Characterization of the actuating response of the graphene oxide/MEO\textsubscript{2}MA hydrogel layer

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Abstract. This study is aimed to characterize the actuating responses of the soft polymeric multilayer, which is composed of a coated graphene oxide (GO) layer and di (ethylene glycol) methyl ether methacrylate (MEO\textsubscript{2}MA) hydrogel layer. The actuating mechanism was based on the swelling and deswelling behaviors of the MEO\textsubscript{2}MA hydrogel that was triggered by the heat generated from the GO layer irradiated with near-infrared (NIR) light. As the swelling and deswelling properties of the MEO\textsubscript{2}MA hydrogel were crucial factors in the performances and responses of the GO/MEO\textsubscript{2}MA multiplayer, the lower critical solution temperature (LCST) and mechanical properties of three different cross-linked MEO\textsubscript{2}MA hydrogels were measured. The measured LCST indicated that the trigger temperature of the GO/MEO\textsubscript{2}MA multilayer was between 20 and 26\degree C. The swelling capability of the MEO\textsubscript{2}MA layer could reach around 12 times, whereas the surrounding temperature was higher than LCST. Three different cross-link ratios of MEO\textsubscript{2}MA samples could afford approximately 1.5 N of force loading. Moreover, the coated GO layer could generate heat to exceed the LCST temperature in a few minutes using 450 mW NIR irradiation. The bending responses of the GO/MEO\textsubscript{2}MA layer were temperature responsive and reversible. Hence, the GO/MEO\textsubscript{2}MA hydrogel might be a promising solution for several applications, such as the artificial muscles and soft gripper.

1. Introduction
Robotic arms have been widely employed in industries or even in medical applications for the past several decades. These arms are popular because of their ability to offer an assistance force during the working time. However, they are still limited with less biocompatibility and dimensions, leading to inconvenient movement. The weight issue and bulky body are still hardly conquered even after using alloy muscles. Therefore, soft artificial muscles are used to resolve this shortcoming [1]. They perform a similar movement and propose a flexible property compared with robot arms used nowadays. Polymer materials are rapidly being used due to their flexible actions. They are used not only as artificial muscles but as bio-scaffolds in tissue engineering.

Indeed, numerous characteristics, such as softness, lightweight, capability of drug loading, and biocompatibility, make the polymeric materials a good candidate for medical application. Indeed, soft actuators performing variant responses are fabricated using various kinds of polymeric materials [2-4]. Polymeric materials are employed for soft actuators due to their multiple dimensions for actuation. High mechanical properties of polymeric muscles could induce the primary action of a human body, including the bending behavior, lifting stretching, and twisting movements. For instance, Li et al. [5] revealed a poly(vinyl alcohol) film grafted with a photomechanical response. Kim et al. [6] employed an electric field–responsive film made with a commercialized Nafion film. Although many approaches applied the
in the fabrication of actuators have been revealed in recent decades, most of them are limited with biocompatibility and idealess mechanical properties. Hence, hydrogels, which are a kind of polymeric materials, have been used in the last ten years to resolve this issue. Hydrogels could provide the variant machine property due to gelatinization with different cross-linkers, resulting in a unique condition needed [7-9].

Graphene oxide (GO) is commonly employed in several applications, such as bioengineering [10]. It is regarded as a heat source to increase the temperature attributed to the excitation of electrons by near-infrared (NIR) light within a specific wavelength (808 nm). Moreover, GO could strengthen the mechanical properties. Using these characteristics, numerous researchers fabricated actuators composed of GO. Cheng et al. [3] made a thin film containing GO, which had the ability of NIR light-stimulated control. The remote control stimulated by light also simplifies the action of actuators, and hence wireless equipment has become the trend in this century. Ultraviolet or NIR light helps to in making hydrogels with different patterns, including deswelling or structural change [7]. Without contact between the base material and the wire, the remote device would simplify the experiments. The di(ethylene glycol) methyl ether methacrylate (MEO2MA) hydrogel is a temperature-responsive scaffold that has demonstrated reversible hydrophilic/hydrophobic properties at lower critical solution temperature (LCST). This temperature is close to the surface temperature of the human skin. Hence, the MEO2MA hydrogels are also used as the bio-scaffold material owing to their adhesion onto the skin.

This study reported the fabrication and characterization of the soft GO/MEO2MA hydrogel actuator. Under NIR irradiation, the atoms in GO were excited to generate heat, which was then transferred to the MEO2MA hydrogel. Subsequently, temperature-responsive MEO2MA hydrogel exhibited the deswelling behavior resulting in bending response as shown in figure 1. When the NIR light was removed, the MEO2MA hydrogel turned to the original state. Repeating the irradiation steps, the GO/MEO2MA hydrogel attained a reversible actuating behavior.

![Figure 1](image-url)

**Figure 1.** Scheme of preparation of the GO/MEO2MA hydrogel samples and actuating operation via the irradiation with near-infrared light.

2. Materials and Methods
2.1 Materials
The monomers of di(ethylene glycol) methyl ether methacrylate (MEO\textsubscript{2}MA, MW = 188.22, 95%), cross-linker, di(ethylene glycol) dimethacrylate (DEGMA, 95%), activator, N,N,N',N'-tetramethylethylenediamine (TEMED, 99%), and GO (powder, 15–20 sheets, 4%–10% edge oxidized) were purchased from Sigma–Aldrich (the USA). The activated alumina, which was used to purify the monomer of cross-linker and initiator, ammonium persulfate (APS) was provided by Wako (Japan). The last but not the least, the solvents for all materials were ethanol (99.5%) and distilled water, which were purified by Millipore (Rephile Bioscience, Ltd).

2.2 Fabrication of GO/MEO\textsubscript{2}MA hydrogel
The MEO\textsubscript{2}MA composite hydrogels comprised the MEO\textsubscript{2}MA monomer, and GO was fabricated by the gelatinization method. Specific amounts of DEGDMA cross-linker (i.e., 10, 20, and 30 mg) were added to each MEO\textsubscript{2}MA solution (3.26 g). Around 100 mg APS was dissolved in 0.5 mL of water/ethanol mixture (V\textsubscript{water} : V\textsubscript{ethanol} : 1:1). The APS solution was then poured into the MEO\textsubscript{2}MA solution as an initiator and placed in a refrigerator at 4°C. After freezing for 2 h, 0.02 mL of TEMED was added to the MEO\textsubscript{2}MA solution to activate the reaction in all chemicals. During the reaction process, the mixture of MEO\textsubscript{2}MA solution was filled into a customized die (1 × 5 × 0.2 cm\textsuperscript{3}) and kept at 4°C for 3 h. Finally, 5 mg GO was cast onto the MEO\textsubscript{2}MA hydrogels.

2.3 A preliminary study of GO/MEO\textsubscript{2}MA hydrogel properties
The temperature-responsive GO/MEO\textsubscript{2}MA hydrogel exhibited various properties. According to the proportion of the cross-linker, each quantity would contribute different amounts of free radicals. Besides, these free radicals could control the properties of the hydrogel, such as transmittance, hydrophilicity and hydrophobicity, load behavior, and degree of bending movement. Therefore, numerous tests were carried out for analyzing the properties of the temperature-responsive MEO\textsubscript{2}MA hydrogel.

2.4 Characteristics of swelling and deswelling on MEO\textsubscript{2}MA hydrogels
The swelling/deswelling behavior is an essential property of MEO\textsubscript{2}MA hydrogels associated with bending force and actuation. \(Q\) relative to the temperature was measured to observe the influence, which was caused by different amounts of the cross-linker in each MEO\textsubscript{2}MA hydrogel. In brief, various MEO\textsubscript{2}MA samples (\(n = 3\)) were cut into circular segments with a diameter of 0.5 cm. The swelling ratio and deswelling ratio were exhibited at a specific temperature and interval time. The \(Q\) of each sample was measured with an electronic balance (BSA224S-CW; Sartorius, Gottingen, Germany) calculated using Eq.(1).

\[
Q = \frac{(m_t - m_0)}{m_0}
\]

where \(m_t\) is the mass of swollen hydrogel at time \(t\) and \(m_0\) is the weight of the dried hydrogel.

2.5 Determination of LCST of GO/MEO\textsubscript{2}MA hydrogel and tensile test
To determine the temperature interval for the LCST of MEO\textsubscript{2}MA hydrogels, the ultraviolet-visible spectroscopy (V-770, JASCO, Tokyo, Japan) was used and operated at 500 nm with a scan rate of 2°C min\textsuperscript{-1}. However, the one-way tensile test was used to measure the mechanical properties of the MEO\textsubscript{2}MA hydrogel. The samples were fabricated in a standard specification tensile scale based on ASTM D638. All samples were tested using a tensile test machine (EX-SX, Shimadzu, Japan) under a loading rate of 100 mm · min\textsuperscript{-1}.

2.6 Measurement of actuating responses of GO/MEO\textsubscript{2}MA hydrogel
About 10 mg GO/MEO\textsubscript{2}MA hydrogel was prepared as shown in figure 2. The NIR light machine (MDL-III-808 nm, Changchun New Industries Optoelectronics Technology Co., Ltd., Changchun, China) was used to stimulate GO within the specific wavelength (808 nm) and increase the temperature. The
distance between the output light source and the GO/MEO\textsubscript{2}MA hydrogel was 5 cm. The power was set at 450 mW, and the current was 0.91 mA. The reversible test was similarly conducted by switching on/off the NIR light system at specific time intervals.

Figure 2. (a) Experimental setting for measuring actuating responses; and (b) photo images of the fabricated GO/MEO\textsubscript{2}MA hydrogel film.

3. Results and Discussion

3.1 Transmittance and mechanical properties of MEO\textsubscript{2}MA hydrogels

The results indicated that the LCST of each sample ranged from 24°C to 28°C (figure 3). Once the GO/MEO\textsubscript{2}MA hydrogel was heated, it changed from a colorless state to a nontranslucent state. The temperature interval increased as the amount of added cross-linker was increased. As shown in figure 4, the GO/MEO\textsubscript{2}MA hydrogels exhibited remarkable mechanical properties evaluated using the tensile test. Especially, a less amount of the cross-linker resulted in the higher displacement of the GO/MEO\textsubscript{2}MA hydrogel but less force for the load. For instance, the GO/MEO\textsubscript{2}MA hydrogel gelatinized using 10 mg of cross-linker showed the softest property, leading to the most flexible hydrogel compared with other samples. Three different cross-linked ratios of samples were characterized to study the machinal property by using the tensile machine. As shown in figure 4, the lower the added amount of cross-linker, the higher the displacement performed. The samples of 10, 20 and 30 mg demonstrated the displacements of approx. 75, 65 and 55 mm, respectively. This finding can be attributed to various amounts of the cross-linker reacting during the gelatinization process. The more cross-linker is used, the more free radicals are generated, resulting in a closer association with MEO\textsubscript{2}MA molecules, and, hence, higher LCST temperature interval and better mechanical properties.

Figure 3. The transmittance of MEO\textsubscript{2}MA with different cross-linker concentrations.

Figure 4. Tensile test of MEO\textsubscript{2}MA with different cross-linker concentrations.

3.2 Swelling and deswelling behavior patterns of MEO\textsubscript{2}MA hydrogels
The GO/MEO$_2$MA hydrogels exhibited different swelling and deswelling behaviors, as shown in figures 5 and 6, respectively. As the temperature increased beyond the LCST, the GO/MEO$_2$MA hydrogels began to shrink and desorb the water. With different ratios of the cross-linker used in the gelatinization process, the water was released with different slopes. For example, 10 mg of cross-linker used in the GO/MEO$_2$MA hydrogel demonstrated lower LCST, cliffy swelling/deswelling slope, and higher water content. The $Q_t$ as the swelling ratio in the swelling test was about 11.5, which surpassed that of the other samples. Overall, the findings revealed that the GO/MEO$_2$MA hydrogel fabricated using 10 mg of cross-linker could rapidly and reversibly react within the changing temperature interval, and hence regarded as a good candidate for actuator application. Based on all conditions mentioned in Section 3.1, the GO/MEO$_2$MA hydrogel gelatinized using 10 mg of cross-linker was used to demonstrate the reversible bending behavior, as shown in figure 7. The results showed that the GO/MEO$_2$MA hydrogel shrank and then recovered to the original state if the NIR light system was switched off. The recorded weight in every 5 min was used to confirm that the swelling and deswelling behaviors did not alter during the repeated operation. Hence, the GO/MEO$_2$MA hydrogel extend and shrink, acting as an actuator.

Figure 5. Swelling ratios of three different cross-linker concentrations of MEO$_2$MA hydrogels.

Figure 6. Deswelling ratios of three different cross-linker concentrations of MEO$_2$MA hydrogels.

Figure 7. Reversible deformation of GO/MEO$_2$MA hydrogel actuated in six cycles.
3.3 Bending and reversibility test of MEO2MA hydrogels
In the bending and reversibility tests, the MEO2MA and GO/MEO2MA hydrogels were compared and separately irradiated with NIR light. As shown in figure 8a and 8b, the shape of the hydrogel without GO was not altered despite irradiation for a long time. On the contrary, the GO/ MEO2MA hydrogel exhibited an apparent bending movement on NIR irradiation after a few minutes, as shown in figure 8c and 8d. On NIR light irradiation, the left side of the MEO2MA hydrogel coated with GO started to shrink and release the water, but no water release occurred on the right side. This resulted in the bending movement. It could be attributed to the increase in temperature caused by the irradiated GO. Once the temperature increased and reached the critical point of LCST, the GO/MEO2MA hydrogel changed from the swelling state to a deswelling state, releasing the water. Therefore, the bending behavior of the GO/MEO2MA hydrogel was believed to be controlled by NIR light. These findings might help in designing the shape of the hydrogel [10-12], which might be applied to the body for assisting in human behaviors. Hence, the GO/MEO2MA hydrogel has excellent potential in soft artificial muscles.

![Figure 8. Bending behavior of the GO/MEO2MA hydrogel stimulated with NIR light. (a) Sample without GO and (b) sample irradiated with NIR, which did not alter the shape. (c) Sample without NIR light irradiation and (d) sample irradiated with NIR light. The current was set as 0.91 mA, and the applied power was 450 mW.](image)

4. Conclusions
In summary, the soft GO/MEO2MA hydrogel actuator was fabricated and characterized, demonstrating the appropriate mechanical and temperature-responsive properties. The GO/MEO2MA hydrogel preformed reversible actuating responses under a repeated switch-on/off NIR irradiation. The GO/MEO2MA actuator was composited of the MEO2MA hydrogel and the thin coated GO layer. The GO layer could generate the heat via the NIR irradiation to operate the actuating responses. While the generated temperature was higher than the LCST of the MEO2MA hydrogels, the deswelling behavior occurred. The LCST of MEO2MA hydrogel was characterized in the range between 24°C and 28°C. The DEGMA cross-linker can affect the swelling, deswelling and mechanical properties of fabricated hydrogel actuators. For example, the GO/MEO2MA hydrogel cross-linked with 10 mg DEGMA demonstrated approximately 12-fold of Qv in the swelling behavior. Overall, the GO/MEO2MA hydrogels might be considered a high potential candidate as an actuator and could be applied for the application [13] of soft artificial muscles.

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