

Effect of Temperature and Graphene Oxide on the Swelling of PAAm-GO Composite Gels

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Abstract - Graphene oxide (GO) is a two dimensional carbon material with similar one-atom thickness, and is a light material having extremely high strength and thermal stability [1]. Thus, GO is an efficient filler for the enhancement of the electrical, mechanical and thermal properties of composite materials [2]. We focused on GO as a nanofiller in polyacrylamide hydrogels and PAAm-GO composites to investigate the effect of temperature and graphene oxide on the swelling. Polyacrylamide (PAAm) hydrogels have been proposed for use as promising biomaterials in biomedical and tissue engineering. The composite gels were prepared by free radical crosslinking copolymerization with GO content varying in the range between 8 and 50 µl of GO. The effects of temperature and graphene oxide on the swelling of the composites were studied. The swelling experiment was performed in the distilled water. Decreasing in pyranine (Py) as a fluorescence probe and emission light intensity (I_{em}) were monitored by steady state fluorescence spectroscopy. Since the increase in I_{sc} corresponds to the increase in turbidity of the swelling composite gel, the corrected fluorescence intensity, I was introduced to analyze the swelling processes. The Stern-Volmer equation combined with Li-Tanaka models was used to explain the behaviour of I during swelling processes. The cooperative diffusion coefficients and time constants were calculated as a function of temperature and GO, respectively.

Keywords: Graphene oxide, Polyacrylamide, Temperature, Swelling, Composite.

1. Introduction

Hydrogels are three-dimensional networks of crosslinked polymer chains swollen in water, having a wide array of applications; including biosensors, sustained drug release, and drug delivery systems. Graphene oxide is a two-dimensional carbon material with similar one-atom thickness but with a large number of hydrophilic oxygenated functional groups [1]. Graphene oxide is a light material having extremely high strength and thermal stability. Therefore, GO is an efficient filler for the enhancement of the electrical, mechanical and thermal properties of composite materials [2]. GO is also used in such applications as nanoelectronic devices, gas sensors, supercapacitors, tissue engineering, and drug delivery systems [3]. pH responsive graphene/polyacrylamide complex via noncovalent interaction have been reported [4]. The resultant complexes show a reversible pH responsive property, although polyacrylamide itself does not possess such characteristics. The swelling properties of GO-polyacrylic acid-co-acrylamide nanocomposites were studied by FTIR, X-ray diffraction, DMA, field emission scanning electron microscopy, and optical microscopy [5]. The swelling capacity of the nanocomposites was compared with pure acrylamide with respect to pH behaviour. We have studied the swelling of polyacrylamide (PAAm)-multiwall carbon nanotube (MWNTs) composite [6], which shows that τ decreased and naturally D increased by increasing temperature. Swelling energies, ΔE were measured and found to be strongly dependent on MWNT content in the composite gels. It is observed that ΔE values first increased up to 1 % (wt) of MWNT, then decreased by increasing MWNT content. Our objective is to study the effect of GO on the swelling process of the PAAm- GO composite by using the steady-state fluorescence technique. The Stern- Volmer equation combined with Li-Tanaka equation to explain the behaviour of the swelling of the PAAm- GO composite at different temperatures. The swelling time constants, τ and cooperative diffusion

coefficients, D , were determined for the swelling of the composite prepared with various GO contents. It was observed that τ decreased and naturally D increased by increasing temperature.

In this paper, the results in this work have shown that the fluorescence method can be used to monitor the swelling kinetics of the PAAm - GO composite in water for various temperatures. This technique was employed to measure the swelling time constants, τ and cooperative diffusion coefficients, D , for composite gels prepared with various PAAm and GO contents. The Li-Tanaka model was applied to measure these parameters. Here basically composite assembly on the basis of intermolecular hydrogen bond or other non-covalent interactions was constructed in the presence of the GOs and PAAm networks, which further affected swelling performances of the composites.

2. Experiment

2.1. Preparation of GO-PAAm Composite

Composite gels were prepared by using 2M AAm (Acrylamide, Merck) with various amounts 8, 20, 30, 40, and 50 μ l of GO (Graphene oxide, Graphenea) contents at room temperature. GO is purchased from Graphenea. Its concentration is 4 mg/mL. The purity of commercial GO is higher than 95 % (wt). Composite gels were formed by free radical copolymerization as follows: 1.42 g of AAm, 0.02 g N'-methylenebisacrylamide (BIS, Merck), 0.016 g of ammonium persulfate (APS, Merck), and 6 μ l of tetramethylethylenediamine (TEMED, Merck) were dissolved in 10 ml distilled water (pH 6.5). The solution was stirred (200 rpm) for 15 min to achieve a homogenous solution. GO is mixed to the solution just before adding TEMED. All samples were deoxygenated by bubbling nitrogen for 10 min just before the polymerization process which occurred in the plastic syringe [7].

2.2. Fluorescence Measurement

The fluorescence intensity measurements were carried out using a Model LS-55 spectrometer from Perkin-Elmer, equipped with a temperature controller. All measurements were made at 90° position and spectral bandwidths were kept at 5 nm. Disc-shaped gel samples were placed on the wall of a 1 cm path length, square quartz cell filled with water for the swelling experiments. We used Py in the PAAm-GO composite as a fluorescence probe. The Py is a derivative of pyrene including three SO_3^- groups which can form bonds with positive charges on the gel. The Py can be attached to the gel by Columbic attractions. The composite was excited at 340 nm during in-situ experiments and emission intensities of the pyranine were monitored at 427 nm as a function of swelling time. As the water diffusion increased, the fluorescence intensity, I_{em} , decreased and the scattered light intensity, I_{sc} , increased due to the increase in turbidity of the swelling gel. Disc-shaped gel samples were placed on the wall of a 1cm path length square quartz cell filled with water for the swelling experiments [8].

3. Theory

3.1. Stern- Volmer Model

The kinetics of photophysical intermolecular deactivation process is defined by quenching mechanism. In this model, the fluorescence intensity is written as [9],

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \quad (1)$$

where τ_0 is the lifetime of the fluorescence probe with no quenching has taken place; k_q is the quenching rate constant, $[Q]$ is the quencher content and I_0 is the fluorescence intensity for the zero quencher content.

In our case, the amount of water diffusion, W is produced over the differential volume when $\tau_0 k_q [Q] \ll 1$

$$W = \left(1 - \frac{I}{I_0}\right) \frac{v}{k_q \tau_0} \quad (2)$$

where v is the volume at the equilibrium swelling state, k_q is the infinity equilibrium value of water diffusion, W , and τ_0 is 5 ns for pyranine molecules. In our system, it is assumed that water molecules are the only quencher for the excited pyranine molecules.

3.2. Li- Tanaka Model

The swelling of a disc gel in axial and radial directions can be solved for small diffusion process [10]. The kinetics of the swelling of a gel can be written in terms of water uptakes W and W_f at time t and equilibrium at large t .

$$\frac{W}{W_f} = 1 - B_l \exp(-t/\tau_l) \quad (3)$$

where B_l is related to the ratio, R [10], which are determined by shear modulus and longitudinal osmotic modulus. The cooperative diffusion coefficient, D_0 at the surface of a gel disc is given by the following relation

$$D_0 = \frac{3a_f^2}{\tau_l \alpha_l^2} \quad (4)$$

where α_l is a function of R only [10], a_f stands for the half thickness of the gel in the final equilibrium state, and τ_l is the swelling time constant, respectively.

4. Results and Discussion

Figure 1 presents the fluorescence spectra of pyranine from the PAAm- GO composite during the swelling process in pure water at 40 °C for 20 μ l of GO at 80 min, respectively. In both cases, as the water uptake is increased, the emission light intensity, I_{em} , decreased and the scattered light intensity, I_{sc} , increased. In order to elaborate the findings, first of all, it has to be mentioned that two different phenomena cause the decrease in the I_{em} ; first one is the quenching of excited pyranine and the other one is the scattering of light from the gel due to turbidity.

Plots of water uptake, W are calculated from Eq. 2. Typical solvent uptake curves, obeying the Li- Tanaka equation is the equation (3) [8- 10]. The logarithmic form of the data was fitted to the following relation produced from equation (3).

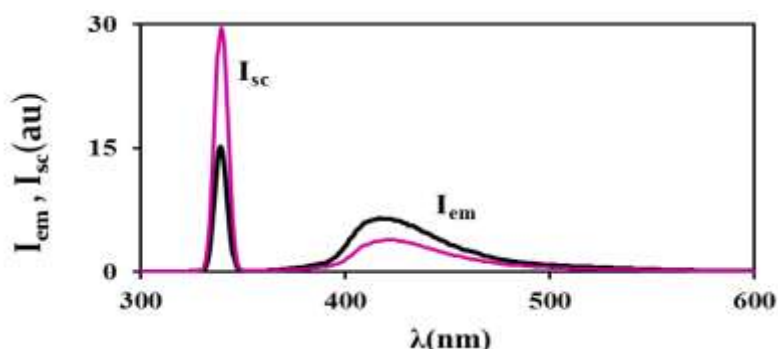


Fig. 1: Fluorescence spectra of pyranine from the hydrogel doped with 20 μ l of GO content samples during the swelling process at 40 °C.

Linear regression of the curves in Figure 2 provided us with B_l and τ_l values. Then, using Eq. (4), cooperative diffusion coefficients, D were determined for these disc-shaped composites and found to be around 10^{-9} m²/s. Experimentally obtained τ and D values at 40 °C at various GO contents are summarized in Table 1.

Table 1: Diffusion coefficients and time constants of PAAm-GO composites at 40 °C at various GO contents.

GO (μl)	τ (min)	D*10 ⁻⁹ (m ² /s)
0	48.50	4.00
8	94.33	1.78
20	111.11	0.6
30	204.08	0.57
40	238.09	0.52
50	263.15	0.46

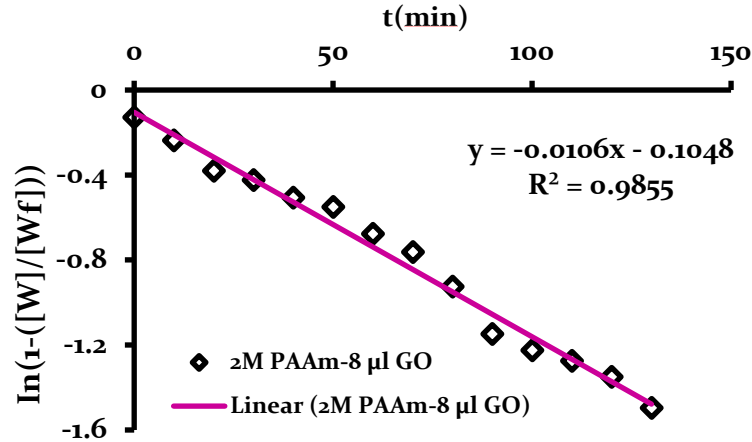


Fig. 2: Linear regressions of diffusion coefficients versus time measured by fluorescence technique for 8 μl of GO content samples.

5. Conclusion

The results in this work have shown that the fluorescence method can be used to monitor the swelling kinetics of the PAAm-GO composite in water for various temperatures, and GO content. This technique was employed to measure the swelling time constants, τ and cooperative diffusion coefficients, D , for composite gels prepared with PAAm and various GO contents. Cooperative diffusion coefficients were calculated by using Li Tanaka's model combined by Stern Volmer's Equations. It is important to note that GO content could act as a multifunctional cross-linker to form more junctions in PAAm-GO composite and increase the density of crosslink, leading to the reduction of swelling capacity.

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