J Mater Sci: Mater Med (2010) 21:2287–2292
DOI 10.1007/s10856-009-3960-5

Influence of multiwall carbon nanotube functionality and loading on mechanical properties of PMMA/MWCNT bone cements

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Received: 17 September 2009 / Accepted: 30 November 2009 / Published online: 20 December 2009

Abstract Poly (methyl methacrylate) (PMMA) bone cement—multi walled carbon nanotube (MWCNT) nanocomposites with weight loadings ranging from 0.1 to 1.0 wt% were prepared. The MWCNTs investigated were unfunctionalised, carboxyl and amine functionalised MWCNTs. Mechanical properties of the resultant nanocomposite cements were characterised as per international standards for acrylic resin cements. These mechanical properties were influenced by the type and wt% loading of MWCNT used. The morphology and degree of dispersion of the MWCNTs in the PMMA matrix at different length scales were examined using field emission scanning electron microscopy. Improvements in mechanical properties were attributed to the MWCNTs arresting/retarding crack propagation through the cement by providing a bridging effect and hindering crack propagation. MWCNTs agglomerations were evident within the cement microstructure, the degree of these agglomerations was dependent on the weight fraction and functionality of MWCNTs incorporated into the cement.

List of symbols

K_{IC}	Critical stress intensity factor (Pa-m$^{1/2}$).
F_{max}	Maximum load at failure (N).
Y_m	Minimum value of the normalised stress intensity factor coefficient, which depends only on the geometry of the test specimen
D	Diameter of specimen (m)
W	Length of specimen (m)

1 Introduction

It is well documented that polymethyl methacrylate (PMMA) bone cement used in total joint replacement (TJR) surgery is susceptible to fatigue-related cracking and impact-induced failure [1]. Failure rates of 67% have been recorded after 16 years in patients younger than 45 years [2]. It is postulated that the annual number of revision total knee arthroplasties performed in the United States will increase 601% to 270,000 by 2030, and the number of total hip arthroplasty revisions will increase 137% to 97,000, with a common cause of implant failure attributed to cement mantle failure [3].

Multiwall carbon nanotubes (MWCNTs) offer the potential to augment mechanical properties of PMMA bone cement due to their strength and aspect ratio. The incorporation of carbon nanotubes (CNTs) into polymers has previously been used to improve mechanical, thermal, and electrical properties, while retaining the structural capabilities of the polymer matrix [2, 4–6]. The addition of MWCNTs to PMMA bone cement has been shown to significantly improve the static mechanical properties [2, 6], and the fatigue performance of MMA-co-Sty copolymer based bone cement [7]. Marrs et al. [2]. investigated the influence of unfunctionalised MWCNTs in PMMA based bone cements. They reported moderate improvements (13–24%) in the static properties when

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2 wt% MWCNTs was incorporated into PMMA bone cement. Marrs [7] reported significant improvements (>300%) in the dynamic properties of methyl methacrylate–styrene copolymer (MMA–co–Sty), a chief component of commercial bone cement when unfunctionalised MWCNTs (2 wt%) were added. However, both studies [2, 7] used non-clinically relevant methods to ensure optimal dispersion of the MWCNTs. The CNTs were dispersed through a molten matrix of pre-polymerised commercial bone cement powder. The two materials were heated and subjected to high-shear mixing. Once the molten composite had cooled and hardened, it was crushed into pellets and hot pressed under vacuum to form films. These films where subsequently machined into testing specimens. Each specimen was then annealed at 125°C for a minimum of 15 h to alleviate any residual stresses that formed during machining.

Wright et al. also reported improved fracture toughness values when woven PMMA fibres were incorporated into PMMA bone cement [8]. Similar to the studies conducted by Marrs et al. [2] and Marrs [7], the method for incorporating fibres into the PMMA cement was not representative of normal surgical protocol for preparation of PMMA cement. The fibres were fabricated using a heat deformation process from PMMA pellets. Flat bar specimens were then produced by weaving PMMA fibres tows around square cobalt-chrome-molybdenum bars. Once the bars had a mantle of PMMA, they were processed into composite materials using a sintering process. A cold cure PMMA was mixed according to the manufacturer's recommendations and poured over the PMMA fibre bars and allowed to cure. Specimens were then prepared by cutting a single notch in the cured woven PMMA-bone cement composite characterised and the fracture toughness was subsequently determined using a non-standardised method [8].

Ormsby et al. [6] incorporated unfunctionalised and carboxyl (COOH–) functionalised MWCNTs (0.1 wt%) into a proprietary PMMA bone cement using three different preparation techniques. CNTs were either added to the liquid methyl methacrylate component of the cement via magnetic stirring or ultrasonic disintegration, or dry blended with the polymer powder component. A contemporary vacuum mixing system was subsequently used to mix the bone cement following the normal protocol for a joint replacement surgical procedure. Improvements in static mechanical properties and thermal properties of the PMMA–MWCNTs nanocomposite cement were observed [6]. Despite these improvements, there were limitations to the study conducted by Ormsby et al. [6]. For example, the effects of adding higher wt% loadings of MWCNTs to PMMA bone cement on the mechanical and thermal properties. Moreover, the influence of using other functionalised MWCNTs (e.g. modification using hydroxyl or amine functionalised groups) are unknown, which could offer greater dispersion and interfacial bonding of the MWCNTs within the PMMA cement matrix.

The objective of this present study was to investigate the incorporation of various concentrations of MWCNTs to PMMA bone cement with differing functional groups to address some of the limitations of our previous study [6]. Subsequently, the bone cement was prepared using a contemporary cement mixing and delivery technique, as per current clinical practice for joint replacement surgery. The mechanical properties of the resultant nanocomposite cements were characterised.

2 Materials and method

2.1 Materials and preparation of the bone cement

Colacryl B866 bone cement (Lucite International Ltd., UK), which consisted of PMMA powder (40 g) and methyl methacrylate (MMA) liquid monomer (20 ml) was used in this study. MWCNTs (0.1, 0.25, 0.5, and 1.0 wt% loadings) were incorporated into the MMA prior to mixing. Carboxyl functionalised (NC3151–COOH) (4% functionalised), unfunctionalised (NC7000C) and amine functionalised (NC3152–NH_2) (0.5% functionalised) MWCNTs (all Nanocyl S.A., Belgium) were used. All types of MWCNTs were grown using chemical vapour deposition and had aspect ratios of the order of 150. The different MWCNTs were incorporated into the bone cement by dispersing the MWCNTs in the MMA monomer using an ultrasonic disintegrator (MSE Ltd. UK) at an amplitude of 10 ± 1 μA for 30 ± 1 s (×3). Subsequently, the MMA monomer and PMMA powder were mixed together under ambient conditions using a commercially available vacuum mixing system (Summit Medical Ltd., UK) according to the manufacturer's instructions. In total 12 different nanocomposite cement combinations were prepared and a control containing no MWCNTs, for comparison. Specimens for mechanical characterisation were prepared in accordance with ISO 5833:2002 [9]. Barker [10] developed the Chevron-Notch Short Rod (CNSR) method for determining plane strain fracture toughness using short rod geometries with machined chevron-shaped slots, creating a double cantilever-type configuration. The CNSR technique was used for quantifying the critical stress intensity factor coefficient (also known as fracture toughness) (K_{IC}) of the novel cements as described by Ryan et al. [11]. Cylindrical specimens of 4.0 ± 0.1 mm in diameter and 8.0 ± 0.1 mm in height were prepared with a custom built system that used two diamond cutting saws to cut: (i) a load line of 1.47 ± 0.1 mm and (ii) the chevron-notch 0.15 ± 0.1 mm.

The specimens were then stored in ambient laboratory conditions (22 ± 1°C) for 24 ± 0.5 h prior to testing. For each mechanical property determined, a total of 18 bone cement specimens (that is, six specimens from three separate mixes for each MWCNT- bone cement combination) were tested. PMMA bone cement without MWCNTs was used as a control in all experiments.

2.2 Mechanical properties

The compressive and bending properties of each bone cement mix were determined in accordance with ISO 5833:2002 [9] using a Lloyds materials testing machine (Lloyds Instrument Ltd., UK). Fracture toughness properties were determined using the CNSR technique using the Lloyds materials testing machine also. The load and deflection were recorded to failure for each specimen and the fracture toughness calculated (Eq. 1) [11]. The maximum failure load denoted by F_{max}, diameter of specimen D, specimen length W and the minimum value of the normalised stress intensity factor coefficient (also known as the geometric factor) represented by Y_m. The geometric factor was previously determined by Lin [12] to be 30.42.

$$K_{IC} = \frac{F_{\max}}{D\sqrt{W}} \times Y_m \tag{1}$$

FE-SEM analysis of the fractured surfaces of the composite materials was conducted using a JEOL 6500 FEG SEM (Advanced Microbe am, Inc., USA) with operating voltages of 5.0 kV used. Specimens were mounted on aluminium discs using a cold cure resin (Extec Corp, Enfield, CT, USA) and allowed to cure for 24 h. The specimens were subsequently sputtered with gold prior to FE-SEM examination.

2.3 Statistical analysis

For each property determined, the results were evaluated for statistical significance using a one-way analysis of variance with p-value <0.05 denoting significance. Post-hoc tests were conducted using the Student–Newman–Keuls and Duncan methods (SAS 8.02; SAS Institute, USA).

3 Results

3.1 Mechanical properties

3.1.1 Compressive and bending properties

The compressive and bending properties are summarised in Table 1 for the control cement and the nanocomposite cements incorporating functionalised (NC3151–COOH and NC3152–NH_2) and unfunctionalised (NC7000C) MWCNTs. The incorporation of NC3151–COOH at lower loadings (≤0.25 wt%) yielded improvements in the mechanical properties of the resultant nanocomposite cement, relative to the control. Significant improvements in compressive strength, bending strength, compressive modulus and bending modulus were observed (p-values < 0.001). As the MWCNT loading increased (≥0.5 wt%) the mechanical properties decreased. Reductions in bending strength and bending modulus were observed (p-values < 0.001), with minor improvements in compressive strength and compressive modulus also recorded (p-values < 0.05). The highest loading of NC3151–COOH (1.0 wt%) significantly reduced all mechanical properties measured (p-values < 0.001). The incorporation of NC3152–NH_2 followed a similar trend with 0.1 wt% loading giving the maximum improvement in mechanical properties. Significant reductions in bending strength, bending modulus (p-values < 0.001), compressive modulus (p-value < 0.05) and an improvement in compressive strength (p-value < 0.01) were observed as the NC3152–NH_2 loading increased (≥0.25 wt%). At the highest loading of NC3152–NH_2 (1.0 wt%), mechanical properties were greatly reduced, with reductions in compressive strength (p-value < 0.05), bending modulus (p-value < 0.001), compressive modulus (p-value < 0.01) and bending strength (p-value < 0.001). Improvements in compressive strength (p-value < 0.001), compressive modulus, bending modulus (p-values < 0.01) and a reduction in bending strength (p-value < 0.05) was observed for the NC7000C–PMMA nanocomposite cement at ≤0.25 wt% loading levels. With the exception of the compressive strength (p-value < 0.001), the mechanical properties measured for the NC7000–PMMA nanocomposite cement were significantly reduced (p-values < 0.001) as the level of MWCNTs loading increased beyond 0.5 wt%.

3.1.2 Fracture toughness properties

All MWCNT–PMMA nanocomposite specimens demonstrated improved fracture toughness when compared to the control cement (Fig. 1). Incorporating NC3151–COOH in PMMA cement improved the mean fracture toughness by ≈12–61% depending on the wt% used, with the 0.25 wt% providing the greatest improvement (≈61%) (p-value $<$ 0.001). Adding NC7000C to the PMMA cement also improved the fracture resistance (≈13–29%), with the greatest increase being recorded at the 0.1 wt% level of loading. The NH_2 functionalised MWCNTs followed a similar trend with improvements ranging from ≈18 to 29% depending on the level of MWCNT loading.

Table 1 Summary of data from mechanical studies (Mean ± SD) of control, unfunctionalised, carboxyl functionalised and amine functionalised MWCNT loaded bone cements

Cement type	CNT loading (wt%)	Mechancial property (MPa)							
		Compressive strength		Compressive modulus		Bending strength		Bending modulus	
Control	0.00	59.8 ± 4.5	% Change	3460.0 ± 831.0	% Change	56.4 ± 7.5	% Change	3012.0 ± 326.0	% Change
NC7000C	0.10	109.0 ± 13.6***	+82.1	3804.0 ± 413.0*	+26.3	56.5 ± 10.3	+0.2	3573.9 ± 382.0**	+25.0
	0.25	95.9 ± 7.7***	+60.2	3499.0 ± 317.0	+16.2	54.1 ± 5.2	−4.2	3084.6 ± 239.0	+7.9
	0.50	80.2 ± 4.9***	+33.9	3633.7 ± 962.0	+20.6	19.4 ± 3.3***	−65.7	496.4 ± 73.1***	−82.6
	1.00	66.8 ± 6.2**	+11.7	2812.0 ± 841.0**	−6.7	41.0 ± 4.4**	−27.3	2413.8 ± 158.0**	−15.6
NC3151COOH	0.10	86.5 ± 6.6***	+44.6	4801.0 ± 447.0***	+59.4	68.8 ± 5.6**	+21.9	3501.0 ± 376.0**	+22.4
	0.25	81.0 ± 8.0**	+35.3	4156.0 ± 385.0***	+38.0	60.4 ± 2.9	+7.0	3053.1 ± 93.0	+6.8
	0.50	75.3 ± 3.8**	+25.9	3549.9 ± 925.0	+17.8	46.4 ± 3.3*	−17.8	2879.4 ± 233.0	−0.7
	1.00	44.2 ± 3.8*	−26.0	3160.0 ± 533.0*	−4.9	31.9 ± 4.9***	−43.5	1757.2 ± 464.0**	−38.6
NC3151NH$_2$	0.10	77.9 ± 9.9***	+30.2	3536.4 ± 407.0	+17.4	54.1 ± 5.5	−4.1	3129.0 ± 213.0	+9.4
	0.25	73.1 ± 4.0***	+22.2	3287.3 ± 625.0	−9.1	48.0 ± 4.7*	−15.0	2781.0 ± 530.0	−2.8
	0.50	62.4 ± 5.3**	+4.3	3463.6 ± 300.0	+1.0	43.8 ± 5.1*	−22.4	2507.2 ± 352.0*	−12.3
	1.00	60.4 ± 6.7**	+1.0	3200.7 ± 521.0	−6.3	35.5 ± 3.3***	−37.1	2105.2 ± 177.0**	−26.4

*** indicates a *p*-value less than 0.001, demonstrating a statistically significant difference between control cement and cements loaded with 0.1–1.0 wt% CNT. ** indicates a *p*-value less than 0.01, demonstrating a statistically significant difference between control cement and cements loaded with 0.1–1.0 wt% CNT. * indicates a *p*-value less than 0.05, demonstrating a statistically significant difference between control cement and cements loaded with 0.1–1.0 wt% CNT

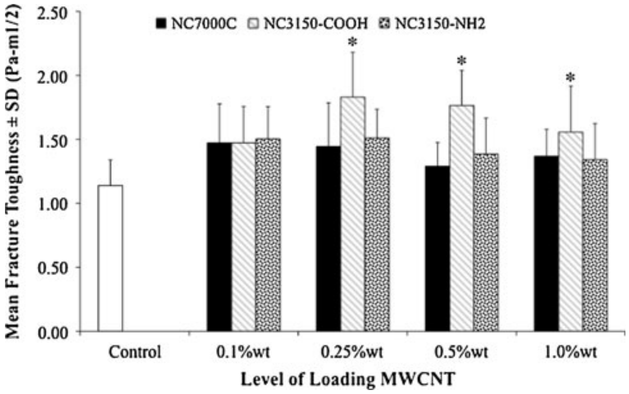

Fig. 1 Mean fracture toughness ± standard deviation (SD) of control and MWCNT loaded bone cements, * implies *p*-value less than 0.001 when compared to control

4 Discussion

The current study investigated the efficacy of adding different concentrations of MWCNTs to PMMA bone cement of varying functionality as a means of improving MWCNT dispersion and thus augmenting the mechanical properties of the PMMA bone cement. Adding MWCNTs at low loadings (≤0.25 wt%) to MMA monomer, prior to cement mixing with a proprietary mixing system, improved the mechanical properties of the resultant nanocomposite cement. Adding –COOH and –NH$_2$ functional groups enhanced the dispersion of the MWCNTs within the cement matrix and potentially increased the interaction between the carbon nanotubes and the cement, thereby improving the mechanical integrity of the resultant nanocomposite cement. These improvements in mechanical strength are potentially significant as mechanical failure of the bone cement mantle remains a prevalent issue in total joint replacement surgery often leading to revision surgical procedures [13]. Adding MWCNTs at higher loadings (≥0.5 wt%) provided a negative effect on the mechanical performance of the nanocomposite cement. This was attributed to poor dispersion of MWCNTs resulting in agglomerations forming within the cement matrix (Fig. 2a). These agglomerations acted as stress concentrations within the cement microstructure, providing a mechanism for premature failure of the cement when subjected to load. In contrast, low loadings (≤0.25 wt%) of MWCNTs were more readily disentangled by the application of ultrasonic energy and homogenously dispersed in the resulting nanocomposite. The presence of well-dispersed MWCNTs in PMMA cement with their anticipated strong nanotube-matrix bonding and high tensile properties, suggests that a percentage of the MWCNTs would be orientated with their longitudinal axis perpendicular to the crack wave. Such MWCNTs were effective in bridging the initial crack and preventing crack propagation, further enhancing the mechanical integrity of the cement mantle (Fig. 2b). These improvements could have clinical benefits for the application of MWCNT–PMMA nanocomposite cement in TJR surgery, due to a reduction in the rate of crack propagation

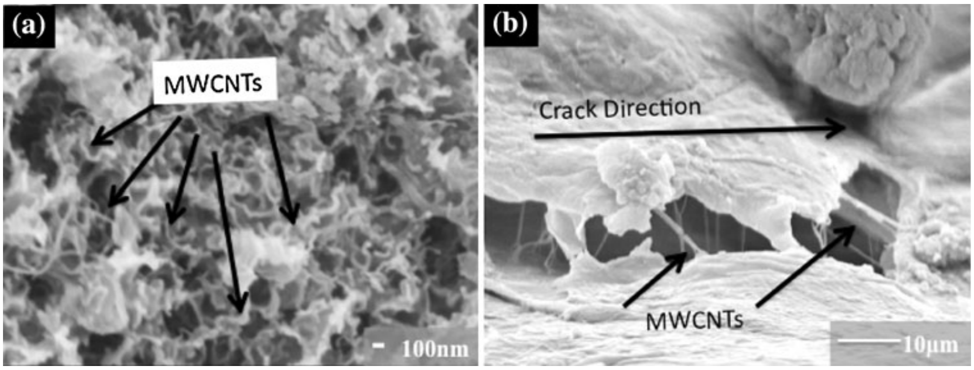

Fig. 2 SEM images showing **a** 0.1 wt% Unfunctionalised MWCNT–PMMA showing an agglomeration of MWCNTs, which was the fracture initiation point for this specimen (×15000), **b** 0.1 wt% COOH Functionalised MWCNT cement in which MWCNT can be seen to bridge a micro-crack on the surface

through the reinforced nanocomposite cement mantle. This effect may have greatest significance for misaligned femoral implants resulting in areas of thinner cement mantle thickness, which continues to be cited as a main factor of cement mantle failure [14].

Gojny et al. [15] reported that the addition of chemical functional groups to the MWCNTs can provide a negative charge to the MWCNTs and thus reduced agglomeration and improve interaction between the nanotubes and the host polymer. The results of this study concurred with the findings of Gojny et al. [15]. The PMMA bone cement with unfunctionalised MWCNTs (NC7000C) exhibited least significant improvements (p-value < 0.05) for all mechanical properties measured. This reduced improvement in mechanical properties was attributed to poor dispersion of MWCNTs within the cement matrix, resulting in the occurrence of MWCNT agglomerations (Fig. 2b). The NC7000C provided a degree of mechanical reinforcement at lower loading ($\leq$0.25 wt%), largely due to the reduced tendency for MWCNT agglomerations. In this study MWCNTs chemically functionalised using either a carboxyl (NC3151–COOH) or amine (NC3152–NH_2) groupings were chosen, as it has been reported the mechanical properties of generic PMMA can be improved using MWCNTs with these functional groups [16]. MWCNTs functionalised with NC3151–COOH groups provided the most significant (p-value < 0.001) improvements in all mechanical properties of the PMMA cement. It is proposed these significant improvements are a result of a homogenous dispersion of the MWCNTs within the PMMA matrix aided by the negatively charged carboxyl groups. This homogeneous dispersion in tandem with interfacial interactions between the functionalised MWCNTs and PMMA matrix could provide improved mechanical properties of the resultant nanocomposite. The MWCNT–PMMA nanocomposite incorporating amine functional groups (NC3152–NH_2) also improved mechanical properties. These improvements were less significant p-value < 0.01 when compared with the addition of NC3151–COOH to PMMA cement. It is postulated that this is due to the lower level of functional groups present on the NC3152–NH_2 when compared with the NC3151–COOH (that is 0.5 vs. 4.0%, functional groups, respectively). This lower concentration of NC3152–NH_2 functional groups may result in a more heterogeneous dispersion of the MWCNTs within the cement matrix, therefore resulting in a less successful transfer of stress through the cement mantle.

Limitations to the present study include the assessment of the dynamic properties of the nanocomposite bone cements. Moreover, investigating how the addition of MWCNTs to PMMA bone cement influences the kinetics of polymerisation was beyond the scope of this study. Finally as this study has utilised MWCNTs, the cytocompatibility of these bone cement nanocomposites will require full characterisation. Such tests are considered essential when considering long-term success of bone cement nanocomposites in vivo, however it must first be proven that such materials offer enhancements in mechanical performance. Notwithstanding these limitations, the results cited from this investigation are clinically valid and work is ongoing to address this shortcoming.

5 Conclusions

Incorporating low loadings of MWCNTs ($\leq$0.25 wt%) to PMMA bone cement improved the mechanical properties of the resultant nanocomposite. Higher loadings ($\geq$0.5 wt%) provided lesser improvements in the mechanical properties, and in some cases significant reductions were recorded. The extent of the effect was dictated by the chemical functional groups added to the MWCNT, and the level of loading used. Improvements in mechanical properties were attributed to the MWCNTs being well dispersed within the PMMA cement, thereby arresting/retarding crack propagation through the cement. The dispersion of MWCNTs within the cement matrix is enhanced by adding chemical functional groups, with the carboxyl functionalised MWCNTs providing the most significant improvements in mechanical integrity.

Aknowledgements The authors acknowledge the support from Nanocyl S.A., Belgium, Lucite International Ltd., UK, and the Department of Education and Learning NI (DEL) for funding.

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