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Material behaviour

Chain extension in poly(butylene-adipate-terephthalate). Inline testing in a laboratory internal mixer

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ABSTRACT

This contribution is concerned with degradation and chain extension in poly(butylene-adipate-terephthalate), PBAT, compounded in a laboratory internal mixer with an epoxydic chain extender additive. Weight-average mass change during melt processing was estimated from temperature-torque-time data recorded by the equipment. The effect of the additive was found to be strongly dependent on processing temperature, and weakly dependent on concentration. Molar mass more than doubled at 230°C with 2% additive. Long induction times and catastrophic failure to mix, occasionally observed with oligomeric additives processed in internal mixers, are discussed. Possible implementation of the procedure for real-time estimate of chain extension is also discussed.

1. Introduction

Degradation of the natural environment by human action is putting pressure on the search for solutions compatible with social and economic growth. One of the major environmental problems created by contemporary civilization in industrial societies is the increase of domestic refuse, of which a significant part is made up by plastic food and other containers (film, foam, bottles, etc.). There are no simple answers to this problem, applicable to several types of products. Recycling of used parts is being explored as a possible solution, and finds increasing application for some classes of relatively large unreinforced plastic products of uniform composition, such as soft drink beverage PET bottles. Recycling, however, is not a universal answer for plastics disposal. Another promising route is the use of biodegradable materials. Biodegradable plastic materials that can be digested by aerobic microorganisms (bacteria and molds) normally present in the soil, and returned to the environment as carbon dioxide and water in a matter of months (and not years or centuries), are an extremely interesting alternative.

The present work is concerned with one of these plastics, a random copolymer of butylene adipate and butylene terephthalate. Poly(butylene-adipate-terephthalate) or PBAT is a synthetic semicrystalline thermoplastic copolyester with mechanical and thermal properties similar to some polyethylenes. PBAT is fully biodegradable in municipal dumps (it is “compostable”). It may be processed in conventional polymer processing equipment (mixers, extruders, injection molding machines, etc.) and is fairly stable under processing conditions. Moreover, it has some interesting barrier properties for a material that may be formed into films for the food packaging industry. Compared with LDPE, neat PBAT has a lower permeability to oxygen (50%) and a much higher permeability to water vapor (80 times) [1–6].

Although PBAT is fairly stable, it degrades at processing temperatures (140–230°C), as most polyesters do, by hydrolysis of the ester bond in the presence of humidity and

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by thermally-induced chain scission, even in the absence of water. As a result, a decrease in average molar mass is observed after processing [7–9].

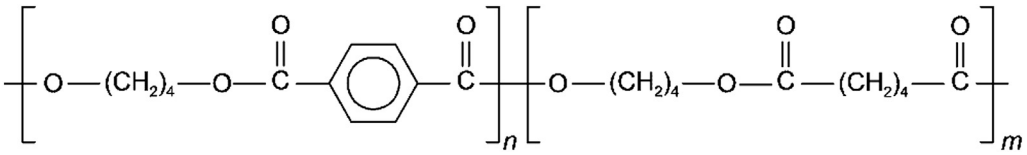
Chain extenders are multifunctional additives that bind to the ends of different macromolecular fragments (carboxyl and hydroxyl groups in the case of polyesters) thus *extending* the chain and increasing the average molar mass of the polymer. Chain extenders do not prevent degradation, but compensate for its effect on the molar mass of the polymer [8,10,11]. There are many low molar mass chain additives described in the literature, and it is not our intention to review them here. In the present work, an epoxydic oligomer, commercially known as Joncryl, widely used to compensate degradation in PET and successfully tested in other polyesters, including PBAT [9,12], will be used as chain extender.

Commercially available PBAT has relatively low molar mass (~50,000 g/mol) and is appropriate for processing as film. Other application (e.g., injection molding or extrusion) may require a polymer with higher molar mass. Chain extension may be a simple way to generate this higher molar mass material, at least for testing applications. While to compensate degradation low concentrations of Joncryl (0.5% to 1.5%) are recommended, higher concentration could be needed to substantially increase the molar mass of the PBAT. Consequently, Joncryl concentrations up to 8% were tested in the present work.

2. Experimental

2.1. Materials

The PBAT or poly(butylene adipate-*co*-butylene terephthalate):



tested in the present work is commercially available as BASF Ecoflex® F BX7011. Although considered as ordinary PBAT in the literature, according to manufacturer's sources [6], Ecoflex is a modified PBAT, containing small amounts of an unknown third multifunctional monomer, which confers a certain degree of branching to the otherwise linear copolymer. According to the manufacturer, Ecoflex contains approximately equal amounts of each co-monomer on a molar basis; 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 melts at 110 to 120°C [6]. DSC measurements in our lab indicate a slightly higher melting point (completing the melting process at 135°C) and a low degree of crystallinity (10 to 15%) [12].

The chain extender additive used is a blend of Joncryl® 4368 and Joncryl® 4370 epoxydic oligomers, commercialized by Polyad Services as Polyad PR-02. Molar mass is typically of the order of 7,000 g/mol and it contains 5 to 10 epoxy reactive functional groups per molecule [13]. Recommended for polyesters, and to be used at temperatures in the range of 170°C to 300°C, the effectiveness of this additive to compensate degradation of virgin and recycled PET was verified in previous work in our laboratory [14]. The chemical structure of Joncryl is shown in Fig. 1 [8].

2.2. Method

Samples of PBAT were processed in a Haake Rheomix 3000 laboratory internal mixer, fitted with high intensity ("roller" type) rotors, operated at a nominal speed $N = 60$ rpm. The processing chamber was 75% full in all cases and its walls were kept at constant temperatures (T_0) between 170°C and 230°C, during each test. Preliminary tests revealed that the polymer is substantially molten after 3 or 4 min processing time. Between 7 and 8 min, the chain extender additive – in quantity sufficient to result in mass fractions (w_A) between 1% and 8% – was incorporated without interrupting the process. The software of the instrument supplies 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.

At constant rotor speed, torque is directly proportional to the rate of mechanical energy dissipation $\dot{E}$ inside the processing chamber:

$$\dot{E} = 2\pi NZ \tag{1}$$

During the melt processing stage, taking into consideration the predominantly shear flow patterns inside the mixer, the rate of mechanical energy dissipation may be expressed – at any given time – in terms of the viscosity of the molten material η, which we may assume to be a

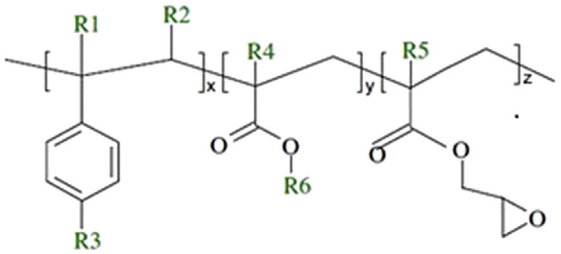


Fig. 1. General structure of the multi-functional oligomeric chain extender family Joncryl; R1–R5 are H, CH_3 or higher alkyl group; R6 is an alkyl group, and x, y and z are each between 1 and 20.