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Role of multi-wall carbon nanotube network in composites to crystallization of isotactic polypropylene matrix

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Abstract

The composites (iPP/CNTs) made of isotactic polypropylene (iPP) and multi-wall carbon nanotubes (CNTs) were prepared by solution blending. To improve compatibility between CNTs and iPP and to enhance dispersion of CNTs in iPP matrix, CNTs were chemically modified by grafting alkyl chains. The chemically modified CNTs had about 6 wt% grafted alkyl chains. Rheological measurements indicated that CNTs caused gelation in iPP/CNTs due to CNT network formation and the critical gelation CNT concentration was about 7.4 wt%, which was considered to be high due to the low CNT aspect ratio in this study. Crystallization behaviors of iPP/CNTs were studied by using optical microscopy (OM) and differential scanning calorimetry (DSC). Radial growth rates of spherulites during isothermal crystallization of iPP/CNTs with CNT concentrations less than 2.0 wt% measured by using OM showed decreasing trends with increasing CNT concentration. Avrami analysis of the exothermic heat flow curves during isothermal crystallization of iPP/CNTs measured by DSC indicated that crystallization rates were accelerated when CNT concentrations were lower than the critical gelation concentration, because CNTs mainly functioned as nucleating agents for crystallization, while crystallization rates did not change obviously when CNT concentrations were higher than the critical gelation concentration, because CNT network could form and mainly functioned to provide restriction to mobility and diffusion of iPP chains to crystal growth fronts.

Keywords: Isotactic polypropylene; Carbon nanotubes; Crystallization

1. Introduction

Isotactic polypropylene (iPP) is one of the most important commodity polymers. It is extensively used in industry to manufacture bottles, films, fibers, etc. However, the application of iPP has been limited by its tendency to brittleness at low temperatures. Therefore, a great deal of effort has been made to modify its mechanical properties such as blending iPP with inorganic fillers [1]. Several studies have been devoted to the uses of carbon nanotubes (CNTs) as fillers to improve performances of iPP or to achieve new properties of the composites, because of high aspect ratios, unusual mechanical and electronic properties of CNTs [2–4]. Because crystallization behavior would have a huge influence on mechanical properties of the filled iPP, several groups reported crystallization behaviors of iPP in the presence of CNTs [5–10]. Most of these studies focused on changes of iPP crystal forms [5,6] or nucleating ability of CNTs for iPP crystallization [7].

One recent study shows that combination of the extended shape, rigidity and deformability of CNTs allows CNTs to be well dispersed in polymer matrix in the form of disordered 'jammed' network structures at above a critical CNT concentration [2]. We predict that this CNT network can affect iPP crystallization in certain ways. Thus, iPP crystallization behaviors may be much different between those prior to and beyond CNT network formation. In fact, there have been several evidences in literatures to support this prediction. Haggenmueller et al. studied crystallization kinetics of polyethylene (PE) in the presence of single-wall carbon nanotube (SWNT) [11]. They found that addition of 1 wt% SWNT

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reduced the half crystallization time ($t_{1/2}$) to 7% of $t_{1/2}$ of neat PE at 122 °C, while additions from 1 wt% to 10 wt% SWNT provided only modest additional decreases of $t_{1/2}$. We consider that 10 wt% SWNT is sufficient for PE/SWNT to form gelation due to the SWNT network according to the SWNT aspect ratio in their study and the SWNT network may affect PE crystallization behaviors. Li et al. studied crystallization kinetics of poly(hexamethylene adipamide) (nylon 66) in the presence of multi-wall carbon nanotubes (CNTs) [12]. They observed that crystallization rate of nylon 66 during isothermal crystallization measured by DSC increased at first and then decreased with increasing CNT content. They suggested that the effect of CNTs on nylon 66 crystallization was twofold: CNTs provided heterogeneous nucleation sites for crystallization while CNT network hindered formation of large-size crystals. At low CNT contents, CNT surface initiated nylon 66 crystallization and the confinement effect was not significant. As the CNT content increased, although more CNTs could provide nucleation surface, the formed robust CNT network imposed a much more significant confinement effect on mobility of nylon 66 chains. This confinement effect overcame the nucleation effect and slowed down the overall crystallization kinetics [12]. Though the effects of CNT network on crystallization of semicrystalline polymers have been proposed, direct evidences are still missing. In the study reported here, we firstly determined the critical gelation CNT concentration for iPP/CNTs by using rheological methods, and then we further investigated the effects of CNT network on iPP crystallization behaviors in the composites.

2. Experimental section

2.1. Preparation and characterization of chemically modified multi-wall carbon nanotubes

To enhance dispersion of CNTs in iPP, commercially available multi-wall CNTs (produced by chemical vapor deposition (CVD) method, Shenzhen Nanotech Port Co., Ltd., China) were chemically modified as follows. CNTs were purified and converted into acid form [CNT(COOH)$_n$] *via* sonication in 1/3 relative volume ratio of nitric acid/sulfuric acid mixture at 40 °C. The resultant solid was washed with deionized water until the pH value was 6 and then an excessive NaOH solution was added until the pH value became 14, converting CNT(COOH)$_n$ into sodium salt form [CNT(COONa)$_n$]. The CNT(COONa)$_n$ nanotubes were recovered by centrifuging at 3000 rpm for 10 min, and then the resultant solid was washed with deionized water until the pH value was 6. Cetyltrimethylammonium bromide (CTAB), $C_{18}H_{37}Br$, CNT(COONa)$_n$ and water were mixed and the suspension was continuously refluxed under vigorous stirring for 12 h. When the stirring was stopped, the suspension separated to form a clear, colorless top solution with a black precipitate on the container bottom. The precipitate was collected and placed in a Soxhlet extractor. Deionized water (200 ml) was added to extract the remained CTAB over a period of 24 h, followed by addition of 200 ml chloroform to remove the remained $C_{18}H_{37}Br$ for another 24 h [13]. The solid material obtained from the Soxhlet extractor was dissolved in chloroform at 1 wt%. The solution was put in a sonication bath for 2 h and then was centrifuged at 3000 rpm for 10 min. The upper solution was collected and distilled to obtain the resultant solid material. Finally, the solid material, alkyl-modified CNTs, CNT(COOC$_{18}$H$_{37}$)$_n$, was dried under vacuum at room temperature for further use. Thermogravimetric analysis (TGA) showed about 6 wt% grafted alkyl chains on CNT(COOC$_{18}$H$_{37}$)$_n$ [13].

Structure and morphology of CNT(COOC$_{18}$H$_{37}$)$_n$ were characterized by using scanning electron microscopy (SEM, Hitachi S-4300, made in Japan). A dilute solution of CNT(COOC$_{18}$H$_{37}$)$_n$ in chloroform was dropped onto a clean aluminum foil to form a thin film after chloroform evaporated, and the thin film was subjected to SEM examination. Length distribution of CNT(COOC$_{18}$H$_{37}$)$_n$ could be obtained from SEM images, which was used to obtain the average aspect ratio of CNT(COOC$_{18}$H$_{37}$)$_n$.

2.2. Preparation of iPP/CNT composites

The iPP sample employed in this work was commercial product of the Aldrich Chemical Company. The iPP sample had mass average molecular weight, M_w, of 340,000 and number average molecular weight, M_n, of 97,000. iPP (3.4 g) was added into 110 ml xylene in a flask. The flask under protection of nitrogen atmosphere was put into an oil bath set at 130 °C. When iPP was dissolved for 20 min, the oil bath temperature was set to 120 °C. The iPP solution was continuously stirred for 1 h before CNT(COOC$_{18}$H$_{37}$)$_n$ xylene suspension was added in. The CNT(COOC$_{18}$H$_{37}$)$_n$ xylene suspension with CNT concentration of 0.25 wt% had been prepared with 2 h sonication. A certain amount of CNT(COOC$_{18}$H$_{37}$)$_n$ xylene suspension was added into iPP solution to determine a suitable mass ratio of CNT(COOC$_{18}$H$_{37}$)$_n$ to iPP. The mixture was continuously stirred for another 1.5 h. Then the mixture was deposited into a large quantity of methanol with a 1/7 volume ratio of the former to the latter. The precipitate of iPP/CNT(COOC$_{18}$H$_{37}$)$_n$ composite was separated and washed with methanol for three times, and then was put in ventilation hood to let solvents evaporate for 48 h. The recovered composite was dried at 60 °C under vacuum for 3 days. By using the above procedure, eight samples were prepared, which possessed CNT(COOC$_{18}$H$_{37}$)$_n$ concentrations of 0%, 0.2%, 0.5%, 1.0%, 2.0%, 3.8%, 7.4% and 9.1%, respectively. CNT(COOC$_{18}$H$_{37}$)$_n$ and iPP/CNT(COOC$_{18}$H$_{37}$)$_n$ composites are abbreviated as CNTs and iPP/CNTs, respectively, for simplicity in this article.

2.3. Determination of critical gelation CNT concentration for iPP/CNTs by rheology

Disk-shaped samples of iPP/CNTs with 1 mm thickness and 25 mm diameter for rheological measurements were prepared by hot-pressing at 200 °C using stainless steel die. A stress-controlled rheometer (AR2000, TA instrument Ltd.) was applied to measure dynamic rheological properties of