cuvette. Absorption spectra were recorded from 200 to 400 nm. UV–Vis spectra of low-MW analogues of aromatic and aliphatic esters and carboxylic acid compounds, *i.e.*, BHET, LA, and acetic acid were analyzed. Alkali-degraded BHET solutions were employed in the construction of a standard curve to quantitatively determine the content of degraded aromatic esters (from the copolymer chains) dissolved in the buffer medium.

3. Results and discussion

3.1. ^1H NMR and FTIR spectroscopy

The chemical structure of PET-co-PLA copolymer and its synthesis reaction is shown in Fig. 2. ^1H NMR spectrum is shown in Fig. 3(a). The band assignments and calculations of MW and microstructure were described earlier [16,17,20]. Proton signals of terephthalate units at 8.1 ppm (aromatic ring), lactate units at 5.0–5.5 ppm (C–H) and 1.3–1.8 ppm ($-\text{CH}_3$), and those of ethylene

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