



The role of particle surface functionality and microstructure development in isothermal and non-isothermal crystallization behavior of polyamide 6/cellulose nanocrystals nanocomposites



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ABSTRACT

Polyamide 6 (PA6)/cellulose nanocrystal (CNC) and aminopropyl triethoxy silane (APS) - modified CNC nanocomposites were prepared by *in situ* anionic ring opening polymerization and subsequent melt extrusion. The morphological observation of these hybrid systems revealed that the non-modified nanocrystals developed a network-like fibrillar structure while the APS-modified CNCs were finely dispersed mostly as individual whiskers. The isothermal and non-isothermal crystallization kinetics was extensively studied with emphasis on the effects of CNC surface functionality and the subsequent microstructure development on crystallization behavior of these novel nanocomposite systems. The non-modified CNC particles with corresponding fibrillar microstructure were found significantly hinder the crystallization process and spherulitic growth of polyamide 6 chains under both isothermal and non-isothermal conditions. On other hand, the surface modified cellulose nanocrystals with improved sub-micron dispersion enhance crystal nucleation in early stages of crystallization while imposing opposite effect in later stages of crystallization resulting in development of relatively smaller defective spherulitic structures.

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1. Introduction

Polyamide 6 (PA6) is one of the most important semi-crystalline engineering thermoplastic materials that has been of great interest both in academic studies and industrial applications due to its superior mechanical strength, chemical resistance towards wide range of solvents and hydrocarbons [1,2] and high stiffness. It is well known that there are two crystalline structures in PA6, the α -type and γ -type polymorphs [3–5]. The α -form is the most thermodynamically stable crystalline form of PA6 consisting of anti-parallel chains connected with the adjacent chains through hydrogen bonds in a planar zig-zag conformation while the γ -form is thermodynamically less stable consisting of pleated sheets of hydrogen bonded parallel chains [6,7].

In the past decade, application of nanomaterials in development of polymer nanocomposites has received much attention in the literature as an effective approach towards controlling the physical and structural properties of the host polymers like their

crystallization behavior and properties. These nanomaterial inclusions include layered silicates [8,9], carbon nanotubes [10,11], graphene [12] and silica nanoparticles [13].

Wu et al. [14] studied the effect of montmorillonite and saponite nanoparticles on the crystallization behavior of PA6. Their results indicated that the addition of these clay nanoparticles acted as effective heterogeneous nucleating agents in the PA6 matrix at lower clay contents indicated by lower crystallization activation energy. In a reported study by Paul et al. [15], it was shown that organically modified clay (O-MMT) significantly reduced the crystallization half time ($t_{1/2}$) of PA6 matrix during non-isothermal crystallization followed by a complicated crystallization mechanism.

Guo and co-workers [16] studied the effect of halloysite nanotubes on non-isothermal crystallization behavior of PA6. Their results revealed that the nanotubes acted as nucleating agents in the PA6 melt while severely restricting the polymer chain mobility. It was also observed that development of γ -phase crystals were significantly promoted in the presence of halloysite nanotubes.

In a series of studies by Li and co-workers [17,18], the effect of carbon nanotubes on isothermal and non-isothermal

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crystallization behavior of PA6 was investigated. It was found that the CNTs accelerated the nucleation phase as indicated by a shift of onset crystallization temperature towards higher temperatures as well as increased the crystallization half-time. However, it is worthy to note that during the isothermal crystallization, the authors reported a shortened crystallization half-time that points to fast crystallization rate, suggesting special effects of the nanomaterials in the crystallization process under the various conditions studied.

In addition, cellulose based nanomaterials in the form of nanofibers and nanocrystals, as in the current study described in this article, have also been the subject of intense study over the past years for application in polymer composites and nanocomposites due to a number of special advantages of the cellulosic nanomaterials over traditional synthetic fibers and fillers. These advantages include such as having lower density, exceptional mechanical properties, bio-renewability, low cost, and potential environmentally-friendly alternative to conventional fillers [19,20]. In a study [21] on polylactic acid (PLA) composites reinforced with up to 10 wt% cellulose whiskers, it was found that the crystallization of PLA is significantly hindered and the overall crystallization of the matrix decreased. Han and co-workers [22] studied the role of cellulose whiskers (CWs) in polyurethane matrix during isothermal crystallization by using Avrami model and found that the CWs act as nucleating agents during isothermal crystallization. This effect was validated by lower activation energies of crystallization as well as shorter half-times of the nanocomposite samples compared to that of the neat polyurethane matrix. Siqueira et al. [23], in a comprehensive reported study of the effect of the shape of the cellulose nanoparticles in the form of micro-fibrillated cellulose (MFC) and CWs on the crystallization behavior of poly (ϵ -caprolactone), showed that both MFCs and CWs can accelerate the crystallization kinetics by acting as nucleating agents under isothermal crystallization condition. In addition, the lamellar growth rate analysis showed that the MFC, and to a lesser extent, the CWs restricted the chain mobility and the lateral growth rate of the spherulites. On the other hand, other authors reported increase in relative crystallinity with addition of nanocellulose. For example, recent reported studies on polyvinyl alcohol reinforced with MFCs either cast from solution [24] or in the form of spun fibers [25] showed an increase in the degree of crystallinity in the composite samples compared to that of the neat matrix.

By contrast, studies on the properties of high melting point engineering thermoplastics such as polyamide 6 reinforced with nanocellulose has been limited due to the thermal degradation of cellulose at typical temperatures of direct melt mixing process that reduces the effectiveness and functionality of cellulose in the matrix. A recent study by Kiziltas et al. [26] showed that incorporation of microcrystalline cellulose (MCC) into polyamide 6 matrix (processed with the aid of lubricant) reduced the overall crystallinity of the matrix upon addition of 2.5–30 wt% of MCCs. The authors just mentioned also reported that the onset and peak crystallization temperature of the PA6 was shifted towards relatively larger values. However, the analysis of the non-isothermal crystallization of these systems via Avrami and Tobin models, showed no significant changes suggesting a poor nucleation activity of the MCC in the PA6 matrix.

In a previous study, we adopted a novel approach of *in-situ* ring-opening polymerization technique to incorporate cellulose nanocrystals (CNCs) in a PA6 matrix that gave PA6/CNC nanocomposites with improved properties such as superior physical and melt property, enhancement obtained even at very low concentration of CNCs reported in our previous publication [27]. This strategy enabled the CNCs to be incorporated in the PA6 matrix prior to processing at temperatures far below the melt processing

temperature of the PA6, significantly minimizing the CNC thermal degradation and improving the CNC dispersion in the PA6 in a subsequent melt processing step. The current study described in this article reports a detailed analysis of the crystallization behavior and kinetics under both isothermal and non-isothermal conditions with specific focus on the effects of CNC surface modification and microstructure evolution in the PA6 matrix, and the results interpreted according to reported polymer crystallization models in the literature.

2. Experimental

2.1. Materials

The caprolactam monomer used in this study is AP-Nylon[®] caprolactam grade (purchased from Brueggemann Chemical, Pennsylvania) with low moisture content (<100 ppm) suitable for anionic ring-opening polymerization. C20, a difunctional hexamethylene-1,6- dicarbonyl caprolactam (the ROP activator), was supplied by Brueggemann Chemical. Ethylmagnesium bromide used as the initiator was purchased from Aldrich. Aminopropyl triethoxy silane (APS) was purchased from Gelest Inc.

2.2. Sample preparation

The cellulose nanocrystals were prepared by sulfuric acid hydrolysis of bleached cellulose paper (obtained from Weyerhaeuser) following the method reported by Capadona et al. [28] with some modifications. The cellulose paper was cut into small pieces and blended with de-ionized water (20 g/L) to achieve a “lumpy” cellulose pulp followed by placement in a glass reactor in an ice bath. Concentrated sulfuric acid (98%) was slowly added to the cold suspension at 35 v/v% of acid in the total suspension. The mixture was then heated to 50 °C and stirred for 3.5 h. The obtained suspension was subsequently quenched with a 10-fold excess of de-ionized (DI) water and filtered over fine fritted glass filter and washed slowly with DI water until the running water showed a pH of ~5–6. The resulting mixture was decanted to remove the unhydrolyzed fibers and then centrifuged (5 cycles) at 3000 rpm for 10 min to concentrate the CNCs. The nanocrystals were recovered by freeze-drying of the suspension and were neutralized with 2 mM NaOH solution to convert the surface sulfonic acid groups to sodium salt (indicated by pH neutrality of the CNC dispersions). The obtained neutralized CNCs were dried overnight to constant weight in a vacuum oven at 90 °C prior to preparation of the nanocomposite samples.

Surface modification of CNCs was carried out using amino propyl triethoxy silane (or APS). Briefly, a suspension of CNC was prepared in DI water with first mixing the CNC followed by sonication for 20 min. In a separate flask, the APS was added (7 wt% of the CNC) to DI water and mixed for 10 min in order to hydrolyze the ethoxy groups into hydroxyls. These separate mixtures were mixed and the final dispersion was allowed to mix for 3 h under continuous agitation. The dispersion was then frozen in liquid nitrogen and freeze dried for at least 60 h to recover the CNC powder with APS adsorbed on the surface. Finally, the polycondensation of APS with the CNC surface hydroxyl groups was carried out in vacuum oven at 120 °C under vacuum for 1 h.

The PA6/CNC nanocomposites were prepared by *in situ* ring-opening polymerization of caprolactam monomer in the presence of CNCs. For this purpose, pristine and surface modified CNCs were dispersed in the monomer at 1, 2 and 3 wt% CNC concentrations by high-speed agitation and sonication for 25 min at 90 °C. This mixture was blended with another master-batch of the activated monomer containing the initiator and activator and the resulting

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