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Crystalline morphology and properties of multi-walled carbon nanotube filled isotactic polypropylene nanocomposites: Influence of filler size and loading

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ABSTRACT

Isotactic polypropylene (PP) nanocomposites with multi-walled carbon nanotubes (MWCNTs) of various diameters (10–50 nm) were fabricated by extrusion and compression-molding techniques and characterized by X-ray diffraction measurements, differential scanning calorimetry, scanning electron microscopy, mechanical test and differential thermal analyses. The pure PP exhibits both the *a*- and *b*-axes oriented α-crystal, whereas the MWCNTs induce the *b*-axis orientation of the α-crystal along with the formation of minor γ-phase crystal in nanocomposites. Crystallinity, long period of lamellae, tensile strength, tensile modulus (*TM*) and microhardness (*H*) of PP considerably change by different loading and sizes of MWCNTs. The estimated values $H/TM = 0.09–0.10$ for all samples approach the predicted value of 0.10 for polymers. The increase in crystallinity has been demonstrated by both XRD and DSC studies. Mathematical models have been invoked to explain the changes in mechanical properties. An increase in thermal stability of polymer matrix occurs with increasing MWCNTs size and loading.

1. Introduction

Isotactic polypropylene (PP) is an extensively used engineering thermoplastic having large variety of physical properties, good mechanical property balances, low cost, easy processability and low density [1]. Despite these advantages of PP, continuous research is still being carried out to further expand its use through the addition of nanoparticles to achieve desired property. In this perspective, some success on nanoparticle-filled PP nanocomposites with improved properties, as driven by the unique properties of the nanoparticles, are notable [2–7]. Since the particle size largely influences the properties of PP based nanocomposites, a variety of nanoparticle morphologies such as spheroidal silica particles [8], platelets clay and graphite particles [9,10], amorphous carbon black [11], and carbon nanotubes (CNTs) [2–4,12,13] have been considered so far to tailor PP for desired performances. Among these, CNTs are used as special types of nanofillers to enable development of lightweight and strong composite materials.

The multi-walled CNTs (MWCNTs) are composed of concentric single-walled CNTs (SWCNTs), which exhibit a unique one-dimensional structure, exceptionally high strength and Young's modulus [14,15]. They have a large aspect ratio and low density and are short enough to allow moldings of complex shapes [16]. The diameter of CNTs ranges from one up to a few nanometers and their length is a few to hundred micrometers. In spite of the promising potential of CNTs, the effect of their size with different loadings on many fundamental properties like crystallinity, nanostructure, mechanical properties and thermal stability of PP is till now to the best of our knowledge neither systematically studied by any researcher nor published in the literature. A few articles regarding the influence of particle size on structures and properties of PP can be mentioned, wherein micro to nanoparticles other than CNTs were used [17–19].

It is well known that the non-uniform dispersion of CNTs in a polymer matrix at higher particle content results in poor mechanical properties of the nanocomposites [20] Therefore, we fabricated injection molded MWCNT-loaded PP nanocomposites after multiple extrusion in previous studies and investigated the influence of particle loading on their crystalline structures and properties [21,22]. Notably, the average length and diameter of the MWCNTs

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used in those investigations were 10 μm and 20 nm, respectively. Considering the effect of particle size on the structure and properties of PP, a series of its nanocomposites with different contents and sizes of MWCNTs have been fabricated in the present study using a compression molding machine after triple extrusions of the mixture of component materials. Thus, the primary aim of the present work is to observe the effects of particle size and loading of MWCNTs on structural, mechanical, micromechanical and thermal properties of the iPP nanocomposites.

2. Experimental

2.1. Sample preparation

Commercial grade PP (density, $\rho_{pp} = 0.91$ g/cm^3 and molecular weight, $M_w = 184700$ g-mol^{-1}) was purchased from BASF, Germany, and MWCNTs powders were collected from Shenzben Nanotech Port Co., Ltd., China. The average diameters of the three different MWCNTs were 10 nm for Particle 1 (range: 5–15 nm), 22 nm for Particle 2 (range: 15–30 nm) and 50 nm for Particle 3 (range: 40–60 nm), but they had the same length ranging 5–15 μm. The MWCNTs powder was of density, $\rho_f = 2.16$ g/cm^3 and was mixed with PP with appropriate ratios. Separate mixtures of PP and 0, 0.05, 0.5, and 2.0 wt% (0, 0.023, 0.231 and 0.925 vol%) MWCNTs content having the aforesaid different sizes were extrusion molded thrice by an extruder machine (Axon AB, Sweden). The extruder has 5 heating zones with blending temperature profiles of 180, 185, 190, 195 and 200 °C. During preparation of samples, the screw rotating speed was 100 rpm. The extrudates were shredded by a chopper machine and again molded in both dumbbell- and bar-shaped dice at 190 °C using a compression molding machine with a load of 100 kN. The compressed melts were rapidly cooled through circulation of water. The neat PP is abbreviated as PP, and 0.05 wt% MWCNTs-loaded PP composites with Particles 1, 2 and 3 are hereinafter coded as 0.05PC1, 0.05PC2 and 0.05PC3, respectively. Similar definitions have been imposed to the case of 0.50, and 2.0 wt% MWCNTs loaded composites.

2.2. X-ray diffraction measurements

The bar samples having the same thickness were used for X-ray diffraction (XRD) measurements. Wide-angle XRD (WAXD) studies were performed by an X-ray diffractometer (model JDX-8P, JEOL Ltd., Tokyo, Japan) using Cu Kα radiation of wavelength, $\lambda = 1.5418$ Å through a step-wise scan over the scattering angle (2θ) from 5° to 50°, with a step of 0.02°. The operating voltage and the tube current of the X-ray generator were 30 kV, 200 mA, respectively. Small-angle XRD (SAXD) measurements of the samples were performed using a rotating anode type high-intensity Rotaflex, RU-300 X-ray generator (40 kV × 200 mA; Rigaku Corporation Tokyo, Japan). The incident X-ray beam, monochromatized by a graphite single crystal, had a wavelength of 1.54 Å. The X-ray beam was passed through a collimation system with a pinhole of 100 μm in diameter. The camera length for SAXD was 460 mm. The diffraction intensity was recorded by a Rigaku Display System imaging plate (IP) (Rigaku Corporation, Tokyo, Japan). The exposure time was set as 60 min in every X-ray measurements.

2.3. Field emission scanning and transmission electron microscopies

The surface morphologies of non-fractured and fractured samples after tensile tests were studied by a field emission scanning electron microscope (FE-SEM) (model-JEOL, JSM-7800F, Japan). For this purpose, samples were placed onto a metal based holder with the help of double sided sticky carbon tape. Prior to observations, samples were coated with platinum by means of a vacuum sputter-coater for ease of conduction. Transmission electron microscopy (TEM) was performed by a Hitachi H-7100 TEM (Japan) with operating voltage of 120 kV to monitor the dispersion of MWCNTs in nanocomposites. For TEM measurements, a plastic crusher machine was used to crush the nanocomposites into powder form, which was subjected to ultrasonication for 30 min with few drops of acetone. After that, drops of MWCNTs powder mixed liquid were put on a copper grid, dried for a few minutes and then studied by TEM.

2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a TA/Q1000 apparatus under nitrogen atmosphere. For monitoring DSC, the samples were initially heated at 30–200 °C with a heating rate 10 °C min^{-1}, then cooled down to 30 °C with a cooling rate 5 °C min^{-1} and re-heated from 30 to 200 °C to monitor calorimetric properties. The degree of DSC crystallinity (χ_{dsc}) of the samples is usually calculated using the heat of fusion of 209 J g^{-1} for 100% crystalline PP including the weight fraction (w_f) of MWCNTs by the following equation [23,24].

$$\chi_{dsc} = \frac{\Delta H_f}{\Delta H_m} \times 100 \tag{1}$$

$$\chi_{\mathrm{dsc}} = \frac{\Delta H_f}{(1 - w_f)\Delta H_m} \times 100 \tag{2}$$

where ΔH_f is the heat of fusion of the sample and ΔH_m is the heat of fusion for 100% crystalline PP. Basically, Eq. (1) is a special case of Eq. (2), which was used to estimate the χ_{dsc} values of the samples prepared for this study.

2.5. Mechanical testing

Tensile tests of the samples were conducted by a universal testing machine (Hounsfield UTM 10KN; ASTM D-638-98) at a crosshead speed of 0.001 m-min^{-1}, keeping a gauge length of 0.06 m. Tensile strength and Young's modulus of the samples were evaluated. Five samples of each composition were used in the mechanical testing.

2.6. Micromechanical testing

A software controlled Vicker's square-based diamond indenter (Shimadzu, Japan) was employed to measure the microhardness (H) from the residual impression on the sample surface after an indentation time of 6 s. Loads of 0.098, 0.245, 0.490 and 0.980 N were used to derive a load independent value of H in MPa by the following relation [25]:

$$H = K\frac{P}{d^2} \tag{3}$$

where d (m) is the length of indentation diagonal, P (N) the applied load, and K a geometrical factor equal to 1.854. At least eight imprints were taken on the surface of the samples for each load, and the H was evaluated from the average value of all impressions.

2.7. Differential thermal analyzer and thermogravimetric measurements

Melting behavior of the samples was monitored by a differential thermal analyzer (DTA) of Seiko-Ex-STAR-6300, Japan. Thermal degradation measurements of them were carried out using a thermogravimetric analyzer (TGA), Q500 V6.4, Germany. Both studies