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ORIGINAL PAPER

Morphology of composite particles of single wall carbon nanotubes/biodegradable polyhydroxyalkanoates prepared by spray drying

Seok Il Yun · Victor Lo · Johannes Noorman · Joel Davis · Robert A. Russell · Peter J. Holden · Gerry E. Gadd

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Abstract Spray drying was investigated as a strategy for producing single wall carbon nanotube (SWCNT)/polymer composites. The spray-drying method produced SWCNT/poly(3-hydroxybutyrate) and SWCNT/poly(3-hydroxyoctanoate) composite particles in which the SWCNTs have been trapped in a well-dispersed state throughout the polymer matrix. Increasing SWCNT content in the composite led to a change in particle morphology from spherical and smooth to rosette shape with angular distortions. The technique shows potential for bulk carbon composite fabrication.

Keywords SWCNT · Composites · PHB · PHO · Spray drying · Powder · Biodegradable

Introduction

Carbon nanotube (CNT)-based biopolymer composites have attracted interest due to their improved electric current conductivity as well as their mechanical properties [1–4]. It has been reported that electrical stimulation, through current-conducting CNT/polylactic acids composites used to assist bone regrowth, efficaciously altered the various biological functions that determine the chemical composition of the organic and inorganic phases of bone, as well as increasing the rate of cell proliferation and, therefore, offering new avenues for stimulation of bone repair [1].

S. I. Yun · V. Lo · J. Noorman · J. Davis · R. A. Russell · P. J. Holden · G. E. Gadd (✉)
Australian Nuclear Science and Technology Organisation, PMB 1, Menai, Sydney,
NSW 2234, Australia
e-mail: geg@ansto.gov.au

S. I. Yun
Jeonju Institute of Machinery and Carbon Composites, Jeonju, Jeollabuk-do 561-844,
Republic of Korea

In regards to the fabrication of polymer/CNT composites, the most critical issue remains the development of methods to homogenously disperse the CNT throughout the polymer matrices [5]. Although high power ultra-sonication can make metastable solutions of nanotubes, it is found invariably that the nanotubes tend to aggregate when slow solvent evaporation is employed, leading to an inhomogeneous distribution of nanotubes throughout the polymer matrix. Another critical drawback in the process engineering of polymer/CNT composite materials is the dramatic viscosity increase of melts due to the large surface area of nanotubes [6]. Highly viscous polymer/CNT melts are difficult to flow and mould or extrude. One of the most commonly used alternative processing methods to compensate for materials with high viscosity is powder or slurry processing [7].

In this study, we have produced powders of polyhydroxyalkanoates (PHA)/single wall carbon nanotube (SWCNT) composites using a spray-drying method. PHAs are thermoplastic polyesters synthesized by micro-organisms, and have become one of the most interesting biomaterials for application in tissue engineering [8–10]. Spray drying is a widely used method which involves rapidly drying a liquid droplet feed by means of a hot gas or air flow [11, 12]. In our previous study on the production of polymer/clay composite particles, rapid evaporation by spray drying effectively minimized agglomeration of the clay, resulting in the clay being dispersed throughout the polymer matrix in the form of tactoids consisting of only a few clay platelets at most [12]. The spraying method used in this study produces micron-sized liquid droplets with a large surface-to-volume ratio which, on account of their small sizes are easily heated in a short time to a temperature where solvent evaporation is rapid. Although sprayed films of CNT or CNT/polymer have been investigated [13, 14], no report has been made of sprayed powders of CNT or CNT/polymer composites.

Experimental procedures

Polymers

Commercial poly(3-hydroxybutyrate) (PHB) (Aldrich) was used as purchased, whilst poly(3-hydroxyoctanoate) (PHO) was synthesized through fed-batch cultivation of *Pseudomonas oleovorans* using octanoic acid (Sigma, Australia) as the carbon source. The synthesis and characteristics (composition, M_w etc.) of PHO used in this study have been discussed in detail elsewhere [4, 15]. PHO dispersions were prepared at room temperature by adding the polymer directly to the solvent, chloroform, and leaving aside for several hours to dissolve. Since the commercial PHB did not dissolve in chloroform at room temperature, PHB was dissolved in chloroform at the elevated temperature of 70 °C. The PHA solution concentration used, was 5% (w/v). The SWCNT was purchased from CNI (Pure HiPco, USA). The CNTs were dispersed in chloroform (3% w/v) using high power sonication from a 600-W, 20-kHz Misonix (USA) ultrasonic liquid processor. The solutions of PHA and SWCNT were then mixed together in the desired proportions and sonicated.

The final PHO/SWCNT and PHB/SWCNT composites were made with different SWCNT contents relative to PHA polymers [0–100 (w/w) %].

Spray-drying technique

A micro-pump (Ismatec) carried the liquid dispersion through teflon tubing to a ultrasonic nozzle (120 kHz; Sonotek, USA) attached to the top of a vertical, heated glass column (~90 mm × 1,000 mm, 100–125 °C). The ultrasonic spray nozzle atomized the liquid stream into a jet of micron-sized droplets (average diameter ~20 μm) into a flow of preheated Ar gas exiting from a specially designed shroud around the tip of the ultrasonic nozzle.

Scanning electronic microscopy

Spray-dried material was directly deposited onto a stainless steel syringe needle aligned parallel to the flow of gas exiting from the spray-dry column. The needle and deposited powders were subsequently coated under vacuum with 50 Å of platinum by electric discharge evaporation for scanning electronic microscopy (SEM) analysis (JEOL JSM-6400 with an attached Noran Instruments Voyager Series IV X-ray microanalysis system. The SEM was operated at an accelerating voltage of 15 kV). This was done so as to minimize charging of the sample during the acquisition of the SEM images. This is a standard procedure known not to introduce any visible artefacts into the examination at the magnifications used here.

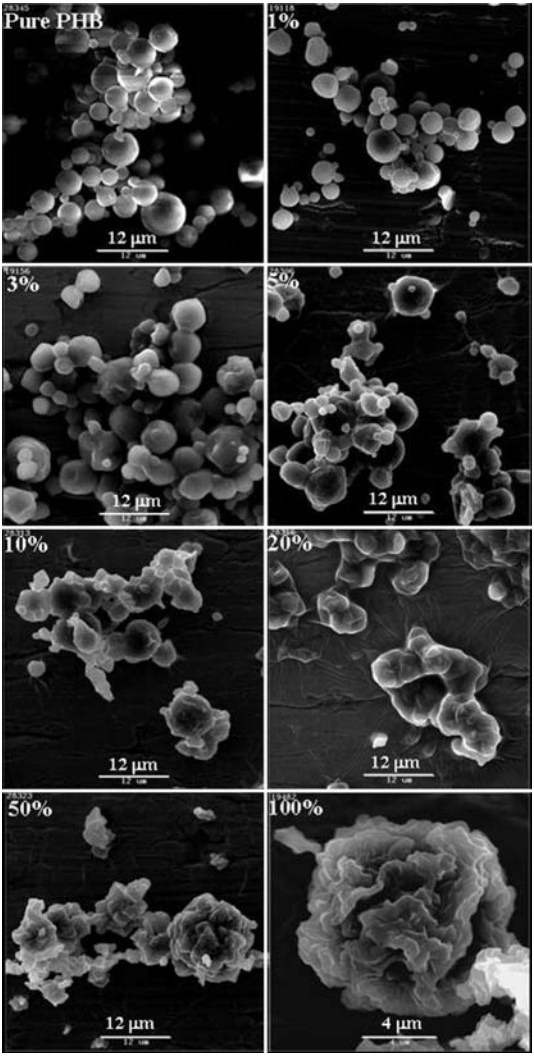
Transmission electronic microscopy

The spray-dried microspherical powder was also investigated with transmission electronic microscopy (TEM; a Joel 2000FXII TEM operating at 100 kV). The spray-dried microspherical powder was set in Buhler's Epo-Thin low viscosity epoxy by vacuum impregnation to extract unwanted air gaps. The set resin was appropriately trimmed to give a small cross section ~0.3 × 0.3 mm before being sectioned by ultramicrotoming using a Leica Ultracut UCT, into sections of approximately 50 nm thick and ~0.3 × 0.5 mm, with a Diatome Ultra 35° diamond knife. Sectioning speed was automated and set at 0.3 mm/s for 50-nm cuts. Samples were then collected and dispensed onto a 3-mm 200-mesh copper based holey carbon TEM grid with 90-μm grid squares.

Results and discussion

Figure 1 shows the SEM images of SWCNT/PHB particles that were produced by spray drying with Ar gas maintained at a temperature of 90 °C, with different SWCNT/PHB weight % compositions. Particles of pure PHB exhibited a spherical

Fig. 1 SEM images of spray-dried PHB/SWCNT particles as a function of SWCNT concentration



morphology. They were typically in the size range of 5–10 μm diameter, and appeared to have a relatively smooth surface. This morphology was consistent up to a SWCNT content of 3% w/w. Beyond this, the morphology of the spray-dried particles apparently changed as seen in the SEM image shown for the 5% SWCNT/PHB spray-dried material. Particle size, however, remained relatively constant. Although the particles were still essentially spherical in nature, the surface showed angular distortions. However, the surface was still relatively smooth on a smaller size scale. At 10% SWCNTs the angular distortions were very evident, and from 20% onwards, the particles showed a structure that could be described as rosette in appearance. The morphology of the spray dried pure SWCNTs was three-dimensional (3D) rosette particles consisting of 2D petal like structures, which indicates a unique ordering of the SWCNT. These pure carbon particles with a rough surface should be readily functionalized over a large surface area and would therefore have potential application in catalytic or sensing nanocomposites.

Unlike hard and brittle PHB polymers, PHO is a very soft elastomer and its T_g (glass transition temperature) is about −40 °C and melting temperature 60 °C, compared to 0 and 180 °C, respectively, for PHB. Consequently, the SWCNT/PHO solutions were sprayed at the reduced temperature of 45 °C. In order to aid evaporation at this temperature, the gas flow was reduced (longer residence time), but in order to prevent saturation of the carrier gas at these reduced flow rates, the liquid feed rate to the ultrasonic nozzle was also appropriately reduced. The softness as well as the very low T_m of PHO made it difficult to prepare well-formed and isolatable PHO particles by the spray-drying method. Bacterial PHO is an optically transparent polymer, and hence, optical microscopy was used in addition to SEM to observe the PHO and PHO/SWCNT composite particles which were deposited on the needle.

Figure 2 shows optical microscopy (a) and SEM (b, c) images for pure PHO. The needle surface was clearly seen as a background through transparent PHO microspheres (Fig. 2a). The side view of deposited PHO particles (Fig. 2c) clearly shows that soft PHO spheres flattened on the needle surface contrary to the much harder PHB spheres.

Figure 3 shows the optical microscopy and SEM images of PHO/SWCNT composite particles. As the concentration of SWCNT increased, the optical transparency of pure PHO spheres was lost, with the particles appearing black as expected from the known black colour of SWCNT. This colour change and the observation that it appears uniform suggest that the SWCNTs were well entrapped and dispersed within the PHO spheres by the spray-drying method.

Figure 4 shows the TEM images of spray-dried particles of PHB/SWCNT (a) and PHO/SWCNT (b). Large agglomerates of SWCNT were not seen in the TEM images, and thin cylinders of SWCNT were aligned in the cutting direction by microtomed slicing. Hairy thin cylinders of SWCNTs were also observed in the TEM image of PHB (Fig. 4). The result qualitatively indicates that spray drying of SWCNT/PHA solutions leads to polymer nanocomposites with an excellent degree of SWCNT dispersion. It is likely that force applied by spraying of the SWCNT/polymer solutions was large enough to separate the bundles of SWCNT in a droplet, and SWCNT did not agglomerate during a rapid evaporation of solvents.

Conclusions

The particles of composite, SWCNTs with PHB or PHO, were prepared by spray drying. Spray-dried powders from the pure PHA solutions adopted well-defined spherical morphology, whilst rosette shapes were observed in SWCNT solutions. As the content of SWCNTs increased, the topology of composite microspheres changed from spheres to the rosette particles. The TEM of SWCNTs/polymer powders shows that the SWCNTs were trapped in a well-dispersed state throughout the polymer

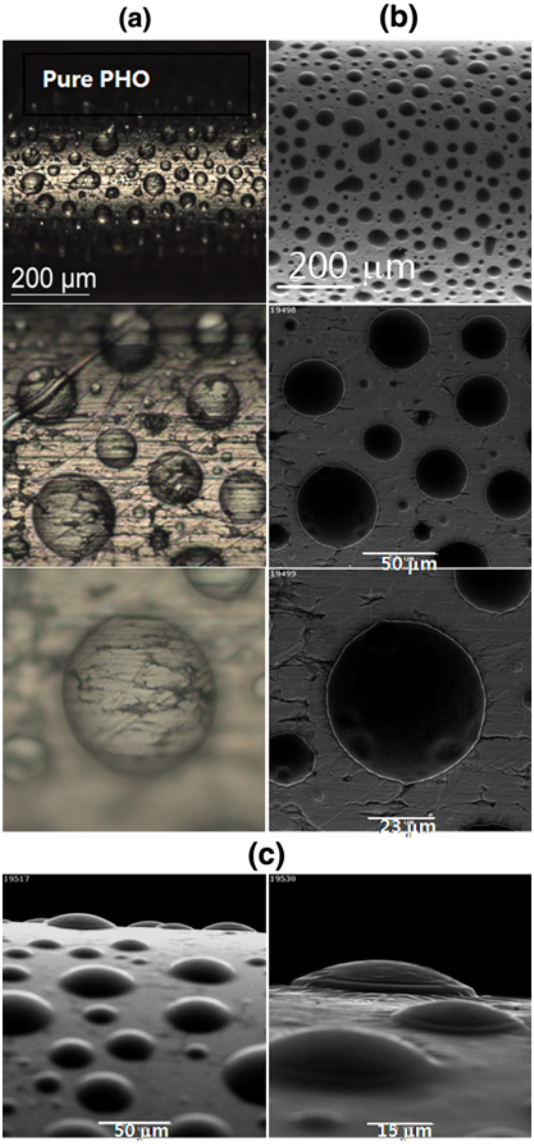


Fig. 2 **a** Optical microscopy; **b**, **c** SEM images of spray-dried pure PHO particles

matrix without the modification of SWCNTs. These composite powders may prove to be very good precursors for further processing such as extrusion or melt blending for bulk composite fabrication. Other advantages of the technique lie in the fact that spray drying is already a well-understood and commonly utilized method in industry, so that infrastructure development is minimized and the technique allows for solvent recovery, and can, therefore, be made environmentally safe and cost effective.

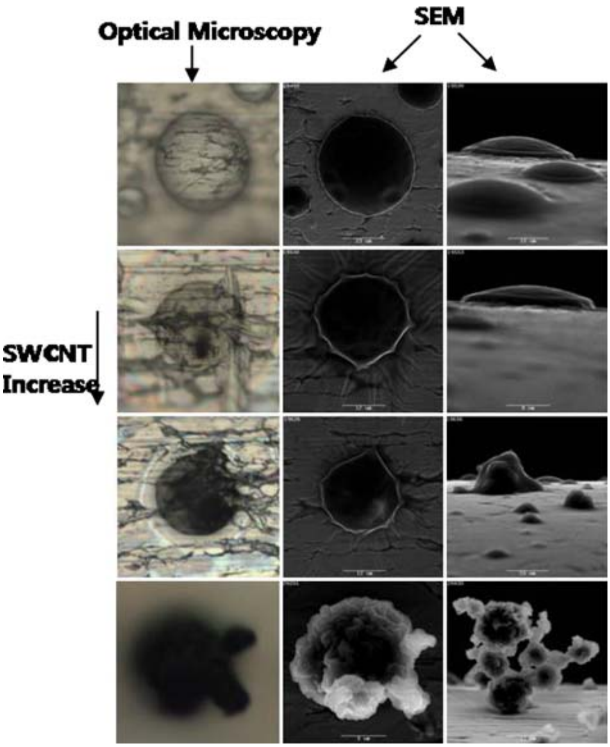


Fig. 3 Optical microscopy and SEM images of spray-dried PHO/SWCNT particles as a function of SWCNT contents

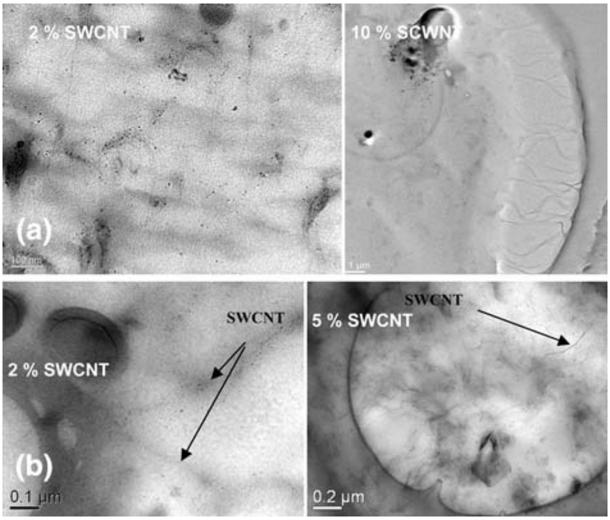


Fig. 4 TEM images of **a** spray-dried PHB/SWCNT particles and **b** spray-dried PHO/SWCNT particles

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