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Dispersion fraction enhances cellular growth of carbon nanotube and aluminum oxide reinforced ultrahigh molecular weight polyethylene biocomposites

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Ultrahigh molecular weight polyethylene (UHMWPE) is widely used as bone-replacement material for articulating surfaces due to its excellent wear resistance and low coefficient of friction. But, the wear debris, generated during abrasion between mating surfaces, leads to aseptic loosening of implants. Thus, various reinforcing agents are generally utilized, which may alter the surface and biological properties of UHMWPE. In the current work, the cellular response of compression molded UHMWPE upon reinforcement of bioactive multiwalled carbon nanotubes (MWCNTs) and bioinert aluminum oxide (Al_2O_3) is investigated. The phase retention and stability were observed using X-ray diffraction, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The reinforcement of MWCNTs and Al_2O_3 has shown to alter the wettability (from contact angle of ~88° ± 2° to ~118° ± 4°) and surface energy (from ~23.20 to ~17.75 mN/m) of composites with respect to UHMWPE, without eliciting any adverse effect on cytocompatibility for the L929 mouse fibroblast cell line. Interestingly, the cellular growth of the L929 mouse fibroblast cell line is observed to be dominated by the dispersion fraction of surface free energy (SFE). After 48 h of incubation period, a decrease in metabolic activity of MWCNT–Al_2O_3 reinforced composites is attributed to apatite formation that reduces the dispersion fraction of surface energy. The mineralized apatite during incubation was confirmed and quantified by energy dispersive spectroscopy and X-ray diffraction respectively. Thus, the dispersion fraction of surface free energy can be engineered to play an important role in achieving enhanced metabolic activity of the MWCNT–Al_2O_3 reinforced UHMWPE biopolymer composites.

1. Introduction

Biomaterials are used to direct, replace or supplement the function of living tissues of the human body. These are bone plates, sutures, heart valves, vascular grafts, joint replacements, intraocular lenses, ligaments, dental implants etc. [1,2]. These may be metals (Ti–6Al–4V, steel), ceramics (HAP, Al_2O_3), polymers (PMMA, polyolefins, nylon) as well as composites. UHMWPE, an engineering polymer, has unique combination of properties such as: highest slurry-abrasion resistance, exceptional impact resistance, low coefficient of friction, self-lubricating properties, outstanding stress-crack resistance, high resistance to cyclic fatigue failures and clearance for use in food and biomedical application [3]. The first hip prosthesis was implanted by using UHMWPE in the 1960s as an alternate to PTFE (polytetrafluoroethylene) and was found to be the best choice for total joint applications only for short term periods (~15–20 years) due to serious problem of wear debris formation and aseptic loosening, which leads to osteolysis [4]. Since the late 2000s profound research work was carried out to develop materials with enhanced tribological performance by crosslinking via gamma-irradiation, sterilizing with ethylene oxide, using cold atmospheric pressure, and gas plasma and organosilane treatment with partial damage of the outer surface of UHMWPE for in vitro as well as in vivo applications [5–7]. To maintain the original properties of materials, some alternative non-destructive routes were also developed to improve the wear performance of the composites. The reinforcement of a polymer matrix with inorganic (Al_2O_3, zirconia) as well as organic (carbon fibers and carbon nanotubes) fillers is the best route to fabricate prosthesis with super performance than virgin polyethylene components in total joint replacements [8,9].

The reinforcement of UHMWPE with 1 wt.% multiwalled carbon nanotubes (MWCNTs) drastically enhanced ductility (~140%) and modulus (~25%) [10]. It is well reported in literature that MWCNTs are extremely strong with tensile strength of ~200 GPa and Young's modulus of ~1 TPa and flexible (with break strain of ~10–30%) [11, 12]. The effective utilization of MWCNTs into a matrix strongly depends on its homogeneous dispersion in the matrix, without destroying the integrity of matrices and MWCNTs–matrix interface bonding, which plays a major role in load transfer across MWCNTs–matrices interfaces during

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application of mechanical stress [13–20]. Toughening of material is also improved by grafting with coupling agents like maleic anhydride (PE-*g*-MAH) and silanes and reinforcing with nano/micro-particles (3% SiC) as well as organic sheets by 0.2–9.0 wt.%, processed via compression molding [17,21–25]. Huang et al. reported that with 3% SiC with different coupling agents, an increase in the flexural strength by ~17% (16.7 to 19.6 MPa) than without a coupling agent was observed. Gupta et al. and Bakshi et al. [26–28], have reported the hybrid composites based on the UHMWPE–HAP–Al_2O_3–MWCNT system and found that an addition of 5 wt.% alumina has led to an increase in the hardness and modulus by 12% and 5.2%, respectively, while, 5 wt.% HAP addition has led to a decrease in the hardness and modulus by 44.5% and 53.8%, respectively, when compared to that of UHMWPE.

Ji-Hoon Lee et al. [29] have reported that reinforcement of silane modified MWCNTs in UHMWPE nanocomposites has resulted in significant lowering of specific wear rate by ~59%, when compared to that of virgin UHMWPE. It was observed that wear debris causes the immature failure of implants since the host cells produce cytokines (precursor of osteoclasts) that start consuming the bone around the implant and result in implant loosening [30,31]. Thus, in order to reduce the formation of wear debris, MWCNTs are reinforced into the UHMWPE matrix due to its lubricating property. It is reported that UHMWPE formed shish–kebab crystalline structure with MWCNTs [32], which enhances the mechanical properties of composites especially tensile modulus and fracture toughness. Enhanced crystallinity is observed after adding MWCNTs into the UHMWPE matrix [33–35]; on the other hand it is shown that the crystallinity of UHMWPE is not affected by the addition of MWCNTs [36].

Hydroxyapatite (HA) is one of the most important bioceramics for medical applications due to the similar chemical composition (Ca/P ratio of 1.67) to the mineral component of the natural human bone [37,38]. Extensive work has been reported on biomedical applications of HA and its composites via filler reinforcements, FGM formation, surface modification, grafting and coating [37–40]. The formation of apatite during incubation (cell culture) is checked by the SBF immersion test that predicts the activity of biomaterials in vitro [41]. Zadpoor and Szubert et al. [41,42] reported the apatite formation test at mica surface supported by physiological mineralization. It was observed that the layers of lipids such as dipalmitoylphosphatidylcholine (DPPC) on the inorganic material surfaces enhance the mineralization and crystal growth at 37 °C [41,42], but systematic quantitative analysis is not reported yet.

Above all, the surface free energy (SFE) of any biomaterial plays an important role in cell adhesion and proliferation, but a systematic analysis which correlates the polar and dispersion fractions of SFE with the density of metabolically active cells and apatite mineralization is not quantified. In the present work, multiwalled carbon nanotubes (MWCNTs) and Al_2O_3 were synergistically reinforced into a UHMWPE matrix in varying percentages via a compression molding process. The phases, chemical, and microstructure of the nanocomposites were characterized by X-ray diffraction analysis, FT-IR, Raman spectroscopy, and scanning electron microscopy. The biocompatibility and cellular response of composites were studied via L929 mouse osteoblast cell line (American Type Cell Collection—ATCC) in vitro cell culture experiments. The cell density was correlated with the surface free energy (SFE) of composites, which indicate that the cell adhesion mechanism in Al_2O_3–MWCNT–UHMWPE biopolymeric composites is strongly enhanced with increasing dispersion fraction of SFE.

2. Experimental section

2.1. Materials and processing

The UHMWPE medical grade powder (GUR™ 1020) with a density of 0.93 g/cm^3 was supplied by Ticona GmbH (Werk Ruhrchemie) Germany. The molecular weight of UHMWPE is 2.7×10^6 with particle size ranging between 10 and 300 μm observed using a scanning electron microscope as shown in Fig. 1A and measured using a laser particle size analyzer (Analysette 22; Fritsch GmbH, Germany). The acicular α-Al_2O_3 (~99.9% purity, particle size of 10–30 μm, see Fig. 1B, and density of ~3.953 g/cm^3) was procured from Allied Hi-tech Products, USA. Multiwalled carbon nanotubes (MWCNTs) (95%+ purity, outer diameter of 30–50 nm, inner diameter of 5–15 nm and length up to 10–20 μm with true density of ~2.1 g/cm^3, Fig. 1C) were procured from Nano-structured and Amorphous Materials Inc., NM, USA. In order to prepare the hybrid composites, varying wt.% values of MWCNTs (2, 5 &10%) with fixed wt.% of Al_2O_3 (15%) were added into the UHMWPE matrix, followed by solvent physical blending for 4 h. It was also found that blending did not change the size and shape of the reinforcements MWCNTs and Al_2O_3.

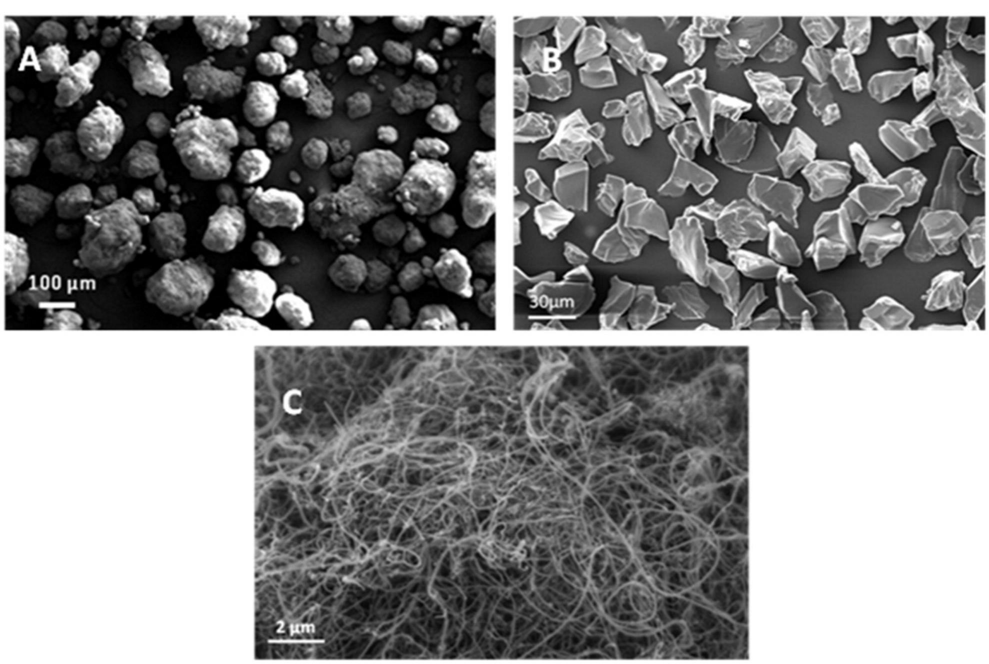

Fig. 1. SEM images of as received (A) UHMWPE, (B) Al_2O_3 and (C) MWCNT powders.