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Microwave sintering and characterization of polypropylene/multi-walled carbon nanotube/hydroxyapatite composites

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ABSTRACT

Low dielectric property of polypropylene (PP) is the main barrier to microwave sintering of PP. In this study, 1 wt% of multi-walled carbon nanotubes (MWCNTs) were incorporated into the PP as the microwave susceptors, together with different amounts (0, 5, 15, and 30 wt%) of hydroxyapatite (HA) to produce PP/MWCNT/HA biocomposites for bone tissue engineering by microwave sintering. A reduction of fabrication time (within 1 min) was achieved and the sintering time decreased with an increase of the HA content. The existence and homogeneous distribution of the HA in the sintered composites were confirmed by X-ray diffraction and back scattered scanning electron microscopy, respectively. Microstructures of these composites were examined and thermal analyses were carried out. The microwave sintering technique developed in this study can be used as an alternative to conventional polymer processing methods for fabrication of microwave transparent PP based composites.

1. Introduction

Microwave processing has attracted great research interest for a variety of materials, such as ceramics and metals [1,2]. This processing technique reduces time and energy [1–3] by direct coupling with materials, under both conditions, i.e., direct [4] and hybrid sintering [5]. The direct microwave sintering takes materials themselves as the only susceptors, while the hybrid sintering uses both the fabricating materials and external susceptors with high dielectric loss to absorb the microwave energy. In addition to the time and energy saving, microwave sintering can enhance bonding strength of the fabricated composite, because of the soldering effect between the filler and the matrix of different dielectric constants [6]. With these advantages, this calls for a technique that could be extended to polymeric materials, which generally have low dielectrics and have dielectric properties that can change with temperature [7].

Owing to the characteristics including dimensional stability, low density, high chemical resistance, polypropylene (PP) has been widely used in construction, automotive and fibre manufacturing industries [8]. In addition to these industrial applications, PP has also been applied in biomedical fields, such as abdominal wall hernia repair, urinary incontinence, prolapsed repair and tracheal replacement [9–11]. The advantages of using PP for tissue replacement include non-biodegradability, durability, high dimensional stability as well as good chemical resistivity [12]. Carbon nanotubes (CNTs) have superior electromagnetic absorbing properties, so that they could be heated to a temperature of 650 °C after irradiation for 10 s [13]. Moreover, CNTs possess extraordinary mechanical properties with their strength ranging from several GPa to 63 GPa [14] and their Young's modulus greater than 1 TPa [15]. CNTs have been reported to be incorporated into polyethylene (PE), which has been accepted for artificial hips and knees applications [16]. PE/multi-walled carbon nanotubes (PE/MWCNTs) composites showed improved mechanical properties like stiffness, strength, and retention of toughness over unfilled PE [17]. Compared with PE, PP is more suitable to be used as the matrix material in the development of biocomposites. It is because PP is a more bio-stable and stiffer non-biodegradable polymer with a lower reduction in mechanical performance at high temperature and better fatigue properties [18]. Bhattacharyya et al. [19] pointed out that CNTs acted as nucleating sites for PP crystallization, and an addition of 0.8 wt% of single-walled carbon nanotubes (SWCNTs) increased the PP crystallization rate by more than an order of magnitude. Another study conducted by Valentini et al. [20] showed that there was an increasing nucleating effect with increasing SWCNTs loading, which was followed by saturation. In addition to the nucleating effects in the PP/CNTs composites, mechanical enhancement of the composites was also observed after incorporation of CNTs into PP [21]. All these studies suggested that CNTs could be a promising candidate to act as susceptors in microwave sintering and a reinforcing phase in a PP composite system. Hydroxyapatite (HA), a typical bioactive ceramic, has attracted

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great research interest due to its chemical similarity to the mineral component of bone and its good ability of generating strong bonding with growing tissue [22]. It also has the ability to stiffen composites and increase their elastic moduli [23]. It is therefore suggested that all the three phases (PP, CNTs, and HA) could be combined to provide composites with improved mechanical and biological properties for potential biomedical applications.

Recently, a great number of composite technologies, such as extrusion, injection moulding, and compression moulding, have been applied for fabricating PP based composites [7,24,25]. However, these conventional polymer processing techniques have some limitations, such as the polymer dissolving problem of solution blending based methods, and time and energy consuming problem of melt blending based methods. Compared with the conventional processing techniques, microwave sintering greatly reduces energy consumption and processing time [26], and avoids the dissolving problem. In this study, microwave sintering was conducted to fabricate PP/MWCNT/HA composites. To overcome the main barrier in microwave sintering of microwave transparent PP, dielectric MWCNTs were chosen as the microwave susceptors and incorporated in the PP matrix. Moreover, MWCNTs also act as the reinforcing inclusion for the PP matrix. Meanwhile, the addition of HA particles was expected to provide good bioactivity, and enhance the stiffness of the composites. X-ray diffractometer (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) were used to characterize the sintered PP/MWCNT/HA composites in terms of chemical compositions, HA distributions, and microstructures of the composites. The crystallization, melting behavior and thermal mechanical properties of the sintered composites were also investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

2. Materials and methods

2.1. Materials

The PP powders were obtained from Goonvean Fibres (Devon, UK), with a density of 0.9 g/cm^3 and particle sizes ranging from 50 to 80 μm. The melting point of the PP was in the range of 150–170 °C. The MWCNTs (catalog No. S-MWNT-1020) were purchased from the Shenzhen Nano-Tech Port Co., Ltd. (Shenzhen, China). The purity of the MWCNTs was >95%. The outer diameter and the length of MWCNTs were 10–20 nm and 5–15 μm, respectively. The as-received MWCNTs were treated with 38% hydrochloric acid for purification for 24 h. The nanosized HA particles, obtained from Kingo Advanced Materials R&D Co., Ltd. (Ningbo, China), were irregular-plate-shaped with 400–2000 nm along the longest direction and nearly 20 nm in thickness.

2.2. Fabrication of PP/MWCNT/HA composites

2.2.1. Powder dispersion

A combination of ultrasonication and mechanical stirring in a solution based condition was selected to uniformly disperse the MWCNTs. An ultrasonicator (CP 2600, Crest Ultrasonic Powersonic), with an average power of 300 W and a frequency of approximate 45 kHz, and a magnetic stirrer (SP18420, Nuova Stir Plate) were adopted. A schematic diagram with detailed parameters values for the powder dispersion process is shown in Fig. 1. First, the three types of particles were ultrasonicated in de-ionized water or ethanol suspension respectively. Second, the three separated suspensions were mixed together by ultrasonication for 30 min. Finally, the mixed suspension was further dispersed by a magnetic stirrer until homogenous dispersion was achieved.

Table 1
Time required for microwave sintering of PP/MWCNT/HA composites with different compositions.

Samples PP:MWCNT:HA (wt%)	100:1:0	100:1:5	100:1:15	100:1:30
Sintering time (s)	50	25	23	22

2.2.2. Powder compaction

The well-dispersed mixtures were dried for compaction. Since the particles tended to agglomerate during the drying process, powder sieving procedure was applied to narrow down the range of the particle size distribution. The particles were sieved by a sieve with opening sizes of 75–120 μm in diameter, and then added into a highly polished mould with an internal diameter of 20.0 mm and lubricant on its inner surface. A 1 Hz sinusoidal load ranging from 10 to 20 N was applied to the mould for particle rearrangement, i.e., from the loosely arrayed condition to a closer packing for increasing the density of the green compact. After particle rearrangement, the PP/MWCNT/HA powder compaction was conducted at a peak load of 40 kN, i.e., 127 MPa, in order to enable the PP particles to go through plastic deformation, and followed by a holding time of 200 s. German [27] suggested that a smaller thickness-to-diameter ratio resulted in a more uniform stress distribution along the axial direction within the sample. In this study, green compacts with an appropriate ratio of thickness to diameter (i.e., 20 mm in diameter and 3 mm in thickness) were prepared.

2.2.3. Microwave sintering of PP/MWCNT/HA composites

The acid-treated MWCNTs, the as-received PP and HA powders were weighed in a ratio of "PP (wt%):MWCNTs (wt%):HA (wt%)" as: 100:1:0, 100:1:5, 100:1:15, and 100:1:30 (the ratios will be used as designations below). Each green compact obtained was placed in a ceramic crucible for sintering in a microwave oven (1100 W, 2.45 GHz frequency magnetron) at full power. The sintering time of each sample was recorded. After sintering, both the oven cavity and the crucible were cooled down to room temperature for next sample sintering.

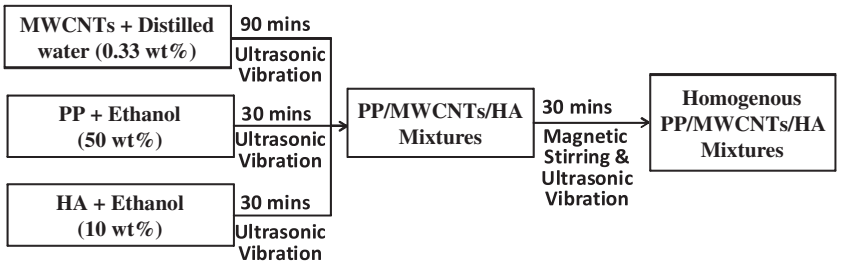

Fig. 1. Schematic diagram for the procedures of powder dispersion.