



Oscillatory shear induced gelation of graphene–poly(vinyl alcohol) composite hydrogels and rheological premonitor of ultra-light aerogels



Ji Eun Kim, Heon Sang Lee*

Department of Chemical Engineering, Dong-A Univ., 840, Hadan-dong, Saha-Gu, Busan 604-714, Republic of Korea

ARTICLE INFO

Article history:

Received 2 August 2013

Received in revised form

10 October 2013

Accepted 10 November 2013

Available online 15 November 2013

Keywords:

Graphene

Hydrogel

Aerogel

ABSTRACT

Time evolution of 3-D structure of GO hydrogels was explored by rheological measurements. We showed that the GO hydrogels were thickened drastically by oscillatory shear flow if and only if both the angular frequencies and shear strain are small. We also showed that the plateau modulus (G_N') of GO hydrogels is rheological premonitory of ultra-light aerogels. The ultra-light aerogel fabricated in this work exhibited low density of 4.0 mg/cm³, low surface resistivity of 6.6 Ω/sq, high specific area of 1069 m²/g, and high recoverable strain of 94% in compression. The glass transition temperature of poly(vinyl alcohol) (PVA) in the aerogel was 49 K higher than that of pure PVA. The thermal stability of the GO/PVA aerogel in air environment was superior to that of dried GO in itself in thermogravimetric analysis (TGA).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

There is fast growing interest in graphene oxide (GO) hydrogels [1–6] and graphene aerogels [7–31]. This may be due to that GO is the “super gelator” in aqueous solution with a critical gelation concentration <0.5 wt.% [5,6]. Since the first report on graphene aerogels in 2009 [7], many researchers have developed graphene aerogels based on the hydrogels composed of GO by freeze-drying [7–10], super critical CO₂ drying [11–17], and microwave-irradiation [18]. Direct synthesis of graphene aerogels by chemical vapour deposition (CVD) has also been reported [19,20]. The researches on graphene aerogels point to various applications such as fiber [9], sensor [12], oil absorber [14], supercapacitor [20], energy storage [15,21], electromagnetic interference shielding [22], microbial fuel cell [23], and water purification [24]. The density of graphene aerogels reported in the literature is about 3–96 mg/cm³ [8,15–17], which are comparable values to those of silica aerogels. Synergistically assembled GO aerogels with organic molecules [14], polymers [25,26], nanoparticles [27], and carbon nanotubes (CNT) [28–31] have been reported. Especially, GO/CNT composites

aerogels show ultra-flyweight density as low as 0.16 mg/cm³ [29], and superelastic and resistant to fatigue [31].

The understanding on the evolution of 3D structures in GO hydrogels is one of the core sciences for the aerogels, too, since many technologies to fabricate graphene aerogels are based on GO hydrogels [7–18]. The evolution of microstructure in dispersions can be monitored by small amplitude oscillatory shear (SAOS) measurements, if stress relaxation is much faster than the time required for structural change [32,33]. The storage modulus (G') reflects the number of network points in the gels, and increases by gelation proceeding. Therefore, many researchers employ SAOS measurements to monitor the degree of gelation of GOs [1–6] and polymers [34–37]. If SAOS affected the structural evolution of gels in measurements, the results could be distorted. In fact, oscillatory-shear induced ordering has often been observed in concentrated colloidal suspensions [38,39]. In this work, we explored the gelation of aqueous dispersions composed of GO and poly(vinyl alcohol) (PVA) through rheological study. Strikingly, our studies showed that SAOS can induce the gelation of graphene dispersions. “Shake gels” has also been reported in polymer dispersions with nano-clay [34,35] and nano-silica [36]. The “shake gels” behavior is the shear induced gelation which is a class of shear thickening phenomena [36]. After cessation of flow, the “shake gels” return to solution [34–36]. While, the SAOS-induced GO hydrogels were stable in this study. It is worth to note that

* Corresponding author. Tel.: +82 51 200 7724; fax: +82 51 200 7728.
E-mail addresses: heonlee@dau.ac.kr, heonlees@gmail.com (H.S. Lee).

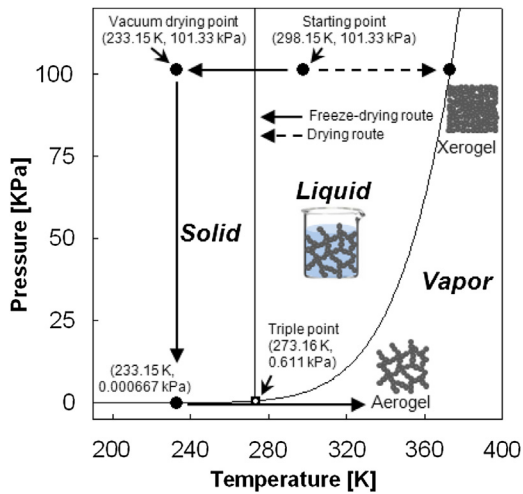


Fig. 1. P - T phase diagram of water and freeze drying path.

SAOS-induced gelation is rarely observed phenomena in condensed matter physics. The rheological properties measured after the completion of SAOS-induced gelation was highly related with the density and the electrical conductivity of graphene aerogels in this study. We anticipate that the SAOS induced-gelation and rheological premonitory of ultra-light aerogels, reported in this work, do a great impact on the further studies on GO hydrogels and aerogels.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA) was purchased from Sigma Aldrich (99 mol% hydrolyzed, $\overline{M}_w = 89,000$ – $98,000$ g). Flake graphite powder (19 μm nominal size) was supplied from Asbury Carbon. GO was synthesized from the purified flake graphite by modified Hummers method [40], following the procedures reported in our previous work [41]. To prepare GO hydrogels, 4.8 ml GO dispersion (5 mg/ml) was added into 1.2 ml PVA solution (4.8–72.0 mg PVA). Aqueous PVA solution was added to the dispersions with various PVA weight ratios to GO ($r_{P/G}$). The mixtures were shaken violently for 3 s to form GO hydrogels. The GO hydrogels were allowed to freeze at -70 °C for about 1 h. The sample was placed onto a precooled shelf -40 °C and then held at this temperature for 30 min. Chamber pressure dropped and leveled off at about 0.000667 kPa. The shelf temperature was ramped from -40 °C to -20 °C for 30 min held for 3 h, was ramped from -20 °C to 0 °C for 1 h and held for 3 h, was ramped from 0 °C to 20 °C for 1 h and held for 3 h and then was ramped from 20 °C to 40 °C for 1 h and held for 51 h at 40 °C. The total duration of the cycle was 67 h and 30 min (Fig. 1).

2.2. Characterization

The rheological measurements were performed using a controlled stress rheometer (model ARG2 from TA Instruments). A parallel plate geometry was used with a gap size of 1.0 mm and a

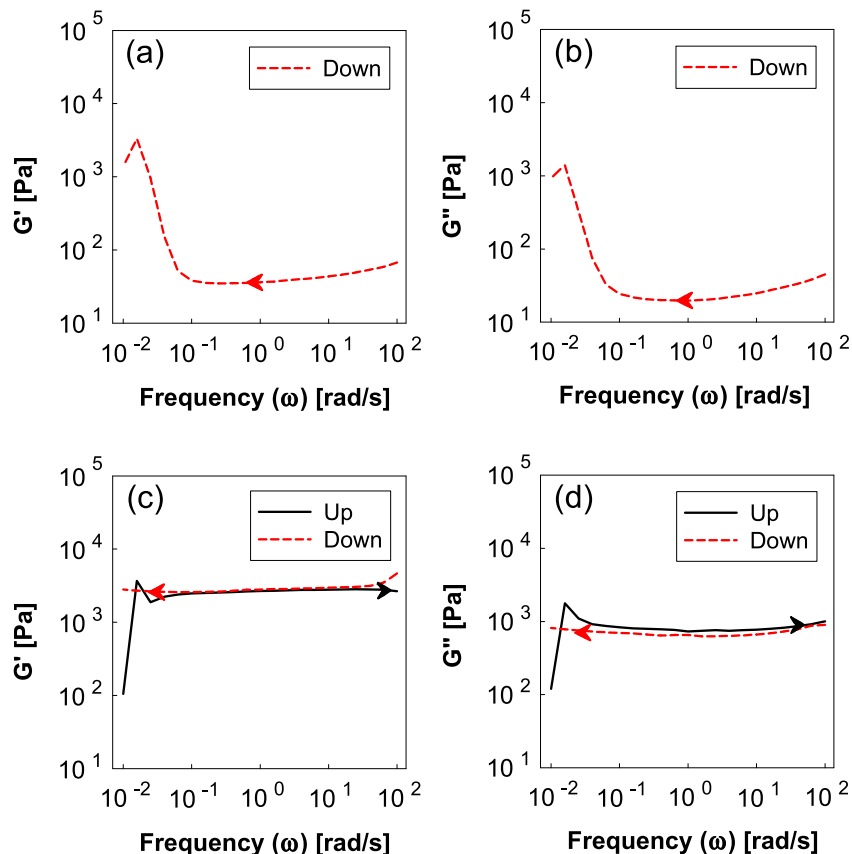


Fig. 2. (a) The storage modulus (G') and (b) the loss modulus (G'') of GO hydrogel with 0.08 wt.% PVA ($r_{P/G} = 1:5$) by frequency down-sweep measurements. (c) The G' and (d) the G'' of the GO hydrogel by frequency up-sweep measurements, followed by frequency down-sweep measurements.

Download English Version:

<https://daneshyari.com/en/article/5181702>

Download Persian Version:

<https://daneshyari.com/article/5181702>

[Daneshyari.com](https://daneshyari.com)