



Chain mobility, secondary relaxation, and oxygen transport in terephthalate copolyesters with rigid and flexible cyclic diols



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ARTICLE INFO

Article history:

Received 11 July 2017

Received in revised form

17 September 2017

Accepted 21 September 2017

Available online 22 September 2017

Keywords:

Polyester

Oxygen permeability

Secondary relaxation

ABSTRACT

High glass transition temperature (T_g) polyesters based on cycloaliphatic diols such as 1,4-cyclohexanedimethanol (CHDM) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) have attracted significant interest as bisphenol-A replacement. Whereas most literature reports focus on synthetic approaches, the present study investigates in depth various structure-property relationships in CHDM- and TMCD-containing novel copolyesters. Significant enhancements in T_g and increases in fragility are observed with the incorporation of bulky CHDM and rigid TMCD as comonomers. Substantial increase in oxygen permeability is measured with the incorporation of CHDM from 14.3 for poly(ethylene terephthalate) to 52.6 cc-mil/100in².day.atm (SPU) for poly(1,4-cyclohexyldimethylene terephthalate). When 35 mol% CHDM is replaced by TMCD as comonomer, the value further increases to 137.0 SPU. In the case of CHDM-containing polyesters, improvements in both sub- T_g molecular mobility (due to additional chair-to-boat transformations) and fractional free volume (FFV) result in an increase in oxygen diffusion. On the other hand, substituting 35 mol% CHDM with more rigid TMCD yields a suppressed β -relaxation. In particular, CHDM-based copolyesters follow a linear correlation between the strength of β -relaxation and diffusivity whereas the TMCD-based copolyester exhibits a significantly positive deviation from the correlation. Therefore, the much higher FFV in TMCD-containing polyester plays a more important role in determining oxygen transport through such polymer. Finally, we demonstrate that copolyesters based on CHDM and TMCD display significantly enhanced resistance to moisture-induced plasticization and the competing penetrant effect.

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1. Introduction

The quest for bisphenol-A (BPA)-free engineering thermoplastics with high glass transition temperatures (T_g) (greater than 100 °C) has inspired research to develop new polymers with specific (co)monomer structures for enhanced polymer backbone stiffness and chain rigidity [1–9]. Due to high T_g , these novel materials offer attractive benefits such as higher heat distortion temperature, reduced creep, lower physical aging rate, and reduced injection molding cycle times [2,6]. Based on homopolyesters such as poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexyldimethylene terephthalate) (PCT) first produced in the 1940's and 1960's, respectively, several copolyester resins have been synthesized and manufactured commercially in order to impart desired material properties. In particular, copolyesters incorporating 1,4-cyclohexanedimethanol (CHDM) comonomers

have been shown to possess superior properties including minimum crystallinity (clear) and improved melt strength and chemical resistance. On the other hand, the T_g s of these copolyesters are relatively low in the range of 70–100 °C, limiting their use in practice [2,4].

In the past decade, a novel copolyester based on a rigid, aliphatic diol, *cis/trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) monomer has been commercialized with significant success as BPA-polycarbonate replacement by Eastman Chemical Company under the brand name of Tritan™ [1–4,6,8–13]. The incorporation of TMCD monomer into the backbone of PCT results in a clear copolyester resin referred to as PCTM (TMCD-modified PCT) with T_g in the range of 100–125 °C [2,4,10]. In addition to an increase in the upper-use temperature as a result of improved T_g , the incorporation of bulky monomer structures leads to films with improved toughness and tear resistance compared to traditional polyester films [1,10]. Other major advantages with PCTM include its enhanced chemical resistance and reduced physical aging rate owing to its

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chemical makeup and higher T_g , making the material attractive for use in a variety of applications [1,4,10]. Past studies have exclusively focused on synthetic approaches for producing TMCD-based copolyesters [1,3,7,8,10,12–14] whereas a fundamental understanding of how cycloaliphatic diols impact polymer chain dynamics and gas transport properties is lacking. Such knowledge is crucial in the design of packaging materials with enhanced performance [15,16].

Studies of small-molecule transport also provide insights on the excess free volume and molecular mobility of amorphous glassy polymers [17]. Polymers do not fully occupy the specific volume due to packing inefficiencies and polymer chain mobility. The unoccupied, free volume is continuously redistributed as a result of thermally stimulated random segmental motions. Driven by a concentration gradient, permeants diffuse through the polymer film via a random walk process that involves small molecules hopping between the transient gaps before desorption from the lower concentration side. Gas transport is thus affected by fractional free volume (FFV) and dynamic free volume resulting from long- and short-range molecular mobility [15,16,18–25]. A few studies have attempted to correlate both short- and long-range motions in copolyesters to macroscopic properties including toughness, yield strength, and gas permeability [17,24–26]; on the other hand, to the best of our knowledge, novel TMCD-based copolyesters have not been examined in their structure-gas transport property relation.

For glassy polymers, long-range motions refer to cooperative segmental motions, i.e., the α -relaxation; short-range motions are more localized (either side chain or segments of the main chain) and involve fewer units, i.e., the β -relaxation [17]. The magnitude of T_g is closely related to structural characteristics such as flexibility, bulkiness, and polarity of the polymer repeat unit [27–34]. On the other hand, the impact of chemical structure on chain flexibility, chain cooperativity, and the α -relaxation dynamics is best elucidated by the fragility parameter of the polymer [27]. Fragility of a system reflects the extent to which properties such as viscosity/relaxation time changes when approaching T_g from the rubbery state. The fragility index, m , is defined as:

$$m = d(\log \tau_\alpha)/d(T_g/T)|_{T=T_g} \quad (1)$$

It essentially characterizes the apparent activation energy of the α -relaxation at T_g normalized by T_g and therefore provides a convenient means to compare different copolyester structures with different T_g values [29].

Far below T_g , localized motions involving fewer main-chain or side-chain segments dominate and create dynamic free volume [15,17]. Sub- T_g , short-range segmental mobility in glasses impacts bulk properties such as the transport of small gas molecules, fracture toughness, and yield [8,15,24,26,35–38]. The β -process in polyesters is often asymmetric with multiple relaxation processes. Several studies have employed dynamic mechanical analysis (DMA), dielectric relaxation spectroscopy, and solid-state NMR techniques to reveal the molecular processes associated with β -relaxation in PET [8,24,26,35,37,39–44]. For example, Illers and Breur attributed the low temperature side of the β -relaxation peak to oscillations of the carboxyl groups and phenyl rings, whereas the high temperature side reflects phenyl ring flipping [37,39]. When antiplasticizers were added in PET, the high temperature side of the secondary transition was strongly suppressed as a result of restricted phenyl ring flipping [35,37,44,45]. In the case of PCT, Chen et al. [26] demonstrated that the β -relaxation involved boat-to-chair transformations of the cyclohexyl ring. Such motions can result in significant volume fluctuations and facilitate shear yielding under high speed impact conditions. More recently, Dennis

et al. [8] synthesized a series of decahydronaphthalene-containing copolyesters that incorporate cycloaliphatic diols. Using dynamic mechanical analysis, they identified complex relaxations associated with the decahydronaphthalate and cyclohexyl rings within the polymer backbone.

Only a few studies have examined the impact of sub- T_g molecular motions (i.e., β -relaxation) on gas permeability of copolyester films [5,8,11,24,25,42,44,46–50]. Almost all of these studies were conducted at temperatures far below T_g and at 0 %RH conditions. Light and Seymour synthesized a series of PET-based copolyesters with different comonomer structures and measured gas permeabilities [42]. They observed that the area under the $\tan \delta$ peak associated with β -relaxation was strongly affected by comonomer structures. For example, poly(ethylene isophthalate) (PEI, a structural isomer of PET) exhibited a significantly suppressed sub- T_g relaxation compared to PET. This is caused by a more restricted phenyl ring flipping process in isophthalate as opposed to in terephthalate. Furthermore, this was the first systematic study that demonstrated a linear relationship between the area under the $\tan \delta$ peak and oxygen diffusivity in copolyesters. A more comprehensive evaluation of gas permeability should take into account effects both from FFV and secondary motions [15]. Kim et al. [25] measured a higher gas permeability in blends based on BPA and tetramethyl bisphenol-A polycarbonates relative to the copolymer counterpart, even though the blends had lower FFV. This was rationalized based on the considerably enhanced secondary motions in the blends that dominated gas permeation properties. More recently, Burgess et al. [38,51] measured a much higher FFV in poly(ethylene furanoate) (PEF) than PET. Nonetheless, oxygen barrier properties of PEF were significantly superior compared to those of PET. This was attributed to a much more suppressed β -relaxation in PEF due to the more rigid furan structure. Furan ring-flipping was thus more hindered compared to phenyl ring-flipping mechanism associated with PET. To the best of our knowledge, these are the only few studies that examined both FFV and secondary motions in determining gas permeation through glassy polymers, all of which showed the latter playing a dominant role.

There is a significant dearth in understanding of how the incorporation of TMCD as a comonomer affects polymer chain mobility and gas transport properties. The present work develops a molecular understanding of the structure-property-performance relationship associated with oxygen transport in a series of industrially relevant copolyesters based on dimethyl terephthalate and EG, CHDM, and TMCD as comonomers. This study is the first to examine the effects of cycloaliphatic diols on the α -relaxation dynamics. The complete amorphous state of the polymers was confirmed through structural characterization via X-ray diffraction. Comparisons of FFV and the strength of β -relaxation among different copolyester systems were made in order to understand how cycloaliphatic diols impact oxygen transport. This work also develops a comprehensive picture of oxygen transport under various temperature and humidity conditions to understand the impact of TMCD and CHDM as comonomers on moisture-induced plasticization in these systems [52,53]. The structure-property relationship revealed here in terephthalate copolyesters with rigid and flexible cyclic diols will aid in the design of improved barrier materials.

2. Experimental

Five high molecular weight polyester and copolyester resins are investigated in the current work (see Table 1 for chemical structure and composition). Pellets are first dried for several days at 60–100 °C under vacuum and compression molded at temperatures in the range of 250–300 °C. Optically transparent films are

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