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Abstract

Hydrogels consisting of the conducting polymer PEDOT:PSS and the biopolymer gellan gum (GG) were characterized using electrical, mechanical and rheological methods. Compression testing and rheological analysis showed that the gels weakened with increasing PEDOT:PSS content. In contrast, the increasing PEDOT:PSS content resulted in an increasing electrical conductivity.

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Electrically Conducting PEDOT:PSS – Gellan Gum Hydrogels

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ABSTRACT

Hydrogels consisting of the conducting polymer PEDOT:PSS and the biopolymer gellan gum (GG) were characterized using electrical, mechanical and rheological methods. Compression testing and rheological analysis showed that the gels weakened with increasing PEDOT:PSS content. In contrast, the increasing PEDOT:PSS content resulted in an increasing electrical conductivity.

INTRODUCTION

Bionic and soft-robotic applications require soft materials which are both electrically conducting and mechanically compliant[1]. Gels based on biopolymers are suitable candidates for such

materials as they are classified as soft materials[2]. Conducting polymers are well-known materials, which can be used to fabricate conducting composites. For example, it has been found that conducting polymers have enhanced the lifetime of neural implants[3] by reducing localized tissue damage. Gellan gum is a linear anionic polysaccharide, derived from the bacterium *Sphingomonas Elodea*[4]. It is a gel-forming biopolymer with a tetrasaccharide repeating unit structure; commonly used as a food additive with Food and Drug Administration and European Union approval (E418). It is cross-linked with cations at high temperatures ($\sim 80^{\circ}\text{C}$) to form rigid hydrogels upon cooling. It has been found that divalent cations efficiently promote the gelation of gellan gum due to the formation of ionic bonds between the carboxyl groups on adjacent chains[5].

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is a block copolymer consisting of anionic PSS and cationic PEDOT. It is a conducting polymer which has been used in applications such as humidity and temperature sensors[6], anti-static coatings[7] and actuators[8].

In this study, gellan gum is combined with the conducting polymer PEDOT:PSS, to assemble electrically conducting gels. These hydrogels are characterized using mechanical compression testing, rheological analysis and electrical impedance analysis.

EXPERIMENTAL

Low acyl gellan gum (GG) was received as a gift from CP Kelco (Gelzan, Lot # 1I1443A). All solutions and subsequent gels were prepared with Milli-Q water (resistivity $\sim 18.2 \text{ M}\Omega\cdot\text{cm}$). Gellan solutions were prepared by adding dry GG powder to heated ($\sim 80^\circ\text{C}$) water under rapid stirring (800 r.p.m) using an overhead stirrer (IKA RW 20 digital). PEDOT:PSS, (conductive grade, 1.3 % solution in water, batch no. MKBJ4242V) was purchased from Sigma Aldrich, Australia.

PEDOT:PSS-GG hydrogels were prepared as follows: PEDOT:PSS dispersions were heated to $\sim 80^\circ\text{C}$, appropriate quantities of hot GG solutions were added while stirring to result in gels with GG concentration 0.5 % w/v. CaCl_2 solution was added such that the composite solution contained 5 mM Ca^{2+} ions. For example, a PEDOT:PSS-GG gel with PEDOT:PSS content of 1.05 % w/v was prepared by combining 15 mL PEDOT:PSS dispersion with 5 mL GG solution (2% w/v) and 100 μL CaCl_2 solution (1M). Hot liquids were poured into plastic molds (diameter 16 mm, height 10 mm), forming gels upon cooling. GG hydrogels were prepared by cross-linking a GG solution (0.5% w/v) with CaCl_2 as described above.

Electrical impedance analysis was carried out using a custom-built instrument. Electrical conductivity (σ) was evaluated from impedance measurements (1 Hz – 100 kHz). Mechanical testing was carried out using a Shimadzu Universal Tester at a rate of 2 mm/min using a 50N

load cell. Oscillatory rheology was performed using an Anton Paar Physica MCR 301 Digital Rheometer (parallel plate tool, diameter 15 mm) at a frequency of 10 Hz while performing a shear strain sweep.

DISCUSSION

Hydrogels were prepared by combining PEDOT:PSS dispersions with GG solutions and cross-linked with Ca^{2+} . GG hydrogels were prepared by cross-linking GG solutions. Electrical impedance analysis was used to evaluate the electrical conductivity of these GG and PEDOT:PSS-GG hydrogels (Figure 1). The GG gels are conducting ($\sigma = 0.138 \pm 0.007$ S/m), even in the absence of PEDOT:PSS, due to the presence of ionic charge carriers. PEDOT:PSS volume fractions were calculated from the PEDOT:PSS (0.8 g/cm^3 [9]), GG ($1.3 \pm 0.03 \text{ g/cm}^3$ [10]) and water densities. The conductivity increased with increasing PEDOT:PSS volume fraction. For example, the conductivity of PEDOT:PSS-GG gel (1.05 % w/v PEDOT:PSS) increased by 128 % compared to the corresponding value for a GG hydrogel, i.e. from 0.138 ± 0.007 S/m to 0.315 ± 0.014 S/m.

Figure 1. Electrical conductivity as a function of PEDOT:PSS volume fraction for rigid PEDOT:PSS-GG samples, measured using a custom-built apparatus for electrically characterizing liquids and gels.

Mechanical and rheological analysis was used to probe the effect of PEDOT:PSS on the mechanical characteristics of GG gels. GG hydrogels (0.5 % w/v) had an average storage modulus of 24.3 ± 0.7 kPa in the linear viscoelastic (LVE) region, prior to the addition of PEDOT:PSS. Figure 2 shows the storage (elastic) modulus in the LVE region as a function of shear strain. For all PEDOT:PSS concentrations, the loss modulus was always lower than the storage modulus in the LVE region, indicating that these materials were true gels. The storage modulus decreases with increasing PEDOT:PSS content. For example, it was found to decrease by one order of magnitude when the PEDOT:PSS volume fraction was increased to 1.05 %. This suggests that addition of PEDOT:PSS weakens the GG network structure.

Figure 2. a) Rheological storage modulus as a function of oscillatory shear strain and b) average storage modulus in the LVE region for rigid PEDOT:PSS-GG hydrogels with varying PEDOT:PSS volume fractions between 0 and 1.05 % v/v.

These observations were further supported by the results from mechanical compression testing. Typical stress-strain curves of PEDOT:PSS gels are shown in Figure 3a. This data is used to calculate tangent modulus (5 – 10 % strain), stress at failure and strain at failure values.

Figure 3b is a plot of the tangent modulus as a function of PEDOT:PSS volume fraction. The depicted decrease in the tangent modulus is indicative of a weakening in the gel structure, as observed in the rheological data. Figures 3c and d exhibit a decrease in both the stress and strain values at failure as a function of PEDOT:PSS volume fraction. These measurements indicate that GG gels are mechanically weakened by the presence of PEDOT:PSS. It is suggested that the reduction in mechanical properties can be attributed to the cationic PEDOT:PSS inhibiting the Ca^{2+} cross-linking of the anionic GG polymer chains by complexation of the available cross-linking sites. This is contrary to previous studies which demonstrated a strengthening effect with the addition of PEDOT:PSS to polyacrylamide (PAAm)[11] and poly(acrylic acid) (PAA)[12]

gels. It was suggested that PEDOT:PSS reinforced these covalently gel networks via entanglement.

Figure 3. a) Stress-strain curves for PEDOT:PSS-GG rigid hydrogels at 0.35 %, 0.70 % and 1.05 % volume fraction PEDOT:PSS. The straight line fits between 5-10 % strain indicate data used to calculate tangent modulus. b) tangent modulus, c) compressive strain at failure and d) compressive stress at failure as a function of PEDOT:PSS volume fraction. The lines in b-d) are to guide the reader's eye.

CONCLUSIONS

The preparation and characterization of PEDOT:PSS-gellan gum hydrogels is presented. It was shown that the electrical conductivity increased proportionally with PEDOT:PSS volume fraction between 0.35 % and 1.05 % to a value of 0.315 ± 0.014 S/m. However, this increase in

conductivity with PEDOT:PSS volume fraction is coupled with a decrease in storage modulus, tangent modulus, stress at failure and strain at failure. This work has shown that conducting hydrogels can be prepared by combining a biopolymer with a conducting polymer.

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