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Structural transitions of nylon 47 and clay influence on its crystallization behavior

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ABSTRACT

Basic diffraction data on nylon 47 pointed out a peculiar structure of hydrogen bonds along two directions. Nylon 47 showed reversible polymorphic transitions during heating/cooling processes that were analyzed by real time synchrotron WAXD experiments. Results indicated that nylon 47 had a first structural transition at low temperature, followed by a gradual Brill transition towards a pseudohexagonal packing.

Nylon 47 crystallized from the melt giving rise to spherulites with different characteristics than those attained with conventional even-even nylons. Interestingly, spherulites crystallized at low supercooling underwent a reversible change in birefringence with temperature. This was due to the reversible structural changes caused by temperature variations and the flat on lamellar morphology.

Intercalated and exfoliated nanocomposites based on nylon 47 were prepared by solution intercalation and melt mixing using Cloisites 25A and 30B. The influence of the final silicate layer morphology on the hot crystallization behavior was investigated. Crystallization rates of the neat polymer and its two nanocomposites were significantly different, mainly due to variations in the primary nucleation.

1. Introduction

Aliphatic polyamides (nylons) constitute a family of polymers with exceptional properties because of their capability to establish strong intermolecular hydrogen-bonding interactions [1], which in addition may condition both molecular conformation and packing preferences. Thus, the crystalline structure of conventional even-even nylons and also of even nylons is based on a stacking of sheets composed of hydrogen-bonded molecular chains with a planar zig-zag conformation (α and β forms) [1–3]. The corresponding X-ray fiber diffraction patterns of such structures are characterized by the presence of two strong equatorial reflections at spacings close to 0.440 and 0.380 nm associated with intrasheet and intersheet spacings, respectively.

Nylons can, however, crystallize according to other arrangements and molecular conformations depending on the parity of the constituent monomers (e.g. the pseudohexagonal γ phase postulated for some odd–odd nylons [1,4]) and indeed the presence of special units like glycine [5,6] (e.g. nylons 2/3, 2/6) and malonic acid [7] (e.g. nylons n,3). Furthermore, nylons can undergo phase transitions during heating and cooling processes, for example the reversible Brill transition typical of nylons having conventional α/β forms at room temperature. [8–17] In this case, the two characteristic equatorial reflections gradually merge on heating into a single one (ca. 0.421 nm), which is indicative of a pseudohexagonal arrangement. On cooling from the melt state, the polymer first crystallized according to a pseudohexagonal packing, and then the characteristic single reflection split into the two above

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indicated reflections at a temperature lower than that observed in the heating process.

A peculiar structure based on the establishment of hydrogen bonds along two different directions has recently been postulated for some nylons derived from diamine and dicarboxylic acid units with different parity (e.g. nylons 69, [18] 65, [19,20] 12,5, [21] 56, [22,23] 5,10 [24] and 92 [25]). These nylons showed X-ray fiber diffraction patterns with two strong equatorial reflections at similar spacings to those reported for the α/β conventional structures. However, as shown in Fig. 1a for a representative odd diamide unit, no good intermolecular hydrogen-bonding interactions could be established when a planar zig-zag molecular conformation was adopted.

The distinctive feature of the new molecular arrangement is the capability to establish good hydrogen-bonding interactions along two different directions with molecules having a practically all trans conformation. Thus, a slight deviation towards 150° (or −150°) for the two torsional angles vicinal to the odd diamide units seems necessary to face all NH and CO groups of neighboring chains. The two amide groups of the odd unit rotated in opposite senses from the plane defined by the methylene carbon atoms, allowing the establishment of a good hydrogen-bonding geometry when neighboring chains became conveniently shifted along the chain axis direction (Fig. 1b). A monoclinic unit cell containing two molecular segments was derived and the chain axis projection corresponded to a rectangular unit cell [18–25].

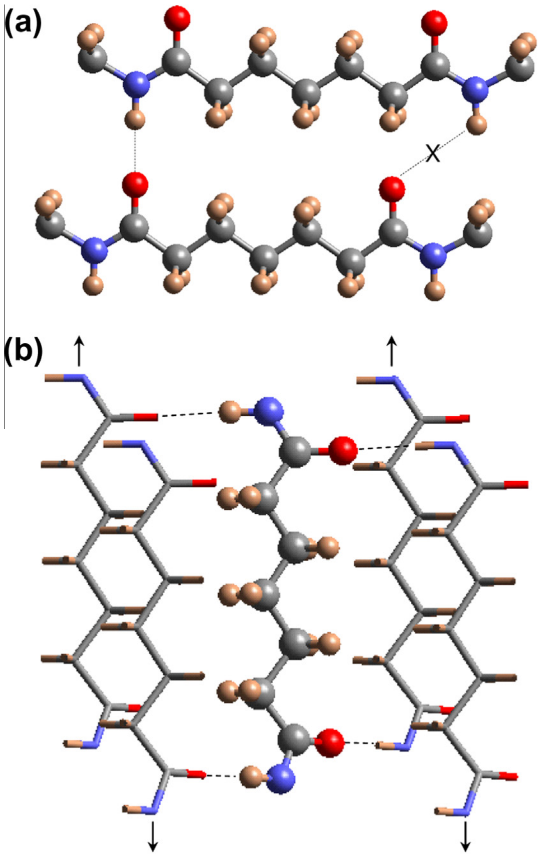

Fig. 1. (a) Scheme of the unfavorable hydrogen-bonding geometry between pimelamide units having an all trans conformation and (b) Scheme showing how hydrogen bonds could be established along two directions when the two amide planes of the pimelamide unit rotate in opposite directions from the plane defined by its methylene carbons. External chains (stick representation) should be shifted along the chain axis direction (see arrows) with respect to the central chain (ball and stick representation), thus giving rise to a monoclinic unit cell. Color code: nitrogen, blue; oxygen, red; carbon, gray; hydrogen, brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Crystallization processes are influenced by the incorporation of phyllosilicate particles as these may affect the overall crystallization rate, crystal growth, nucleation type and morphological features. In fact, crystallization is determined by different factors which may be favored or disfavored when clay particles are added. Thus, previously published results suggest that the crystallization process strongly depends on the type of clay dispersion (e.g. exfoliated or intercalated) and even on the interactions between clay and polymer matrix [26–30]. It seems, therefore, interesting to obtain new data on the crystallization behavior of composites based on polyamides having different intermolecular interactions from those of conventional nylons as it is the case of nylon 47, an even–odd polyamide whose structural transitions will be also studied.

2. Experimental section

2.1. Materials

Nylon 47 was synthesized by interfacial polycondensation of 1,4-diaminobutane and pimeloyl chloride using toluene as organic solvent and sodium hydroxide as proton acceptor and following the procedure previously described for similar nylons [19]. The polymer was purified by precipitation with water of a formic acid solution. Nylon 47 was obtained with a yield of 55% and an intrinsic viscosity of 0.85 dL/g (determined in dichloroacetic acid at 25 °C).

Dimethyl hydrogenated-tallow 2-ethylhexyl ammonium montmorillonite (CLOISITE 25A, Southern Clay Products, 2MHTEX) and methyl tallow bis(2-hydroxyethyl) ammonium montmorillonite (CLOISITE 30B, Southern Clay Products, MT2EH) (tallow ($\sim$65% C18, $\sim$30% C16, $\sim$5% C14)) were used as received.

2.2. Preparation of nanocomposites

Nanocomposites containing 3% of C25A or C30B clay particles were prepared by a two-step melt mixing process using a co-rotating tightly intermeshed twin-screw extruder (DSM Xplore 5 ml microcompounder). The processing temperature, screw rotation and cycle time were 260 °C, 100 rpm and 3 min, respectively.

Alternatively, nanocomposites were also prepared by the solution-intercalation film-casting technique. Specifically, 100 mg of nylon 47 were dissolved in 10 mL of 1,1,1,3,3,3-hexafluoroisopropanol and mixed with a clay dispersion (<0.1 wt%) in 1,1,1,3,3,3-hexafluroisopropanol.