



Nucleation and crystallization of random aliphatic-butylene terephthalate copolyester

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ABSTRACT

Aromatic component of biodegradable aliphatic–aromatic random copolyester crystallizes. A strong self-nucleation is active with self-nuclei stable below 160 °C. Without self-nuclei the peak crystallization temperature decreases by 25 °C during subsequent cooling. The activity of self-nuclei was incentive to find artificial nucleating agents. Green phthalocyanine, blue phthalocyanine and talc were found to be effective nucleating agents for aliphatic–aromatic copolyester in absence of self-nuclei, increasing both the peak crystallization temperature and the density of nucleation. Crystallization of aliphatic–aromatic copolyester led to the formation of spherulites filling the entire volume of the material although aromatic crystal amounted to 10% of entire volume. SAXS analysis and AFM imaging showed that crystals are neither lamellar nor aligned in stacks. Instead, the crystals are formed as narrow, 3–4 nm thick fibrils radiating from spherulite centers. Crystallization of nucleated copolyester proceeds during cooling in a very peculiar way: first long fibrils are formed that partially immobilize the rest of material. During further cooling partially confined melt crystallizes in the form of short fibrils, however, in significantly smaller amount. The strangest outcome of artificial nucleation is that the crystallinity degree of nucleated copolyester is lower than nonnucleated. By short annealing at 70 °C long fibrils decompose by partial melting and capillary instability freeing the material from constraints.

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1. Introduction

Biodegradable materials are among the most promising solutions for the environmental problems connected with plastic waste [1]. A major role with respect to the industrial relevance is played by different polyesters, especially the aliphatic ones due to their susceptibility to degradation by enzymes and microorganisms [2]. According to the origin biodegradable polymers can be briefly classified into two categories: “bacterial” polymers and synthetic polymers [3]. The former ones include poly(hydroxyalkanoate)s (PHA), for instance polyhydroxybutyrate (PHB) [4]. The latter consists mainly of synthetic aliphatic polyesters such as: poly(ϵ -caprolactone) (PCL) [5], polylactide (PLA) [6], poly(butylene succinate) (PBS) [7] and poly(butylene adipate) (PBA) [8]. Their mechanical properties are not adequate for many applications, thus the aromatic units were introduced into main chains to create more mechanically resistant copolymers [9,10], which, nevertheless, remain biodegradable.

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Biodegradability, exactly its rate, is an important property for practical application. The materials should be stable enough while being used, yet the waste should be susceptible to biodegradation. In addition it should be remembered that physical properties and biodegradability of polymers are affected by their crystallinity and morphology.

Recently, we have developed a new aliphatic–aromatic copolyester (PBAGST) based on three aliphatic comonomers (succinate, glutarate and adipate dibutyl esters) and one aromatic (butylene terephthalate) comonomer. The morphology and thermal properties of PBAGST have been recently described by us [11]. This copolymer was also successfully used for toughening of polylactide [12].

It was found that PBAGST was a nearly random copolymer. During solidification, only butylene terephthalate blocks are able to crystallize forming crystals with the unit cell characteristic of poly(butylene terephthalate) (PBT) crystals. Nonisothermal crystallization of PBAGST revealed peak of crystallization at a rather low temperature of 70 °C during cooling at the rate of 10 °C min⁻¹, while melting peak of those crystals occurred at 108 °C upon heating at the rate of 10 °C min⁻¹ [11]. This was in contrast to PBT homopolymer that melts and crystallizes at much higher temperatures: 228 °C and 193 °C, respectively, during heating and cooling at the rate of 10 °C min⁻¹. PBAGST crystallizes in the form of thin fibrous crystals, few nanometers thick. It was determined that the main reason of depression of the melting temperature of those crystals in comparison to PBT homopolymer was their small thickness [11]. Although the crystallinity degree is low (around 20% of aromatic component) the fibrous crystals form spherulitic aggregates, around 7 μm in radius, filling the entire volume of the material. Apparently, the spherulites are nucleated on heterogeneities that are present in the material and activated in the amount of $9 \times 10^6 \text{ mm}^{-3}$ during cooling when approaching 80–70 °C. This is in contrast to PBT homopolymer in which the nucleation occurs during cooling slightly below 200 °C. This large temperature difference for crystallographically identical crystals indicates that the primary nucleation in PBAGST can be modified and there is a possibility to alter the number of seeds and their activity in PBAGST. The other important parameter besides the number of nuclei is their thermal activity. The crystallization temperature during cooling, that is very important for polymer processing, is controlled by the activity of nuclei. Therefore, the investigation of solidification during nonisothermal crystallization is very important for optimization of the processing conditions and the end-properties of products.

Generally, the crystallization of polymers consists of nucleation and growth steps. Nucleation is a process of the formation or activation of seeds on which crystalline aggregates can grow. Three kinds of nucleation are distinguished [13]: homogeneous nucleation, heterogeneous nucleation, and self-nucleation. Homogeneous nucleation occurs as the result of random fluctuations of order and density in the undercooled melt and usually it requires large undercooling. Heterogeneous nucleation occurs on or near foreign surfaces of impurities or nucleating agents added to a polymer on purpose. The surfaces reduce the free-energy barrier to primary nucleation [14] and provide sites where nuclei are formed. In general, the action of a substrate is to enhance the nucleation due to lowering the free energy of activation by means of a force field near the surface. This force field is a function of the chemical constituents of the substrate and also their geometrical arrangement. Thus, generally, the incorporation of nucleating agents increases nonisothermal crystallization peak temperature, and therefore the crystallinity. Simultaneously, the crystallization is accelerated and spherulites sizes are reduced. Higher crystallization temperature is advantageous for shortening of processing cycles. Moreover, higher crystallinity of a polymer is reflected in increased elastic modulus and yield stress, whereas the decreased grain size is beneficial for toughness and ultimate mechanical properties. Lotz and Wittmann [15] pointed out the importance of epitaxy in the heterogeneous nucleation.

The term self-nucleation or self-seeding has been introduced by Blundell et al. [16] to describe the nucleation of folded-chain crystals grown from solution on high molecular weight remnants of its own crystals that remained undissolved throughout the dissolution step. The term self-nucleation is understood nowadays as the nucleation of macromolecular melt or solution by remnants of crystals that escaped complete melting or dissolution [14]. The term “melt memory” has been employed to describe the observation that a polymer sample may be considered molten but retains somehow a partial memory of its former crystalline structure which is closely related to the existence of precursors of crystallization nuclei [17]. The investigation described in this paper dealt with the study of nucleation of crystallization of aliphatic–aromatic copolyester PBAGST. The effect of self-nucleation and nucleating agents on crystallization was of particular interest.

2. Experimental

2.1. Synthesis of copolyester

PBAGST copolymer was prepared by a two-step melt polymerization method: transesterification followed by polycondensation. A mixture of dicarboxylic acid dimethyl esters, which contained 31% of dimethyl adipate (DMA), 14% of dimethyl succinate (DMS), and 55% of dimethyl glutarate (DMG) was the aliphatic part that amounted to 60 wt.% of polymerizing comonomers mixture. Dimethyl terephthalate (DMT) was added in the amount of 40 wt.%. An excess of 1,4-butanediol was added to the polymerizing constituents. The excess of 1,4-butanediol ensures a high yield (90%) of the first stage of the process and prevents escaping the volatile components in the second stage, when the pressure is decreased. Detailed description of PBAGST copolyester preparation and its molecular characterization is presented in [11]. PBAGST sequence analysis showed that a molar fraction of aromatic units is equal 45% but not the initial 40% because of escaping of some volatile components during the second stage of polycondensation.

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