Thermochimica Acta 590 (2014) 40–50

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Humidity response of poly(butylene adipate-co-butylene terephthalate) copolyesters and their composites with wood flour determined by dynamic mechanical analysis

Angela Milinkovic [a], Pastorek Miroslav [b], Adriana Gregorova [a,*]

[a] Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, Graz, Austria
[b] Centre of Polymer Systems, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic

ARTICLE INFO

Article history:
Received 13 March 2014
Received in revised form 16 May 2014
Accepted 11 June 2014
Available online 14 June 2014

Keywords:
Aliphatic–aromatic copolyesters
Crystallinity
Dynamic mechanical analysis
Mechanical properties
Relative humidity
Viscoelastic properties

ABSTRACT

This study investigated the mechanical and viscoelastic properties of poly(butylene adipate-co-butylene terephthalate) copolyesters, P(BA-co-BT)s and their composites, P(BA-co-BT)–WF with 20 vol.% of beech wood flour (WF) at dry (N_2) and in humid atmosphere (50% RH) using a large temperature range from 20 to 90 °C. The melting behaviour of P(BA-co-BT) copolyesters were studied with differential scanning calorimetry (DSC) and wide-angle X-ray analysis. The increase of the aromatic moiety as well as reinforcement with WF improved stiffness of copolyesters. The ambient testing environment with the increased temperature negatively impacted the stiffness and strain properties of P(BA-co-BT)s as well as P(BA-co-BT)–WF composites. The loss of mechanical properties was accelerated in humid atmosphere due to hydrolytic degradation of the ester linkage in copolymers. It was determined that wood flour used as a reinforcement slightly contributed to the hygrothermal aging of P(BA-co-BT) composites. Understanding the effect of humid atmosphere combined with dynamic changed temperature provides useful information for the assessment of the hygrothermal stability of biodegradable polyesters.

1. Introduction

The major advantage of biodegradable polymers is their ability to degrade under special conditions supported by the action of microorganisms and thus to contribute to the reduction of plastic waste thrown in landfills. Enzymes play the role of catalysts for the degradation but hydrolysis is further predominant mechanism occurring mainly in polyesters. Practical applications for the use of biodegradable polymers are mainly in the fields of packaging materials, engineered fabrics, hygiene products and agricultural film sheeting. The associated disadvantages such as higher costs, greater brittleness and lower thermal stability in the comparison to those of the common non-biodegradable synthetic polymers (e.g. polyolefins) are hampering factors that decelerate a wider utilization of biodegradable polymers. The improvement of the physical properties of biodegradable polyesters was announced by the syntheses of aliphatic–aromatic copolymers such as poly (trimethylene decanedioate-co-trimethylene terephthalate), poly (butylene adipate-co-butylene terephthalates) (P(BA-co-BT)s), poly(butylene cyclohexanedimethylene succinate terephthalates) [1–3]. In the context of the biodegradation, it is known that an aliphatic moiety in aliphatic–aromatic copolyesters enhances the hydrolytic as well as biological degradation susceptibility [4]. Investigations showed that the biodegradation of aliphatic–aromatic copolyesters can be controlled by adjusting the molar ratio of monomers [3,5,6]. The complete degradation under composting system conditions of commercial aliphatic–aromatic copolyester, Ecoflex, with the 22.2 mol% of aromatic moiety was approved [7]. Other factors affecting the biodegradation of polymer sample are molecular weight and crystallinity degree, degree of surface hydrophilicity, geometric parameters, and the outdoor conditions as well as the selection of microorganisms [3,5,8]. It was reported that the physical properties of aliphatic–aromatic copolyesters such as solubility, molecular weight, thermal and mechanical properties can be modified by the variation of aliphatic and aromatic moiety (by a concentration ratio or by an alteration of additives) [1,3,9,10]. Moreover, the effect of blending with other biodegradable polymers or reinforcing with fillers on the physical properties of aliphatic–aromatic polyesters based blends or composites was evaluated [11–15]. Renewable materials were considered to be attractive fillers due to their large

---

[*] Corresponding author. Tel.: +43 316 873 32305; fax: +43 316 873 32302.
E-mail addresses: adrianagregorova@yahoo.com, adriana.gregorova@tugraz.at (A. Gregorova).

http://dx.doi.org/10.1016/j.tca.2014.06.010
0040-6031/© 2014 Elsevier B.V. All rights reserved.

abundance, sustainability, non-abrasiveness, low density and low price [16]. However, the chemical and physical properties of filler influence its compatibility with the copolyester matrix and so limit the final thermal and mechanical properties of composites [16–22]. It was well recognized that ester groups contribute to hygrothermal aging of polyesters. Nevertheless, until now only few papers have investigated the impact of ambient moisture and temperature on the final rheological and mechanical properties of biodegradable polyesters or copolyesters [14,23–26]. Partini et al. [24] studied the change in complex viscosity of dried (drying at 50 °C for 72 h) and wet (stored at 70% RH, 30 °C for 7 days) biodegradable polyesters in a melt state at different temperatures as a function of time. This study puts forward the hypothesis that the moisture present in the sample is an important factor influencing the degradation kinetics. Plasticization by water can theoretically increase the values for elongation properties. As shown in the study of hygrothermal aging of blends based on poly (lactic acid) (PLA) and poly(caprolactone) (PCL), time and temperature are additional considerable parameters to moisture that limit ductility of samples [25]. Audic and Chaufer [14] studied the effect of relative humidity of 53% RH on mechanical properties of poly(butylene adipate-co-terephthalate) blended with sodium caseinate and plasticized with glycerol or triethanolamine. The samples were conditioned for 2 weeks at relative humidity of 53% RH and temperature of 23 °C before mechanical testing. It was observed that mechanical properties of blends without plasticizers were comparable at both relative humidity conditions of 0 and 53% RH. However, addition of plasticizer decreased elastic modulus by above 50% [14]. Among other factors influencing the impact of hygrothermal aging of polyester, hydrophilic filler based reinforcement can also be considered. On the other hand, it was reported that the priority role in the hydrolysis of composites has cleavage of ester groups present in the polymer matrix [23].

The sensitivity of polyesters and copolyesters to hydrolysis limit their durability and long-term behaviour under humid conditions. The objective of the present work is pursuing viscoelastic and mechanical properties of poly(butylene adipate-co-butylene terephthalate) copolyesters by dynamic mechanical analysis combined with relative humidity (DMA–RH). DMA–RH allows combining multiple parameters such as frequency, temperature, time, load, and humidity during a single measurement and such simulate hygrothermal aging at static or dynamic conditions [27]. It is well known that the ratio of aliphatic and aromatic moiety modify the mechanical properties of copolyesters [28]. Additionally, based on the high susceptibility of aliphatic ester bonds to hydrolysis, we hypothesize that the variation of aliphatic/aromatic moiety concentration may influence the viscoelastic properties of copolyesters in humid atmosphere. Moreover, the presence of hydrophilic filler in copolyester can also modify the final response of the composite to hygrothermal aging [29]. The aim of this work is to study an effect of humid atmosphere combined with temperature change (hygrothermal aging) on mechanical and viscoelastic properties of pure poly(butylene adipate-co-butylene terephthalate) [P(BA-co-BT)] copolyesters with varying concentrations of the aliphatic/aromatic moiety. Finally, in this study, an effect of 20 vol.% of beech wood flour on hygrothermal aging of aliphatic–aromatic polyesters is determined.

2. Experimental

2.1. Materials

Dimethyl terephthalate, 99% (DMT) was supplied by Fluka, and adipic acid, 100% (AA) by Merc. Tetrabutylorthotitanate, 100% (TBOT) and 1,4-butanediol, 99% were supplied by Sigma–Aldrich (Germany). Chloroform, 99% and methanol, 99.5% were used as obtained from Carl Roth (Austria). For NMR spectroscopy deuterated chloroform ($CDCl_3$) with 0.03% of tetramethylsilane (TMS) from Sigma–Aldrich (Germany) was used. Hydrothermally pre-treated beech wood flour (BWF) [30] with a density of 1.25 g/cm^3 was used as filler. Particle size of WF (measured by CILAS 1064 instrument) was 18.8 μm (diameter at 90% in volume).

2.2. Synthesis of copolymers

Aliphatic–aromatic poly(butylene adipate-co-butylene terephthalate) copolyesters with butylene adipate (BA) and butylene terephthalate (BT) molar ratio of 70:30 [P(BA-co-30-BT)], 60:40 [P(BA-co-40-BT)], and 50:50 [P(BA-co-30-BT)] were prepared according to the procedure described by Gan et al. [10]. Synthesis was accomplished in three steps (see Fig. 1). The resulting product was cooled down to room temperature and dissolved in chloroform. The copolymer solution was precipitated by chilled methanol. The precipitate was filtrated and dried at 65 °C for 48 h under vacuum.

2.3. Preparation of copolymer and composite sheets

Conical co-rotating twin-screw Haake MiniLab II microcompounder was used for melt compounding of P(BA-co-BT) composites with 20 vol.% of beech wood flour. The following processing conditions were used: temperature of 120 °C, time of 3 min, mixing of 50 rpm. Dried copolyesters and compounded composites were thermoformed by thermohydraulic press (Collin P 200PV) at melting temperature, pressure of 10 MPa, pressing time 6 min and cooling time of 10 min till 30 °C. From the thermoformed films with a thickness of 100 μm were cut rectangle-shaped specimens with dimensions of 7 mm × 3 mm × 0.1 mm and those were stored in a desiccator before analyses.

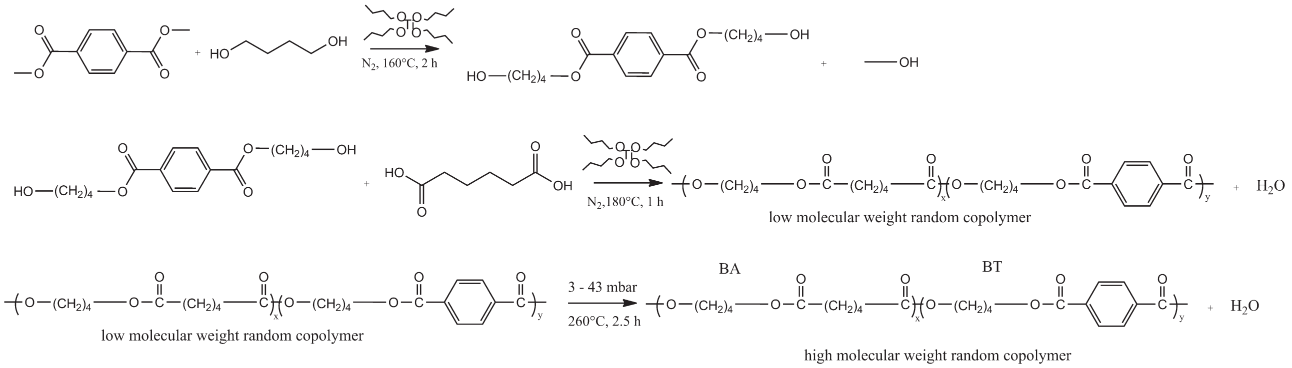

Fig. 1. Scheme of synthesis of P(BA-co-BT) copolymers.