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European Polymer Journal 41 (2005) 1380–1390
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Influence of a cooling rate on a structure of PA6

S.S. Pesetskii [a], B. Jurkowski [b,*], Y.A. Olkhov [c], S.P. Bogdanovich [a], V.N. Koval [a]

[a] *Laboratory of Chemical Technology of Polymeric Composite Materials, V.A., Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus, 32a Kirov Street, 246050 Gomel, Belarus*
[b] *Institute of Material Technology, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland*
[c] *Institute of the Problems of Chemical Physics of Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia*

Received 19 May 2004; received in revised form 11 December 2004; accepted 16 December 2004
Available online 10 February 2005

Abstract

The structure of the plate specimens obtained from the molten PA6 that was cooled at rates between 2 and 2000 °C/min have been studied. The cooling rate of 2000 °C/min did not ensure a complete amorphization of the specimens. The amorphous phase created by supercooling is unstable and at room temperature undergoes a noticeable cold crystallization. The access of water to the specimen from the surrounding air accelerates this process.

Variations in the cooling rate of the melt reflect in rearrangement of the amorphous phase of PA6. Owing to the effect of interaction with the crystalline phase, the amorphous regions undergo changes in molecular weight and MWD of the chain segments between junctions in topological regions, temperatures of the glass transition and β-relaxation, compaction, etc.

Keywords: Polyamide 6; Crystallization; Amorphous phase; WAXS; DSC; Relaxation spectrometry; TMA

1. Introduction

Amorphous and crystalline structures with different degree of order, packing density, and crystal perfection may be formed in PA6 [1–8]. This process depends on the conditions of cooling the melt, a presence of crystallization nuclei and plasticizers, mechanical stresses, electromagnetic fields, or other factors. Fast cooling may result in amorphous (or δ) structure [9–11] with density 1.097–1.10 g/cm^3 [12–14]. It is characterized by a low degree of ordering of the structural elements. The arrangement is mainly one-dimensional owing to low concentration of hydrogen bonds between –NH– and =CO groups in adjacent chains. A two-dimensional arrangement can be obtained in certain situations [9,15,16]. The transition from unstable structures into stable crystalline ones is studied extensively [2,10,15,17–20]. PA6 at supercooling of its melt develops a crystalline γ*-form that is unstable toward thermal exposure [2]. It could be transformed into a monoclinic one above 150 °C [4,16,17,21,22].

Polymorphic structures and their transformations in PA6 are usually studied by the X-ray technique [23]. In PA6 objects is observed a structure consisting an amorphous phase and the two crystalline forms. The

* Corresponding author. Tel.: +48 61 6652 776; fax: +48 61 6652 217.
E-mail address: boleslaw.jurkowski@put.poznan.pl (B. Jurkowski).

0014-3057/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.12.009

diffraction maxima of the different crystals and that of amorphous regions overlap because they are within the same range of $2\Theta = 15–20°$ angles. The amorphous portion is characterized by diffuse scattering only.

The information concerning the production of amorphous PA6, thermal and other conditions at which the material structure changes from amorphous to crystalline is rather contradictory. The nuclei of crystallization present in the melt prevent the structure from getting amorphous even at fast cooling rates. The nuclei could break down completely, but only during annealing the melt at 280 °C (the equilibrium melting point of PA6) for 90 min [11].

Supercooling of a thin layer of the melt makes it possible to produce a transparent film of PA6 [9] having an amorphous structure that is stable at room temperature. The film specimens heated at 110 °C for 3 h does not show any crystallization. When heated at 175–180 °C for 3 h, PA6 has crystallized fast and showed equilibrium of crystalline structures. According to another study [10], the chain segments in amorphous PA6 underwent ordering and nematic, smectic or pseudohexagonal (γ*) structures are formed when the material is heated up to 50 °C, i.e. to a temperature close to T_g.

The PA6 structures are usually studied on fiber or film specimens. Information on the structure of PA6 plates is limited [16,23]. The amorphous structural features of a plate of PA6 with different crystallinity degrees and perfection degree of the crystals have been studied inadequately. The technological capabilities of producing amorphous material as plates are not clear as well as the kinetics and thermal conditions necessary for changing δ-amorphous form to crystalline one. The aim of present work is to perform an analysis of structural changes, particularly referring to the amorphous phase, in PA6 plate specimens prepared from the melt that had been cooled at different rates.

2. Experimental

2.1. Materials

Polyamide 6 (PA6) was supplied by the Khimvolokno Company, Grodno, Belarus. The relative viscosity of the material in H_2SO_4 is 2.6; the melting point is 222 °C.

2.2. Specimen preparation

Test specimens were obtained from the melt ($T_m = 240$ °C) by injection molding in the laboratory machine of piston type (injection volume 3 cm^3). The cooling rate of PA6 melt was changed by varying the initial temperature of the mould. It was determined by using thermocouples to measure the temperature of the mould near its cavity that filled with the polymer. A slow cooling rate was about 2 °C/min; an intermediate one was about 100 °C/min. The fast cooling (at about 2000 °C/min) was conducted as follows: the metallic plates were cooled in liquid nitrogen; then molten PA6 in the form of jet that had been heated up to 240 °C was run between the steel plates having an initial temperature of about −100 °C. In this case, variations in the cooling rate within the specimen are possible. In central zone of the specimen where the thermocouples were now located, a quenching runs at the lowest rate due to the lowest heat transfer. Consequently, structural transformations there occur deeper than those in outer zones contacting a steel surface. Because of this, a cooling rate in central zone (about 2000 °C/min) is accepted as the main for the studied process.

For the cooling rates of 2 and 100 °C/min, the specimens for DSC and WAXS investigations were as strips 5 mm wide and 4 mm thick. For the relaxation measurements, test strips in a size of $50 \times 5 \times 1$ mm were used. In the case of cooling rate of 2000 °C/min, for all the tests, specimens in the form of plates of about 1 mm thick were cut with a punching die.

2.3. X-ray analysis

The X-ray analysis was performed by the WAXS method using the diffractometer DRON (Nauchpribor Co., Orlov, Russia) with CuK_α—radiation source ($\lambda = 0.1542$ nm) and Ni filter (slot 10 μm) (Cu anode, voltage 40 kV, current 30 mA). The diffractograms were recorded for angles (2Θ) between 10° and 30°.

2.4. DSC analysis

The structural changes in specimens were estimated with respect to thermal effects of melting and crystallization by differential scanning calorimetry (DSM-10M, Institute of Biological Instruments, Russian Academy of Sciences). The specimens as slices were cut from the central region of PA6 plates; the weight was 7 mg; the heating and cooling rates were 16 °C/min. The temperature was measured within the accuracy of ±0.2 °C. The crystallinity degree was evaluated from the melting (crystallization) heat of PA6. The working standard was In ($T_m = 156$ °C, $\Delta H_m = 28.45$ J/g) [24].

2.5. Relaxation measurements

The relaxation transitions were studied by dynamic-mechanical loss method using the reverse torsion pendulum device designed at MPRI NAS of Belarus [25]. The pendulum frequency was 1 Hz. The specimens were heated at the rate of 1.5 °C/min within temperature range from −150 up to 200 °C. The temperature measurement accuracy was ±0.1 °C.