



Unique crystallization behaviors of isotactic polypropylene in the presence of MWCNT supported β nucleating agent: Lower temperature $T(\alpha\beta)$ - $T(\beta\alpha)$ interval and fast cooling preferred formation of β crystals



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ABSTRACT

Simultaneous improvement of stiffness and toughness of isotactic polypropylene (iPP) has caught tremendous effort for decades and previously we have shown that the modification of iPP with combined nanofillers and β -nucleating agent (β -NA) is an efficacious way to balance its stiffness and toughness. However, simultaneous introduction of reinforcing fillers and β -NA generates nucleation competition in the crystallization process and generally the formation of β crystals is depressed, while the nucleation competition induced by β -NA grafted onto the surface of reinforcing fillers was not clear yet. In this work, a kind of novel β -NA for iPP, N,N'-dicyclohexyl-1,5-diamino-2,6-naphthalenedi-carboxamide, was supported onto the surface of multi-walled carbon nanotubes (MWCNTs) through chemical bonds. The α and β nucleating competition among iPP nucleated by β -NA, physically mixed MWCNTs and β -NA (MWCNT + NA), and MWCNT supported β -NA (MWCNT-NA) was systematically investigated. Interestingly, in the presence of MWCNT-NA, iPP showed unique crystallization behaviors. The nucleation competition between α - and β -crystals became intensified and showed temperature dependence, and the relative content of β -crystals increased with increasing cooling rate, which is opposite to the general understanding of crystallization behaviors of semicrystalline polymers, but is highly desired in practical productions. A possible interpretation for this unusual crystallization behavior of iPP is provided.

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1. Introduction

Isotactic polypropylene (iPP) is one of the most important thermoplastic polymers owing to its relatively low manufacturing cost and rather versatile properties. It is a typical polymorphic thermoplastic with several crystalline forms including monoclinic (α), trigonal (β) and or thorthombic (γ) [1–3]. Among these crystalline forms, β -form iPP (β -iPP) shows excellent toughness and thermal performance [4–7] and has received much attention in scientific research and industrial applications. Generally, α -form crystals are obtained under common processing conditions, while β -form crystals can only be generated under some special conditions, such as quenching [8], abrupt temperature gradient [9],

shearing or elongation deformation [10–14], introducing homogeneity fibers at certain temperatures [15,16], and the addition of β -nucleating agent (β -NA) [5,7,17,18]. Among these methods, the addition of β -NA is the most effective and accessible to obtain high content of β -form crystals. However, the yield strength and stiffness of β -iPP are generally lowered down compared with those of α -form iPP (α -iPP) [19].

Modification of iPP with reinforcing fillers and β -NA may be a possible path to balance the stiffness–toughness of iPP. But simply compounding reinforcing fillers and β -NA with iPP is hard to improve the strength and toughness of resulted iPP materials at the same time [20]. The modification of iPP with nanofiller grafted β -NA, which can induce a tough β crystal layer surrounding the stiff nanofillers, is an efficacious way. In our previous work, a kind of β -NA, calcium pimelate was supported onto the surface of MWCNTs, which largely improved the impact toughness without significant loss of the stiffness and strength of iPP composites [6,21]. Recently, a kind of novel β -NA, N,N'-dicyclohexyl-1,5-diamino-2,6-

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naphthalenedi-carboxamide, was supported onto the surface of graphene oxide (GO) by π - π conjugation, and iPP samples modified by this compound GO- β -NA showed simultaneously enhanced toughness and tensile strength [22].

The reinforcing fillers, such as carbon nanotubes and carbon fibers, have α nucleating ability for iPP [23–25]. It is well known that the coexistence of reinforcing nanofillers and β -NA induces the growth competition between α -crystal and β -crystal in iPP matrix [26–29]. When β -NA was supported on the nanofillers, the crystallization competition between α -crystal and β -crystal may be different from that induced by physical blending of nanofillers and β -NA, which is very important for achieving high-performance of iPP through tailoring crystallization by β -NA supported nanofillers. However the α - and β -nucleation competition in β -NA supported fillers is not clear yet.

In this work, the novel β -NA for iPP synthesized by our group [30], N,N'-dicyclohexyl-1,5-diamino-2,6-naphthalenedi-carboxamide, was supported onto the surface of MWCNTs by chemical bonding, after MWCNTs were grafted with polyacrylic acid (PAA) chains through reversible addition-fragmentation chain transfer (RAFT) polymerization. The crystallization behaviors of iPP modified by β -NA, physically mixed β -NA and MWCNTs (MWCNT + NA), and MWCNT supported β -NA (MWCNT-NA) were systematically studied. Because of the dual nucleating ability of MWCNT-NA, α and β nucleating competition induced by MWCNT-NA became more intensely and induced unique crystallization behaviors of iPP composite. The nucleation competition also showed temperature dependence, and the relative content of β -crystals increased obviously with increasing cooling rate, which is opposite to the general understanding of crystallization behaviors of semicrystalline polymers, but is highly desired in practical productions. A possible interpretation for this unusual crystallization behavior of iPP is also presented here.

2. Experimental section

2.1. Materials

iPP with the trade name of T30s and a melt flow rate of 2.3 g/10 min (230 °C, 2.16 kg load) was purchased from Lanzhou petroleum Chemical Co, Ltd. (PR China). The used β -NA, N,N'-dicyclohexyl-1,5-diamino-2,6-naphthalenedi-carboxamide, was synthesized according to the procedure reported in our previous work [30]. Amino-functionalized MWCNTs (MWCNT-NH₂, trade name XFM62), with an average diameter of 8–15 nm and length of 50 μ m, were purchased from XFNANO Inc. (Nanjing, China). According to the supplier, the content of -NH₂ is 0.45wt%. Other reagents, including methylene chloride, thionyl chloride, tetrahydrofuran (THF), triethylamine, acrylic acid, dimethyl formamide (DMF), were purchased from Chengdu Changzheng Chemical Glass Apparatus Co, Ltd. (PR China). Methylene chloride, THF, acrylic acid, DMF were purified by vacuum distillation.

2.2. Synthesis of MWCNT supported NA (MWCNT-NA)

Reversible addition-fragmentation chain transfer polymerization was adopted to graft β -NA onto the surface of MWCNTs. The RAFT agent, *S,S'*-Bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate (CTA) was prepared using John's method [31].

282 mg (1 mmol) CTA was dissolved in 20 ml anhydrous methylene chloride in a 500 mL three-necked and round bottom flask, and 5 mL thionyl chloride was added into the flask dropwise. The mixture was refluxed under stirring for 6 h at 60 °C. Reduced pressure distillation was then performed to remove excess thionyl chloride. 500 mg amino-functionalized MWCNT (MWCNT-NH₂)

was dispersed in 300 mL anhydrous THF under ultrasonication for 30 min, and then were added into the flask. The mixture was then refluxed under stirring for 12 h at 60 °C and vacuum filtered. The obtained powder was washed with THF via high speed centrifugation for more than five times to remove excess CTA. The MWCNT-CTA was obtained after the resulting powder was vacuum dried at 60 °C for 24 h.

300 mg MWCNT-CTA, 3.6 g acrylic acid, and 4.1 mg of 2, 2-azobisisobutyronitrile (AIBN) in 10 ml THF were added into a 50 ml flask and sealed under vacuum. Then the flask was ultrasonication treated for 30 min and then placed in an oil bath at 65 °C and kept stirring for 24 h [32–35]. The products were washed with distilled water via high speed centrifugation for more than five times. The MWCNT-PAA was obtained after the resulting powder was vacuum dried at 60 °C for 24 h.

200 mg MWCNT-PAA was dispersed in 50 mL anhydrous THF and 10 mL thionyl chloride was added into the flask dropwise. The mixture was refluxed under stirring for 12 h at 60 °C, and then reduced pressure distillation was performed to remove excess thionyl chloride. 100 mg N,N'-dicyclohexyl-1,5-diamino-2,6-naphthalenedi-carboxamide in 40 mL anhydrous DMF were then added into the flask, and the mixture were stirred at 65 °C for 12 h. The products were washed with DMF via high speed centrifugation for more than five times. The final products were dried at 40 °C under vacuum for 24 h, yielding MWCNT supported β -NA (designated as MWCNT-NA).

2.3. Preparation of MWCNT-NA nucleated iPP composites

The iPP pellets and MWCNT-NA (0.5, 1.0, 2.0 wt%) were compounded with a mini extruder at 190 °C and 60 rpm. For comparison, pure iPP, iPP composites with 1.0wt% MWCNT-NH₂ and MWCNT-PAA were also prepared with the same procedure. The content of grafted β -NA on the surface of MWCNT-NA was calculated from the XPS spectra to be about 10wt%. Then in the sample containing 0.5wt% MWCNT-NA, the content of β -NA was about 0.05wt%. In order to find out the effect of grafting on the nucleating ability of β -NA, we also prepared iPP composites with 0.05wt% β -NA, 0.45wt% MWCNT-NH₂ and 0.05wt% β -NA, 0.45wt%MWCNT-PAA and 0.05wt% β -NA (marked as 0.05NA, MWCNT + NA and MWCNT-PAA + NA, respectively) with the same procedure. In these four specimens, the content of β -NA was nearly the same. The β -NA in MWCNT-NA was grafted onto the surface of carbon nanotubes through the amidation reaction with PAA, whereas the β -NA was simply mixed in the other three samples.

All these samples were compression molded at 220 °C and 10 MPa into 0.4 mm thickness sheets. The cooling process of compression molding was recorded by a temperature probe, and the cooling rate was about 140 °C/min in the temperature range of 140–100 °C (see Fig. S1).

2.4. Characterizations

2.4.1. Fourier transform infrared spectroscopy (FTIR)

The chemical structures of MWCNTs and its derivatives were analyzed with a Nicolet 6700 Fourier transform infrared spectrophotometer (Nicolet Instrument Company, USA). Specimens for the measurements were mixed with KBr and pressed into plates. The FTIR spectra were recorded in the wavenumber range of 4000–400 cm⁻¹ with a 4 cm⁻¹ resolution over 16 scans.

2.4.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed to study the elemental composition of MWCNTs and its derivatives using an X-ray photoelectron spectrometer (XSAM800, Kratos Company, UK).

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