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Morphology and physical properties of graphene nanoplatelet embedded poly(vinyl alcohol) composite aerogel

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ABSTRACT

Three dimensional carbon nanomaterial reinforced composite aerogel was fabricated using a freeze-drying method. Graphene nanoplatelets (GNPs) were used as the reinforcement and poly vinyl alcohol (PVA) as the organic binding material to produce the composite aerogel. Two different methods were employed to control the internal structure of the aerogel: a variation of solvent composition and the formation of cross-linking. The internal structure of the aerogel was affected by the types and composition of the solvent. In addition, the subsequent cross-linking of the aerogel influenced the morphology and physical properties. It is expected that this study can provide a simple and efficient way to control the internal structure and resulting properties of the GNP aerogel.

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1. Introduction

Recently, carbon aerogels attract considerable attention by scientists as a new three dimensional form of material with a wide range of applications, such as oil-absorption device [1,2], thermal insulator [3], gas sensor [4,5], battery electrode [6], and supercapacitor [7-9]. Various types of carbon materials such as carbon nanotube (CNT) [10,11], carbon nanofiber (CNF) [12,13], graphene [14-16] have been introduced as the base material for the aerogel due to their superior mechanical, electrical, and morphological properties. For example, M. B. Bryning et al. prepared CNT aerogels using wet-gel precursors and demonstrated that CNTs could be bound with the use of PVA [10]. Ye et al. fabricated graphene oxide/epoxy aerogel via the freeze-drying method [17]. In addition, Haiyan et al. reported a CNT/graphene hybrid aerogel with low density [18]. On the other hand, graphene nanoplatelets (GNPs), two dimensional disc shaped particles, are produced by exfoliating natural graphite flake and have advantages such as lower cost and higher production rate than CNT or graphene [19].

It is important to control the internal structures of aerogel, including the fraction, size and the shape of pores since they determine the properties of the aerogel [20]. In general, the template based methods such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) are two common methods to produce highly ordered structure. However, it is difficult to apply the template based methods to the commercial applications due to their complicated preparation procedure and high cost. On the other hand, a freeze-drying method does not require any template and can be applied to mass production. In this respect, the freeze-drying method has been used for the fabrication of carbon aerogels. For instance, Kim et al. reported graphene coated CNT aerogel with extraordinary elasticity and fatigue resistance [21]. Furthermore, additional epoxy coating improved the mechanical properties of the aerogel [17].

In this study, we fabricated GNP/PVA aerogel using the freeze-drying method. The internal structure of the aerogel was manipulated by controlling the solvent composition and cross-linking the polymer. A mixture of water and ethanol was used as the solvent and maleic acid was used as the cross-linker. To the best of our knowledge, there was no report on the morphology control for aerogel by applying either solvent or cross-linker. The morphology of aerogel was identified with cryo-SEM and FE-SEM. The thermal conductivity and mechanical properties were also evaluated.

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2. Experimental

2.1. Preparation of GNP/PVA aerogel

GNPs (C grade) were purchased from XGScience (Michigan, USA) and had a true density of 2.2 g/cm^3 and a surface area of 750 m^2/g. PVA with a molecular weight of 89,000–98,000 and a degree of hydrolysis of 99+% and Maleic acid were supplied by Sigma Aldrich.

PVA was dissolved in DI water under vigorous stirring. The weight fraction of PVA was varied from 1.00 wt% to 2.00 wt%. The GNP powder was added to the PVA solution and suspended under sonication. The solution was poured into a cylindrical mold and quenched in the liquid nitrogen. Thereafter, the sample was freeze-dried for 48 h in order to maintain the internal structure of the solid parts in the suspension. Two different compositions of solvent were applied: one was pure DI water and the other was aqueous ethanol solution with a volume fraction of 20%. Maleic acid was mixed the GNP/PVA suspension with help of a mechanical stirrer. The content of maleic acid was 30% w/w PVA. After freeze-drying, the volume and mass of aerogel were measured directly. The porosity of aerogel was calculated by the following equation.

$$V_g = \frac{\rho_m - \rho_{air} - \rho_f}{\rho_m - \rho_{air}} \quad (1)$$

where V_g denotes the porosity of aerogel, ρ_m is the density of the added materials, ρ_{air} is the density of air, and ρ_f is the density of aerogel. The experimental conditions, density, and porosity of the GNP aerogel are summarized in Table 1.

2.2. Characterization

The size distribution of GNPs in the suspension was analyzed with a dynamic light scattering spectrophotometer (DLS-7000, Otsuka Eletronics CO. Ltd, Japan). A cryogenic scanning electron microscope (Mira-3 FEG, Tescan, USA) was used to investigate the microstructure of the GNP suspension in liquid state. The frozen DI water suspension was sublimed at −100 °C for 5 min after fracture, whereas the frozen DI water/ethanol suspension was sublimed at −100 °C for 10 min to prevent recrystallization of frozen water. The morphology of the GNP/PVA aerogel was observed with a scanning electron microscope (JSM-6390LV, JEOL, Tokyo, Japan) at room temperature. Fourier transform infrared attenuated total reflection spectroscopy (Nicolet 6700, Thermo Sciencific, Epsom, UK) was applied to identify the cross-linking reaction of PVA. The thermal conductivity of the aerogel was measured by using a thermal analyzer (C-Therm TCi, C-Therm Technologies Ltd, New Brunswick, Canada) based on a modified transient plane source method. The compressive strength was examined with a universal tensile test machine (Instron 3365, MA, USA) at room temperature.

Table 1
Density and porosity of the prepared GNP/PVA aerogels with respect to different experimental conditions.

Sample	PVA:GNP (weight ratio)	Solvent composition	Maleic acid (w/w PVA)	Density (g/cm^3)	Porosity (%)
GP1	1:1	Water	–	0.03057	98.1
E-GP1	1:1	Water+EtOH	–	0.01306	99.2
GP2	2:1	Water	–	0.09742	93.4
X-GP2	2:1	Water	0.3	0.11696	92.2

3. Results and discussion

3.1. Dispersion of GNP

Dynamic light scattering (DLS), also known as photo correlation spectroscopy or quasi-elastic light scattering, is a technique used widely for analyzing the particle size and the size distribution [22]. This technique is based on the Brownian motion of spherical particles which causes a Doppler shift of incident laser light. The hydrodynamic diameter, d_h measured by using DLS, is presented in Fig. 1. The GNPs suspended in DI water had the mean diameter of about 900 nm, whereas those in the mixture of water and ethanol possessed a mean diameter of 360 nm. This discrepancy showed that the addition of ethanol led to a better dispersion of GNP in the suspension, which could affect the formation of ice crystal and then the microstructure of GNP/PVA aerogel. The enhanced particle dispersion could entail the generation of smaller pores and the improvement of porosity in the aerogel. Therefore, the E-GP1 aerogel shows higher porosity than the GP1 aerogel as listed in Table 1.

3.2. Microstructure of the aerogel

The cryo-SEM observation was performed to investigate the internal structure of suspension in the liquid state. When the suspension sample was quenched with the use of liquid nitrogen, the heterogeneous nucleation sites were formed on the mold surface and ice crystals, which were larger than the critical size, were grown along with temperature gradient. Since the crystal growth along the c-axis of hexagonal ice was two orders of magnitude slower than the growth along the a-axis and b-axis, the lamellar structure of ice crystal was generated [23]. The GNPs were redistributed during the nucleation and the growth of ice crystal and relocated between the generated ice crystals. After freeze-drying, the ice crystals were sublimed, and the remained GNP particles formed lamella network structure with the organic binder. As a result, the ice crystal structure was transferred into the microstructure of the GNP/PVA aerogel [24].

Fig. 2a and b show cryo-SEM images of the GNP suspensions. The lamellar ice crystals were observed and the GNPs were placed between the ice crystals. It was found that the sample prepared with the water/ethanol mixture had smaller crystal size, i.e., closer interlayer distance of the ice crystals than the one prepared with DI water. This discrepancy in the crystal size was also observed for the pure DI water and the water-ethanol mixture without GNPs (Fig. S1.). The addition of ethanol into water increased the number of nucleation sites and subsequently decreased the crystal size. The microstructure of the crystal was determined depending on the composition of the suspensions. The agglomerates of the GNPs were identified in Fig. 2a. This implies relatively poor dispersion of the GNPs in water, which is in agreement with the aforementioned DLS result.

The SEM images of the GNP/PVA aerogels are presented in Fig. 3a and b. The samples were freeze-dried to fix the microstructure of crystal. Similar to the cryo-SEM observation, the water/ethanol mixture yielded more complicated microstructure with smaller pore than the DI water. It is worth noting that internal structural factors such as porosity, size, and shape of pore are determined by the nature of solvent.

Fig. 4a and b demonstrate the effect of cross-linking of PVA with maleic acid on the microstructure of the aerogel. The solvent used was water, and the ratio of GNP and PVA was 1:2. The thickness of strut was increased after the cross-linking of maleic acid. The increase of strut could lead to an enhancement of the mechanical properties.

The change in the chemical structure is identified with the FT-IR spectra. Fig. 5 presents the spectra of the cross-linked GP2 aerogel. The characteristic peak of PVA was observed between 3000 and

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