



Classification of aliphatic-butylene terephthalate copolyesters in relation to aliphatic/aromatic ratio



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ARTICLE INFO

Article history:

Received 11 November 2016

Received in revised form

13 February 2017

Accepted 14 February 2017

Available online 20 February 2017

Keywords:

Copolyesters

Random

Aliphatic-aromatic

Mechanical properties

Crystallization

ABSTRACT

Aliphatic-aromatic copolyesters containing: butylene terephthalate ester and a mixture of butylene esters: adipate, succinate and glutarate, (PBASGT), were synthesized and classified according to their chemical composition and physical performance. Several such mixtures of aliphatic dimethyl esters are available on the market. Structures and properties of PBASGTs were characterized by various techniques including ¹H NMR spectrometry, calorimetry, x-ray scattering and diffraction, dynamic mechanical analysis and tensile testing. All copolyesters were nearly random copolymers. Surprisingly, only the aromatic component is able to crystallize in the form characteristic for poly (butylene terephthalate). The increase of aromatic units content did not change the crystallographic form, however, a stronger crystallinity develops. The dramatic changes of thermal and mechanical properties of PBASGT were observed with the increase of aliphatic units content, e.g. from brittle to tough behavior. Copolyesters with aromatic content of 30% and below exhibit single relaxation peak of aliphatic rich amorphous components. At the concentration of 40% and above the aromatic component is segregated while the amorphous aliphatic units form joint pools. A partial segmental miscibility of aromatic and aliphatic components is suggested. It was shown that PBASGT with 40% of aromatic units is biodegradable.

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1. Introduction

Increasing problems with domestic waste at the end of XX century directed the polymer research toward development of biodegradable plastics. Linear aliphatic polyesters are biodegradable and able to crystallize, however, their crystals melt at low temperature (T_m , from ambient to about 70 °C) while their amorphous phase is characterized by low glass transition temperature (T_g). The mechanical properties including the strength and toughness can be significantly improved at higher temperature by introducing aromatic units into polymer chains [1–6]. However, the main aim of developing such aliphatic-aromatic copolyesters (AAC) was to combine good material properties with biodegradability. Copolyesters are usually prepared by copolymerization of a mixture of co-monomers. The copolymerization reaction and copolymer structure are controlled by the ratios and reactivity of reagents and catalysts [6,7].

The most well-known binary systems are butylene succinate-

co-butylene terephthalate, (PBST), and butylene adipate-co-butylene terephthalate, (PBAT), copolyesters. Li et al. [5] demonstrated that molecular weight of synthesized PBST decreases with the increase of butylene terephthalate (BT) comonomer content in the composition leading to lower viscosity copolyesters. However, with the increase of BT units, the phase transition temperatures (T_g , T_m , T_c – crystallization temperature) and decomposition temperature (T_d) of PBST [8] and PBAT [9,10] copolyesters tend to increase. The increase of BT comonomer fraction causes a gradual shift from monoclinic crystal structure, characteristic for poly (butylene succinate), (PBS) or poly (butylene adipate), (PBA), to triclinic one, characteristic for poly (butylene terephthalate), (PBT). The transition of PBST [5,11] and PBAT [10,12] crystal lattice was observed for aromatic content higher than approximately 30%.

The increase of BT content causes the largest changes to the tensile properties, the higher the content of BT units, the higher the initial modulus of the PBST sample and the higher ultimate strength. However, the elongation at break decreases with the increase of BT co-units [13]. Kang et al. [14] conducted the studies about developing random poly(butylene adipate-co-butylene succinate-co-butylene terephthalate), (PBAST), synthesis. The higher

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the mixing time was applied the more random structure of the copolyester was obtained. However, the authors [14] could not find any trend between BT content and the degree of randomness. It was also reported that the increase of BT content in composition increases the average aromatic block length. It was observed that the viscosity was influenced by the BT content, mixing time and temperature. The copolyester composition affects the crystal structure: copolymers with higher aliphatic unit content exhibit monoclinic crystal structure (characteristic for aliphatic homopolymers), whilst copolyesters with a dominance of BT units possess triclinic crystal lattice. So, it was suggested that when a dominant component crystallizes, the lesser component is excluded completely from the crystal formation. In fact only amorphous halo was found for copolyesters containing less than 40% of BT units while mechanical properties of PBAST were inferior as compared to aliphatic poly (butylene adipate-*co*- butylene succinate), (PBAS).

Witt et al. [7] reported that random copolyesters PBAT having the average aromatic block length 3 and below 3 were biodegradable. This observation was confirmed by Shi et al. [15] for random PBAST copolyesters. PBAST exhibited one broad melting peak with the maximum at around 110 °C. Moreover, it was presented that WAXS pattern of PBAST is similar to PBT α -form pattern. Shi et al. [15] also studied the mechanical properties, which revealed a rubber-like behavior of PBAST. The presence of aliphatic units caused a development of elastomeric properties and a decrease of tensile modulus and strength of PBAST as compared to PBT. There are also known examples of copolyesters with more than three comonomers, for instance containing butylene adipate, succinate, glutarate and terephthalate, (PBASGT). Park and Kang [16] prepared block copolyester of PBASG-*b*-PBT by transesterification during melt processing. The mixing time and the content of PBT influenced the transesterification degree. However, the randomness of copolyesters depended mainly on the mixing time and not on the aromatic polyester content. Moreover, an increase of melt mixing time caused a gradual decrease of melting temperature. However, the melting point was shifted to higher values together with the increasing amount of aromatic units. Additionally the heat of fusion became higher. Furthermore, synthesized copolyesters with aromatic unit content above 40% exhibited 2θ wide angle X-ray scattering (WAXS) pattern characteristic for triclinic crystal form of PBT. It is worth to underline that all copolyesters showed progressive changes of properties together with the changes in concentration of comonomers.

Recently, we have reported the studies of the properties of aliphatic-aromatic copolyester containing three different aliphatic comonomers: butylene adipate, butylene succinate and butylene glutarate, and one aromatic butylene terephthalate comonomer at the concentration of 40%, (PBASGT) [17]. It was shown that even though the copolymer was found to be random it was still able to crystallize in the form characteristic for PBT.

This study focuses on copolymers synthesized based on a mixture of aliphatic comonomers with aromatic-butylene terephthalate having concentration from 0 to 100%. Such mixtures of aliphatic dimethyl esters are available on the market at relatively low price, e.g.: DBE (Du Pont), Santosol (Monsanto), Estasol (Chemox), Uniestrol (Synthos, formerly by Organika, Sarzyna). They are usually byproducts in fabrication of dimethyl adipate ester and they are commonly used as solvents for uncured epoxy, polyester, urethane, acrylic, phenolic and styrenic resins. Availability of mixtures of dimethyl aliphatic esters inspired us to use them for copolymerization with aromatic dimethyl terephthalate ester. A range of copolyesters with concentration of aromatic component from 0 to 100% were synthesized with the aim of classification of the copolyesters. The variety of properties in connection with copolyesters composition will be presented.

Copolymers with homogeneous comonomer distribution are excellent vehicles for fundamental studies of structure–property relationships in semicrystalline aliphatic-aromatic copolymers. One of the questions is whether aromatic copolymers should crystallize as fringed micellar crystals when the crystallizable sequences are not long enough to chain fold into lamellar crystals. It is of interest to determine whether the copolymers similarly form fringed micellar crystals if the crystallizable sequences are short. The combined observations of solid-state structure and properties maybe used to understand the behavior of these materials and to develop a classification scheme based on comonomer content. Moreover, it will be shown whether the compromise between polymers ability to crystallization and the average crystallizable sequence length at around 3 and below, that guarantee biodegradation, can be achieved.

2. Experimental

2.1. Raw materials used for synthesis

Dimethyl terephthalate (DMT) was purchased from Mogilev-khimvolokno, Mogilev (Belarus); 1,4-butanediol (BD) was obtained from PPH Standard Co., Ltd. (Poland); and a mixture of aliphatic comonomers, Uniestrol, was delivered by Pilot Plant “Organika” Co., Ltd. (Poland). The Uniestrol is a mixture of dicarboxylic acid dimethyl esters, which contain 31% of dimethyl adipate (DMA), 14% of dimethyl succinate (DMS), and 55% of dimethyl glutarate (DMG). The catalyst, tetrabutyl orthotitanate ($\text{Ti}(\text{OBU})_4$) was supplied by Sigma Aldrich Co. All chemicals were used as received.

2.2. Synthesis of copolyesters

The scheme of reactions leading to copolyesters was already presented in our previous report concerning copolymerization of PBASGT containing 40% of aromatic comonomer [17]. Copolymers consisting from 0 to 100% of aromatic comonomer were prepared by a two-step melt polycondensation method. Exemplary recipe for PBASGT copolyester with 10% of aromatic comonomer molar content is as follows: into 9 dm³ acid resistance reactor warmed to 140 °C with nitrogen atmosphere were introduced: 23 g of DMT, 150 g of BD, 173 g of Uniestrol and 0.05 g of $\text{Ti}(\text{OBU})_4$ as the catalyst. The reactor was then warmed up to the temperature in the range from 165 °C to 225 °C under ambient pressure. Simultaneously methanol was distilled out the reactor. Subsequently, 0.15 g $\text{Ti}(\text{OBU})_4$ was added, the pressure was slowly decreased to 0.53 hPa and the reaction temperature was raised to 250 °C. Excess of 1,4-butanediol was distilled out in this period. The copolymerization reaction was followed by observing the torque on the stirrer blade. The reaction is presented schematically in Fig. 1 and it was finished after approximately 80 min. Then the molten polymer was extruded out the reactor in the form of 2–3 mm thick strings and pelletized.

The series of copolyesters were synthesized as presented in Table 1. The synthesis procedure for others copolyester compositions was the same as described above for 10% of aromatic component except for various components ratios (see Table 1).

2.3. ¹H nuclear magnetic resonance (¹H NMR)

To investigate the chemical composition of synthesized copolyesters and the sequence distribution of comonomers, ¹H NMR measurements were conducted under ambient temperature using a Bruker Avance DRX500 spectrometer operated at a resonance frequency of 500 MHz. Copolyester pellets were dissolved in deuterated chloroform (CDCl_3). For copolyesters with aromatic

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