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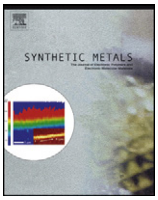

Preparation and characterisation of graphene composite hydrogels

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ABSTRACT

Stable dispersions containing graphene and gellan gum are used to form composite films. Incorporation of graphene into the gellan gum matrix results in mechanical reinforcement and electrical conductivity at low and high graphene loading fractions, respectively. Graphene-containing gellan gum hydrogel films are prepared by immersion of composite films in Ca^{2+} cross-linking solutions. The resulting hydrogels are electrically conducting and exhibit reinforcement compared to the corresponding gellan gum hydrogels.

1. Introduction

Graphene, in its purest form, exists as a single 2D monolayer of sp^2 carbon atoms in a hexagonally arranged crystal lattice. Within the graphene network, the carbon–carbon sigma bonds are one of the strongest observed within nature, giving rise to their exceptional properties and a significant interest amongst the scientific community. Its separation as a single-monolayer, however, has only recently been examined in 2004 [1], despite its role as the constituent material of carbon nanotubes (CNTs) and buckministerfullerene. Defect-free graphene sheets possess an array of remarkable thermal, electrical and mechanical properties, comparable to those of CNTs [2]. Graphene can be produced using, mechanical cleavage of highly ordered, pyrolytic graphite crystals [3], epitaxial growth using chemical vapour deposition (CVD) on silicon carbide [4], through thermally expanded graphite with relatively good yield [5], and through electrochemical reduction of graphite oxide [6]. A more practical approach utilises the chemical reduction of exfoliated graphite oxide (GO) sheets to form isolated chemically converted graphene (CCG), which can be prepared in organic and aqueous solvents in good yield [7,8]. These dispersions are desirable, as they can be readily processed using solution based techniques to prepare composite materials [9–11]. Graphene hydrogel films are a new class of materials which are being developed for applications such as electrodes and capacitors [12–17].

Gellan gum (GG) is a high molecular weight, linear anionic extracellular polysaccharide secreted by the bacterium *Sphingomonas elodea* (ATCC 31461) [18]. Structurally, it is built up of tetrasaccharide repeat units containing β-D-glucose, β-D-glucoronic acid and α-L-rhamnose monomers. The natural form is partially acetylated with L-glycerate and *O*-acetate groups substituted on one glucose residue [19]. In aqueous environments at elevated temperatures, the polysaccharide exists in a random coil conformation. Cooling below a critical transition temperature promotes a thermally-reversible conformational change to ordered double-helices. The formation of this double-helix is believed to be stabilised through internal hydrogen bonding between the hydroxy methyl groups of 4-linked D-glucosyl units and adjacent hemiacetal oxygen of the L-glycerate on adjacent chains [20]. This conformational transition has been characterised by a vast array of techniques including rheometry [21], differential scanning calorimetry [22], nuclear magnetic resonance spectroscopy [23], circular dichroism [24], and more recently by atomic force microscopy [25]. The temperature at which this transition occurs has been found to be within the biologically relevant region of ~30 °C, and is shifted considerably depending upon variations in the polymer molecular weight [26], pH [27], and particularly the presence of cationic species such as Na^+, K^+, Ca^{2+} and Mg^{2+} [28].

Further to this conformational change, a more permanent change is induced through a temperature-dependant, cation-induced gelation. Upon cooling below the transition temperature in the presence of sufficient monovalent (K^+ or Na^+) or divalent

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cations (Ca^{2+} or Mg^{2+}), gel junction zones are formed [29]. The aggregation of double helices as a result of charge screening and bridging between carboxyl groups on neighbouring chains. This transition establishes multiple junction zones between surrounding double helices, forming a three-dimensional network, and bridging the polysaccharide backbone [30].

GG has been approved in the US (FDA) and in the EU for food and medical usage as a gelling, stabilising, and suspending agent [18]. It is commonly used within foods such as dessert gels, icings, puddings and glazes [31] and its ideal film forming properties led to its use in coatings and preservation of fruits [32]. GG's unique dispersing ability has been utilised in the processing of carbon nanotubes by film casting [33–36], vacuum filtration [37], inkjet printing [38] and extrusion printing [39].

In this paper, graphene dispersions added to a gellan gum solution have been used to prepare graphene-containing films and hydrogels. We show that the presence of graphene can provide mechanical reinforcement in the films and hydrogels. It is demonstrated that incorporation of graphene in the films results in electrical percolation.

2. Experimental methods

2.1. Preparation of solutions and dispersions

Solutions of gellan gum (GG) were prepared by adding the appropriate mass of gellan powder (Gelzan CM, CP Kelco, Lot #9A5250A) to 100 mL of Milli-Q (MQ) water (Millipore, resistivity 18.2 MΩ cm) under mechanical stirring for 90 min at 80 °C.

Graphene (CCG) dispersions were prepared by hydrazine reduction of a graphite oxide (GO) precursor. The GO was produced through oxidation/exfoliation of natural graphite powder (SP-1, Bay Carbon) via the modified Hummer's method [40,41]. The reduction of GO to CCG was carried out as follows. An appropriate mass of GO precursor material was added to a 1 L vessel, diluted with MQ water, followed by addition of 1 mL hydrazine (35% w/v in water, Aldrich) and 7 mL of ammonia solution (28% w/v in water, Crown Scientific) to create a 0.05% w/v dispersion of GO sheets. The resulting homogeneous GO dispersion was then vigorously shaken for a few minutes and the vessel was placed in a water bath and maintained at 95 °C for 1 h, yielding a colloidal dispersion (CCG, 0.05% w/v).

Composite dispersions were prepared by adding the required volume of CCG to a heated (50 °C) gellan gum solution. The dispersions were stirred for 10 min with heating (40 °C) and then centrifuged (2000 rpm, 15 s) to remove entrapped air. The resulting GG–CCG dispersions were prepared such that the CCG concentration was between 0.0025 and 0.045% w/v with a GG concentration of 1% w/v.

2.2. Dispersion characterisation

The homogeneity of the CCG dispersions was assessed by optical microscopy. Specifically, a small volume of the dispersion was placed onto a glass microscope slide and covered with a cover slip to ensure appropriate imaging thickness, and to prevent drying. Images of the dispersions were obtained with an optical microscope (Leica Z16 APO).

The zeta potential of CCG dispersions as a function of pH and Ca^{2+} ion concentration was obtained using a zetasizer (ZetaSizer Nano ZS, Malvern Inc). Measurement of the zeta-potential as a function of pH change was performed by preparing 10 mL dispersions of 10× diluted CCG, followed by the addition of an appropriate volume of 0.1 M HCl (from 37% AR Grade, Aldrich) to obtain a range of dispersion pH from approximately 6–11. In a similar manner, the measurement of zeta-potential as a function of added Ca^{2+} ions was made by preparing 10 mL dispersions of 10× diluted CCG with a small-volume addition of 0.5 M $CaCl_2$ (from $CaCl_2.2H_2O$ salt, Aldrich) to achieve Ca^{2+} concentrations up to 100 mM. The solutions were homogenised by inverting, before pipetting into a clean disposable zeta cuvette (DTS1060C). Three measurements were accumulated for each representative sample composition and the mean and standard deviation determined.

2.3. Preparation of hydrogels

GG–CCG dispersions (60 °C) were stirred whilst the required volume of hot (60 °C) 1 M $CaCl_2$ was added such that the Ca^{2+} concentration in solutions was varied between 5 mM and 20 mM, followed by stirring for another 5 min. The dispersions were then cooled below the gelation temperature (30 °C).

2.4. Preparation of films and hydrogels films

GG and composite GG–CCG dispersions were prepared, and stirred under moderate heat for 5 min to homogenise. The hot dispersions were transferred into polystyrene petri dishes (diameters ~5.5 cm or 12 cm) and dried in a convection oven (40 °C) for 24 h. After drying, the films were peeled off the substrate to yield free-standing films which were stored under controlled ambient conditions (21 °C, 45% RH). The films were then hydrated and cross-linked by immersion for up 180 minutes in $CaCl_2$ solution, followed by rinsing with Milli-Q water (to remove excess ions), and blotting between filter paper to remove excess water. The water content of these films was determined (WC) was calculated using (Eq. (1)),

$$WC = \frac{m_w - m_i}{m_w} \tag{1}$$

where m_i and m_w are the initial mass and the mass of the hydrated film at different time points. Measurements of the mass of the hydrated film were made by removing films at regular time intervals, blotting between filter paper to remove excess liquid, and re-weighing.

2.5. Microscopy

The morphology of the composite films was examined using a JEOL 7500FA scanning electron microscope (SEM). The samples were prepared for imaging by drying in a 60 °C vacuum oven, with representative sections cut from the sample and mounted onto brass stubs using conductive tape. Some samples were coated with a nanometre thick gold layer prior to imaging to prevent charge accumulation.

2.6. Spectroscopy

Raman spectra of the starting materials (graphite, GO and CCG) and dried GG–CCG films were obtained using a Jobin Yvon Horiba HR800 Raman spectrometer. The spectra were measured between 500 and 3000 cm^{-1} using a 638.5 nm laser source with a 950-line diffraction grating.

2.6.1. Electrical characterisation

The electrical resistance of dried and hydrated films were evaluated using a two-point probe method. Films were mounted on a glass slide and contacted with high purity silver paint (SPI) and two copper tape (3 M) contacts. The current–voltage (I–V) characteristics of the films (channel length 0.1 cm, temperature 21 °C, 45% RH) were measured by applying a sawtooth DC potential (1–10 V amplitude, 100 mHz frequency) from an Agilent waveform generator (33220 A), and measuring the current flow through the circuit via an Agilent multimeter (34410 A).