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Composites: Part A

Graphene for flame-retarding elastomeric composite foams having strong interface

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ABSTRACT

It is a great challenge to make elastomeric polymer foams antistatic, flame-retardant and mechanically robust. The challenge was addressed herein by in situ polymerizing polyvinyl alcohol, formaldehyde and graphene sheets. The graphene sheets – each in average being ∼5 nm thick – had a carbon to oxygen atomic ratio of 9.8 and a Raman I_D/I_G of 0.03. The sheets proved to react with formaldehyde building up a strong interface for the composites, and the reaction promoted the exfoliation and dispersion of graphene sheets in the matrix. They were found to create a large number of fine pores to the composites. Graphene sheets at 0.12 vol% increased the foam water retention rate from 346% to 784%. These composites had a percolation threshold of electrical conductivity at 0.023 vol%. The composites reached a limiting oxygen index of 59.4, implying an exceptional self-extinguishing performance.

1. Introduction

Of all engineering materials, polymers have seen the largest increase in industrial applications over the past decades because of their relatively high specific strength and low manufacturing costs. However, polymers are limited by high flammability [1] and inability to dissipating static electric charges [2] that relate to catastrophic explosions in underground mining and chemical environments [3–10]. Therefore, it is of significance to develop anti-static, flame-retarding polymers. Commercial polymers have surface resistivity 10^{12}–10^{17} Ω/square [2,11], and it requires 10^6–10^{12} Ω/square to dissipate static charge [2,11]. Utilizing functional fillers is the most cost-effective method to make polymers anti-static and flame-retardant.

Polymeric foams are produced by introducing microscopic voids and/or gas bubbles through polymerization. They are increasingly more used in construction and packaging industries [12–15], because of favourable properties – light weight, thermal and acoustic insulation, energy absorption and cost effectiveness [16–18]. Practical applications such as packaging require these foams to be mechanically strong, anti-static and flame-retarding; this poses a formidable challenge.

Polyvinyl formaldehyde (PVFMH) is a product of polyvinyl alcohol and formaldehyde by condensation. PVFMH-based foams are relatively new in comparison with those foams based on polyurethane, but they are more advantageous in terms of environmental friendliness. Neat PVFMH [19,20] and its composite foams containing alginate [21], chitosan [22] have shown promise in biomedical industry. A chelating PVFMH foam [23] was reported for environmental protection, where the foam surface was modified by a methacrylate and hydroxylamine solution via grafting polymerization; the modified foam showed adsorption capacity 73.23 mg/g for Cu^{2+} from water [23].

These studies are respectable, but they are associated with three limitations (i) low rate of water absorption, (ii) unsatisfactory mechanical robustness – a neat foam just disintegrates itself after absorbing and removing water for 30 cycles, and (iii) lack of anti-static and flame-retarding performance; these severely limit the application. A hypothesis made herein was that compounding PVFMH with graphene sheets should address these limitations, because the sheets are exceptionally stiff and strong, have high electrical conductivity and flame-retarding property, and would react with formaldehyde likely creating a strong interface for the composites. CVD-grown graphene has been recently reported to create foams for various applications such as supercapacitors, absorbents and energy harvesting [24,25]; but its costs prevent the application in industry.

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We in this study develop PVFMH/graphene composite foams starting from graphene sheets, polyvinyl alcohol and formaldehyde via *in situ* polymerization. The foams not only demonstrate anti-static performance and a high rate of water absorption, but remain remarkable structural integrity even through 150 cycles of absorbing and removing water. More importantly, limiting oxygen index measurement proves the composite foams to be highly flame-retardant.

2. Materials and methods

2.1. Raw materials

Flake graphite of ∼160 μm in lateral dimension was purchased from Baoding Carbon Co. Pty Ltd, China. Potassium dichromate (90.0 wt%), concentrated sulfuric acid (98.0 wt%), peroxyacetic acid, formaldehyde (37.0 wt%), polyvinyl alcohol (99.0 wt%) and *n*-pentane (95.0 wt%) were ordered from Tianjin Hongguang Chemical Co. Pty Ltd.

A graphite intercalation compound (GIC) was prepared according to previous studies [26,27]. In brief, 1.30 g of potassium dichromate, 18.40 g of sulfuric acid and 5.00 g of peroxyacetic acid were carefully moved into a 250-ml flask that sat in a water bath with magnetic stirring; then 5.0 g of flake graphite was added into the mixture, with the temperature controlled at 45 °C for 30 min. The mixture was subsequently washed through filtration until being neutral, followed by drying at 60 °C for 30 min; this produced a graphite intercalation compound.

The compound was thermally treated in a normal atmospheric-pressure furnace as detailed below. A crucible was preheated in the furnace at 800 °C for 10 min. Then 1 g of GIC was transferred into the crucible and treated in the furnace for 1 min, which created a loose pile of graphene sheets. The crucible was taken out and left in a fume cupboard to allow the product to cool down. The process should be conducted in a fume cupboard, and the operator must wear safety glasses, specific heat resistant gloves, protection cloth and closed shoes.

2.2. Fabrication of neat polyvinyl formaldehyde foam and its graphene composite foam

Polyvinyl formaldehyde (PVFMH) was synthesized taking advantage of the reaction between the hydroxyl groups of PVA and the carbonyl groups of formaldehyde in Scheme 1; this reaction was reported and proved before [28]. In specific, 10.0 g of

polyvinyl alcohol was dissolved in 90.0 g of distilled water by magnetic stirring at 300 rpm; the polymer was observed to dissolve completely after 60 min. A mixture of 5.0 g concentrated sulfuric acid and 34.5 g formaldehyde solution was added into the PVA solution, followed by 30 min of stirring at 65 °C; this produced a PVFMH solution for the following.

A PVFMH foam was fabricated by using *n*-pentane as a foaming agent, because *n*-pentane has low cost and boiling temperature. 4.50 ml of *n*-pentane was added into the PVFMH solution with magnetic stirring at 300 rpm and then the mixture was immediately poured into a mold, followed by heat treatment in an oven at 60 °C for 90 min. This produced a disk-like foam of ∼12.0 cm in diameter.

A series of PVFMH/graphene composites were prepared by *in situ* polymerization. As described above, 10.0 g of PVA was dissolved in 90.0 g of distilled water, into which 5.0 g concentrated sulfuric acid, 34.5 g formaldehyde solution and a desired quantity of graphene were added, followed by 30 min of stirring at 65 °C; this produced PVFMH/graphene composites. These composite were transformed into disk-like foams by using a similar process to the fabrication of neat PVFMH foam. Through varying the ratio of graphene to PVFMH, we prepared composite foams at graphene weight fractions 0.45–2.63 wt%. In order to obtain volume fractions (V_f), Eq. (1) was adopted:

$$V_f = \frac{\rho_m W_f}{\rho_f(1 - W_f) + \rho_m W_f} \tag{1}$$

where W_f, ρ_f and ρ_m respectively refer to weight fraction, matrix density and filler density. The density values of graphene sheets and foam were taken as 2.2 and 0.114 g/cm³. The density of neat foam was measured based on weight and volume of three replicas.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed by a SPECS SAGE XPS system with a Phoibos 150 analyzer and a MCD-9 detector. Non-monochromated Mg Kα radiation was used and set at 10 kV and 200 W. A circular spot of 3 mm in diameter was investigated. Ratios of C/O were determined by calculating the peak area of C1s and O1s *via* OriginLab® software. Raman spectra were obtained using a Renishaw inVia Raman microspectrometer by a laser excitation of 633 nm in wavelength.

Atomic force microscopy was performed to obtain the thickness of graphene sheets by an NT-MDTSPM instrument with an NSG03 non-contact golden cantilever. Graphene sheets were immersed in
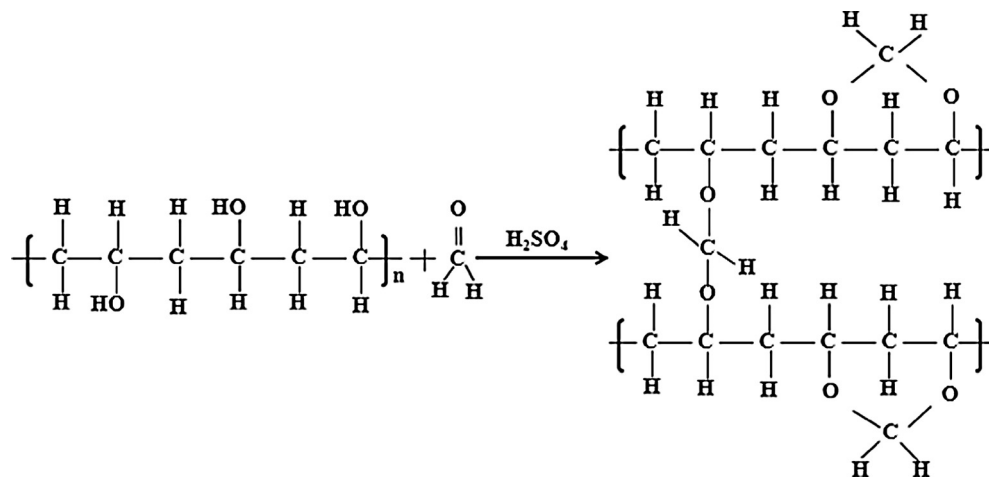
Scheme 1. Synthesis of polyvinyl formaldehyde, where both intermolecular and intramolecular crosslinking occur.