



Kinetics of the deformation induced memory effect in polyamide-6



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ARTICLE INFO

Article history:

Received 5 July 2015

Received in revised form 28 September 2015

Accepted 29 September 2015

Available online 6 October 2015

Keywords:

Crystallization

Memory effect

Polyamides

Polymorphism

ABSTRACT

Nascent polyamide-6 shows a peculiar and irreversible effect; the quiescent crystallization kinetics on cooling are accelerated upon deformation in the melt, even after full relaxation of the melt. This phenomenon, known as the orientation (or better, deformation) induced memory effect of polyamide materials, is explored in a step-by-step manner using in-situ wide-angle X-ray diffraction. For this purpose, unique polyamide-6 samples were used, which were created by compression moulding the virgin pellets just below the average melting temperature, defined by the peak position in a DSC-curve. The experimental data shows that only the imposed strain level controls the irreversible change in the quiescent crystallization kinetics. During cooling of the undeformed melt, an unusual crystallization behaviour is observed, i.e. the stable α -phase converges into the less stable β -mesophase. Possible causes for the memory-effect are discussed and related to hypotheses from the literature.

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1. Introduction

Polyamide-6 (PA-6) is a semi-crystalline polymer mainly used for engineering applications. The physical properties of the material are significantly influenced by the crystalline morphology within the sample, which, in turn, is controlled by the conditions during processing [1–5]. Two different polymorphic structures may form upon crystallization from the relaxed melt, namely, the monoclinic α -phase [6] and, at high cooling rates or upon cold-crystallization, a pseudo-hexagonal β -mesophase [1,7–9]. Both polymorphs exhibit a strong dependency on the intermolecular hydrogen bonding between different amide groups. The most stable α -structure contains fully extended, anti-parallel chains and is characterized by sheet-like hydrogen bonding. The less stable β -mesophase is described as an aggregate of parallel and straight but conformationally disordered chain segments with cylindrical symmetry. The structure of the β -mesophase is much alike the stable pseudo-hexagonal γ -phase, which can be obtained by an iodinating treatment of PA-6 [10,11], spinning fibres at high speeds [12] or crystallization in confined systems [13]. The existence of the β -mesophase and the γ -phase easily leads to confusion, mainly because the profiles obtained with wide-angle X-ray diffraction (WAXD) are similar. Only a technique based on infrared spectroscopy is able to distinguish between both structures [11,14], although this is not easy. Some authors summarize that, based on the setting of the hydrogen bonds and chain conformation, the β -mesophase can be viewed as an intermediate structure between the α - and γ -phase [2,12]. This suggests that the difference between the γ - and β -mesophase can only be found in the degree of crystal perfection [3,15].

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The overview above briefly illustrates the complexity of the different polymorphs present in PA-6. However, what remains is that in the case of quiescent crystallization, for a relaxed polymer melt, the crystallization rate on cooling depends on the temperature dependent nucleation density and growth rate of the crystal aggregates [16,17]. Melt-memory effects may occur when, prior to (re-)crystallization, a sample is brought to a low temperature or when the annealing period is short. Eventually, this leads to an increase in the crystallization rate [18,19] or a change of the final crystal morphology [20,21]. It is well known that for most semi-crystalline systems, prolonged time in the melt prior to crystallization reduces these effects of the original structure by gradual destruction of the crystal aggregates [18,22]. For polymers with strong hydrogen bonding, such as polyamides, stronger melt-memory effects are reported because the structures are harder to relax [23,24]. In addition to these *temperature* controlled memory effects, a large difference exists between the crystallization temperature of raw reactor material and mechanically treated polyamides [25–28]. Upon cooling at 10 °C/min, a shift upwards of 15 °C was reported for extruded PA-6 samples. The PA-6 used is produced in a continuous process where shear deformation exposed to the bulk of the material during this process is negligible compared to the shear deformation during later melt treatments as described in this paper. Indeed, it is shown many times in literature that a PA-6 sample, polymerized on lab scale or on a larger more commercial scale, shows a mechanical induced irreversible upward shift in crystallization temperature [13,25–31]. This memory effect is known to be also molecular weight dependent [18]. The molecular weight should be high enough; memory effects are not observed for oligomers. For the material we used this is definitely the case.¹ This irreversible phenomena is often called the *orientation* induced memory effect, but for obvious reasons shown in this work is referred to as the *deformation* induced memory effect. This matter forms a long-lasting research topic including ongoing debate on the (molecular) origin. In literature, different treatments are classified based on the induced shift in crystallization rate, ranging from untreated virgin material (no shift) to solution precipitation (maximum shift) [29]. Despite the abundance of work published on this topic, no systematic study on the influence of melt deformation on virgin material is reported *during* solidification and/or melting. The reason for this is found in the fact that dedicated experimental setups always require samples of specific dimensions. Hence, raw reactor material is mechanically deformed prior to structural investigation, erasing the original material behaviour. Subsequently, only the *thermally* induced memory effect can be studied instead [32].

The work reported here was inspired by the work of Janssens [31], who studied the deformation induced shift of the crystallization kinetics of virgin material in a step-by-step manner using RheoDSC. After a careful sample preparation procedure, we obtained unique disk shaped samples with crystallization and melting kinetics similar to the raw reactor material. These samples were examined using a shear cell setup combined with WAXD in a synchrotron. Crystallization and melting of virgin material is monitored in-situ after various shear pulses with different strength and total strain. In addition, the effects of delay time and shear temperature were investigated. Possible causes for the measured change in crystallization kinetics are discussed and related to hypotheses from the literature. So the main goal of this work is the rationalization of the experimental observation in order to come with a scientific sound hypothesis in an attempt to explain the experimental observations.

2. Material and methods

2.1. Sample preparation

The material investigated is a commercial polyamide-6 Akulon grade (DSM, the Netherlands). As-received granular material, from here on referred to as virgin material, was dried for 48 h in vacuum at 80 °C according to the specifications supplied by the manufacturer. Disk shaped samples of 32 mm in diameter and approximately 1.4 mm thick were compression moulded at a relatively low temperature of 204 °C for one minute under low pressure. The samples were sandwiched between two thin aluminium layers coated with silicon free release agent to minimize any adherence between the polymer and the aluminium. Each sample was removed from the mould and quenched between two metal plates of room temperature. Immediately after, the sample was sealed in a small aluminium bag, enclosed with standard silica bags to prevent moisture absorbance by the sample. Since sample preparation is a crucial aspect within this work, more details are included in the results section.

2.2. Thermal analyses

Differential scanning calorimetry (DSC) was used to investigate crystallization and melting of the virgin and mechanically deformed samples under non-isothermal conditions. Use was made of a Mettler-Toledo 823e/700 module in combination with a Cryostat intracooler. Razor blade cut samples of approximately four mg were placed in standard 40 µm aluminium crucibles. Two subsequent heating and cooling runs were performed, always at a rate of 20 °C/min and in the range of 25–260 °C. The highest temperature was held for five minutes to erase any thermal history. In between both runs an equilibration period of one minute was used at the lowest temperature.

¹ The material used is a commercial grade with a $M_n \sim 24$ kg/mol, $M_w/M_n \sim 2$ and zero shear viscosity $\varrho(10^3)$ Pa s. More information cannot be provided due to confidential reasons.

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