

Conductive double-network hydrogel composed of sodium alginate, polyacrylamide, and reduced graphene oxide

Byongyeon Kim[‡], Junggeon Park[‡], and Jae Young Lee[†]

School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Korea

(Received 9 July 2022 • Revised 28 September 2022 • Accepted 5 October 2022)

Abstract—Conductive hydrogels have garnered considerable attention as novel materials for biomedical devices and tissue engineering because they exhibit electroactivity and tissue-like softness. Various composites and manufacturing techniques have been developed in this regard. However, conductive hydrogels often exhibit poor mechanical properties (e.g., low toughness), which impedes their biomedical application. In this study, we fabricated double network (DN) hydrogels composed of sodium alginate (SA), polyacrylamide (PAAm), and graphene oxide (GO) to promote elasticity, toughness, and mechanical strength. Subsequently, we reduced the composite hydrogels to improve electrical conductivity by converting GO to more conductive reduced graphene oxide (rGO). The electrical, electrochemical, and mechanical properties of the produced hydrogels, r(GO/SA/PAAm), were characterized. Particularly, crosslinking density and reducing time were varied to obtain optimal conditions. The produced r(GO/SA/PAAm) demonstrated excellent electrical conductivity, mechanical strength, and toughness compared to homopolymers and unreduced DN hydrogels. We demonstrated that conductive DN hydrogels are suitable strain sensors. Electrically conductive and mechanically strong hydrogels will be beneficial in various biomedical applications, such as tissue engineering scaffolds and bioelectrodes.

Keywords: Conductive, Hydrogel, Double Network, Graphene, Strain Sensor

INTRODUCTION

Hydrogels are three-dimensional networks composed of hydrophilic polymers [1,2] that are excellent biomaterials owing to their soft and hydrated nature. In addition, to fabricate multifunctional hydrogels, other properties such as electrical conductivity and biological activity have been introduced [3,4]. Recently, conductive hydrogels with appropriate electrical conductivity and tissue-like softness have been highlighted as new multifunctional biomaterials [5,6]. These unique properties have made conductive hydrogels useful in wearable sensors, soft electronics, and tissue-engineering scaffolds.

Conductive components are composed of hydrophilic polymers to formulate conductive hydrogels. Various materials can be employed as conductive components, including carbon-based materials (e.g., carbon nanotubes or graphene derivatives), metallic nanoparticles, and conductive polymers (e.g., polyaniline and polypyrrole) [7]. Among them, carbon-based nanomaterials offer multiple advantages, such as low price, stability, conductivity, and a high surface-to-volume ratio [8]. In particular, graphene offers high conductivity, high thermal and chemical stability, flexibility, and large surface area to mass ratio [9]. Graphene oxide (GO) is widely used in biomedical applications owing to its availability and dispersity in aqueous solutions. GO is typically obtained from the oxidative exfoliation of graphite. GO possesses oxygen-containing functional

groups, such as carboxyl, hydroxyl, and epoxy groups in its basal planes and edges [10,11]. GO is hydrophilic and miscible with hydrophilic polymers [10,12,13]. However, owing to its defects in sp^2 carbons, GO has poor electrical properties. Hence, it is commonly reduced to rGO to improve its electrical properties [14]. Restoration of sp^2 carbons improves the electrical conductivity of rGO [10,15]. However, the hydrophobicity of rGO limits its use in aqueous solutions and formulations with hydrophilic substances.

To produce conductive hydrogels, these issues of conductivity and water dispersion of GO and rGO, respectively, must be addressed. Our previous study prepared rGO-incorporated hydrogels via sequential polymerization and chemical reduction [16]. For example, GO/PAAm hydrogels were prepared to form composite hydrogels. Subsequently, mild chemical reduction was employed to convert the internal GO to rGO while preventing the aggregation of rGO within the composite hydrogels. The resultant hydrogels displayed excellent electrical conductivity and softness, which were compatible with myoblast culture. However, conductive hydrogels still exhibit poor mechanical properties, such as brittleness. The reliability, toughness, and flexibility of conductive hydrogels are required for their application in dynamic environments.

Therefore, this study aimed to improve the mechanical properties of rGO-incorporated conductive hydrogels by creating a double network (DN). DN refers to a polymeric network in which two polymers are not covalently bonded to each other but interpenetrate each other as separate networks [17,18]. DN hydrogels commonly show significantly improved mechanical properties compared to single network polymer hydrogels [19], such as excellent mechanical strength and fracture toughness based on an internal fracture mechanism. Generally, DN hydrogels consist of a brittle first net-

[†]To whom correspondence should be addressed.

E-mail: jaeyounglee@gist.ac.kr

[‡]These authors contributed equally.

Copyright by The Korean Institute of Chemical Engineers.

work and ductile second network. When deformation stress is applied to the DN hydrogel, the second network structure maintains its structure, whereas the first brittle network breaks down to dissipate the stress. The increased toughness of DN hydrogels is attributed to the facilitated dispersion of a large amount of energy when the first network protects the second network [20].

Specifically, we produced GO-containing DN hydrogels using PAAm, SA, and GO, in which SA and PAAm served as the first and second networks, respectively. The composite hydrogels were further reduced by mild chemical reduction to enhance their electrical properties. SA is the sodium salt of alginate which is a natural linear polysaccharide copolymer obtained from brown algae that is widely used in biomedical applications because of its biocompatibility, low cost, and low toxicity [21]. Importantly, SA readily forms an ionic gel in the presence of divalent ions such as calcium and barium ions [22]. These DN hydrogels contain a physically cross-linked alginate (first) network that displays recoverable and tough characteristics with reversible non-covalent bonds, and a chemically crosslinked PAAm (second) network that displays mechanical strength [20,23]. We prepared various r(GO/SA/PAAm) DN hydrogels and carefully characterized their mechanical characteristics in comparison with single-network hydrogels. Both electrical and toughness characteristics of the hydrogel are especially important for mechanical sensors. For example, Jiang et al. prepared poly(vinyl alcohol)/sodium alginate hydrogels by freezing/thawing and subsequent immersion in the saturated NaCl solution [24]. The hydrogels exhibited excellent mechanical strength and toughness and electrical conductivity. Hence, we tested the rGO-based double-network hydrogel as a potential strain sensor.

MATERIALS AND METHODS

1. Materials

Acrylamide (AAm), N,N'-methylenebis(acrylamide) (MBA), ammonium persulfate (APS), alginic acid sodium salt from brown algae, calcium chloride, and L-ascorbic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Aqueous GO solution (6 mg/mL) was purchased from Graphene Supermarket, Inc. (Calverton, NY, USA).

2. Fabrication of Conductive DN r(GO/SA/PAAm) Hydrogels

The GO aqueous solution (4 mL) was first transferred to a 20 mL glass vial. AAm, SA, MBA, and deionized (DI) water were added to the vial containing the GO solution. The solution contained final concentrations of 80 mg/mL AAm, 10 mg/mL SA, 3 mg/mL GO, and various concentrations of MBA (AAm:MBA ratios were 29, 59, or 89). The individual solutions were completely dissolved by stirring at 4 °C. APS was subsequently added to each mixture and completely dissolved by stirring at 4 °C. Each mixture solution was transferred into two parallel glass plates with a 2 mm gap and incubated at 60 °C for 4 h to polymerize PAAm. The hydrogel was incubated in a 4 wt% CaCl₂ aqueous solution for 24 h for ionic crosslinking and washed with DI water. Finally, the GO/SA/PAAm hydrogel was chemically reduced by incubation in an aqueous L-ascorbic acid solution (4 mg/mL) at 37 °C for various time periods. The prepared r(GO/SA/PAAm) hydrogel was washed with DI water.

3. Raman Spectroscopy

The Raman spectra of each hydrogel were obtained using a Raman spectroscope (LabRAM HR Evolution, Horiba, Ltd., Japan) with a 532 nm laser. The fabricated hydrogels were punched to produce 1.2 cm diameter discs. The reduction of GO was examined by comparing the intensity ratio of the peaks of the D band (1,350 cm⁻¹) and G band (1,580 cm⁻¹) in the Raman spectra [25-28].

4. Electrical and Electrochemical Properties

The electrical conductivity and electrochemical impedance spectra (EIS) of the samples were recorded. Hydrogels were punched to produce 1.2 cm diameter discs. For the conductivity measurements, a 4-point probe method was employed using a computer-assisted potentiostat (VersaSTAT3, Princeton Applied Research, Princeton, NJ, USA). The sheet resistance of the hydrogels was measured at a scan rate of 100 mV/s, and the conductivity was calculated using the following formula [29,30]:

$$\sigma = 1/(R_s \times t) \quad (1)$$

where σ is the conductivity, R_s is the sheet resistance and t is the hydrogel thickness. For the EIS measurements, the hydrogel disc was placed between the gold-coated glass. Impedance was measured in the range of 10⁻¹-10⁵ Hz by applying an alternative sinusoidal potential of 10 mV using a computer-assisted potentiostat.

5. Mechanical Properties

For the tensile tests, the specimens were prepared in a rectangular shape with a length of 40 mm, thickness of 2 mm, and width of 10 mm. Tensile tests for each specimen were performed using a universal testing machine (Unitest M1, TEST ONE, Republic of Korea) with a crosshead speed of 100 mm/min, a load cell of 10 kN, and an initial gauge length of 15 mm.

6. Strain Sensor Application

The electrical sensitivity was measured as a potential application of conductive DN hydrogels for strain sensors. A rectangular sample (length: 40 mm, thickness: 2 mm, and width: 10 mm) was loaded on the universal testing machine and the two ends of the sample were connected to a computer-assisted potentiostat. The sample was stretched to a strain of 300% and returned to initial state (strain of 0%), and the resistance of the sample was measured during the elongation. The gauge factor (GF) was calculated using the following formula [31,32]:

$$GF = \frac{\Delta R/R}{\varepsilon} \quad (2)$$

where R is the resistance, and ε is the applied strain.

7. Statistical Assessment

All experiments were performed in triplicate, unless otherwise noted. Statistical significance was examined using one-way ANOVA with Tukey's post-hoc comparison of the means using Origin Pro 9.3 software. Differences were considered statistically significant at $P < 0.05$.

RESULTS AND DISCUSSION

1. Fabrication of r(GO/SA/PAAm) Hydrogels

Conductive DN hydrogels consisting of alginate, PAAm, and rGO were fabricated using i) composite preparation, ii) chemical

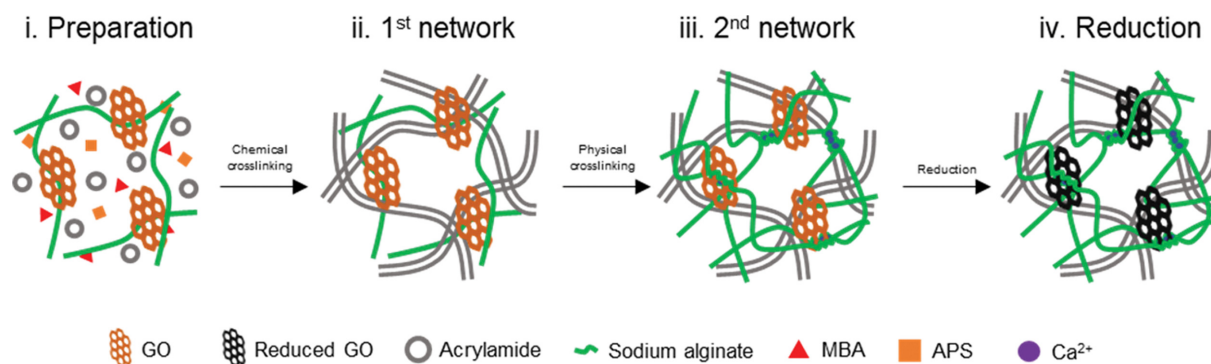


Fig. 1. Schematic illustration of synthesis of the r(GO/SA/PAAm) double network hydrogel.

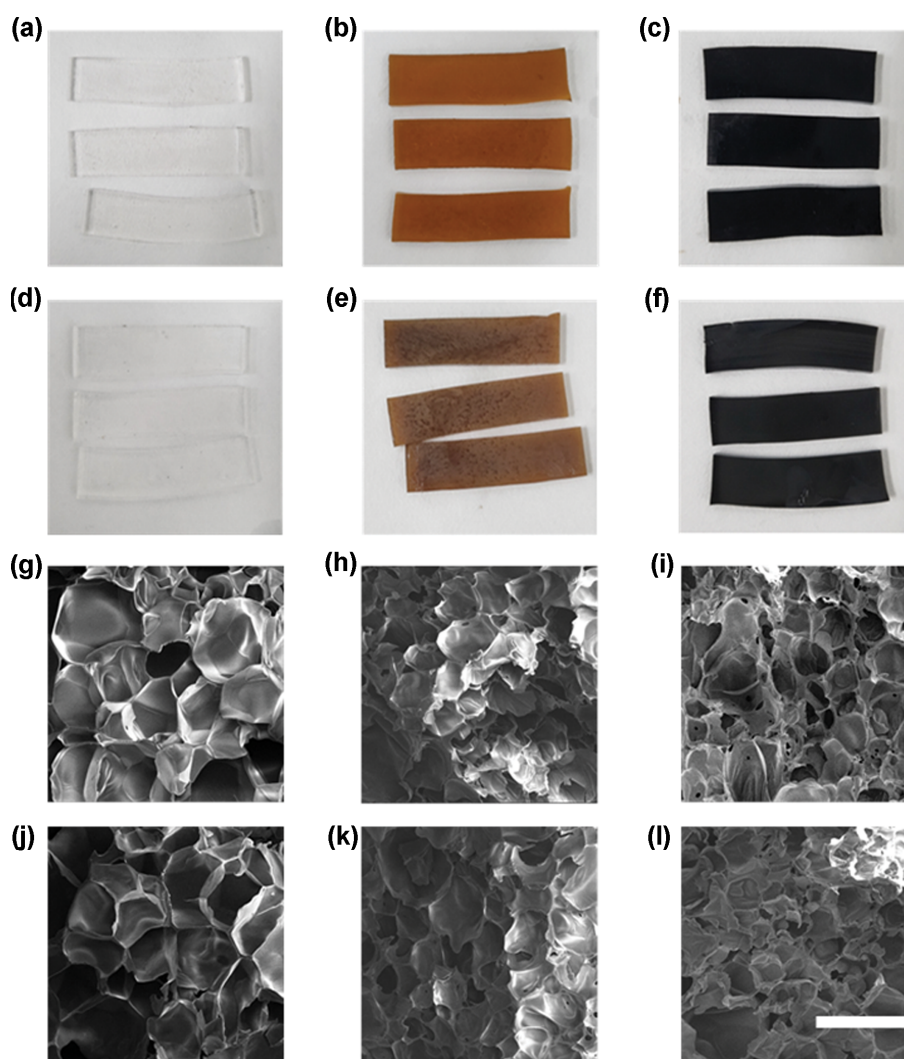


Fig. 2. Photographs (a)–(f) and scanning electron micrographs (g)–(l) of the hydrogels. (a), (g) PAAm; (b), (h) GO/PAAm; (c), (i) r(GO/PAAm); (d), (j) SA/PAAm; (e), (k) GO/SA/PAAm; (f), (l) r(GO/SA/PAAm). The hydrogels were prepared at a ratio of monomer: crosslinker to 29:1. (c) and (f) samples were prepared by reduction for 24 h from (b) and (e), respectively. Scale bar: 100 μm .

polymerization of PAAm, iii) ionic crosslinking, and iv) chemical reduction (Fig. 1). The PAAm network was formed by thermal polymerization at 60 °C for 4 h. Ionic crosslinking involved immersion in 4 wt% CaCl_2 solution for 24 h. Mild chemical reduction was

employed to convert GO into conductive rGO within the polymeric matrices, without severe aggregation of rGO. Various controls were also prepared, including PAAm, SA/PAAm, GO/PAAm (unreduced), r(GO/PAAm) (reduced and alginate-free), and GO/

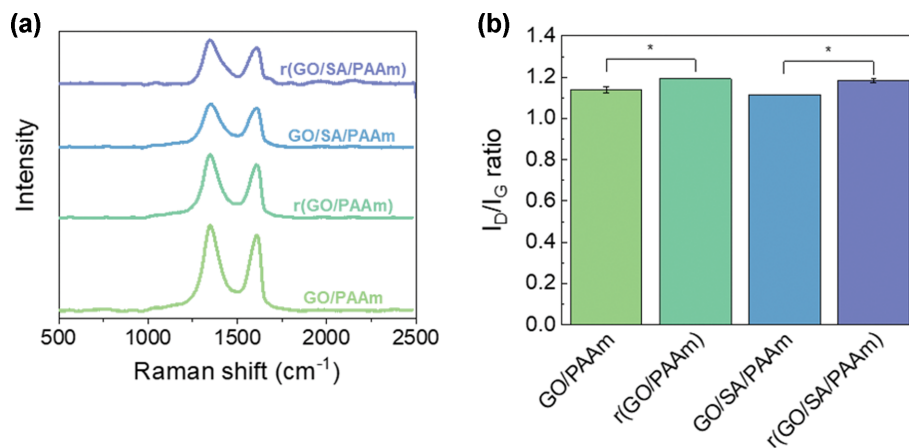


Fig. 3. (a) Raman spectra of hydrogels - PAAm, GO/PAAm, r(GO/PAAm), SA/PAAm, GO/SA/PAAm, and r(GO/SA/PAAm). (b) Plot of the ratio (I_D/I_G) of the intensities of the D-band and G-band in Raman spectra. The hydrogels were prepared at ratio of monomer: crosslinker to 29:1. r(GO/PAAm) and r(GO/SA/PAAm) were prepared by the reduction for 24 h from GO/PAAm and GO/SA/PAAm, respectively.

SA/PAAm (unreduced), to examine the effects of DN on the material properties.

GO-free hydrogels (i.e., PAAm and SA/PAAm) are transparent; however, GO-containing hydrogels are brown but turn black after mild chemical reduction (Fig. 2). The brown color and its change to black indicate GO incorporation and reduction, respectively. Because of the considerable defects in sp^2 carbons, GO is typically brown. Restoration of the conjugated sp^2 orbitals in GO results in black color [15]. Fig. 2 shows scanning electron microscope images of various hydrogel groups. All hydrogel groups show porous structure. No aggregate of graphene derivatives was visible from scanning electron micrographs of GO incorporated hydrogels. In particular, the well-dispersed rGO network in the hydrogel matrix can contribute to its high electrical properties [16].

2. Raman Spectroscopy

Raman spectroscopy was performed to examine the reduction of GO components in r(GO/PAAm) and r(GO/SA/PAAm) (Fig. 3). The peak intensity ratio of the D band to G band (I_D/I_G) was used as an indicator of the degree of reduction. The I_D/I_G ratios increased at low-defect regions because elastic scattering occurs more at high-defect regions [26,28]. Accordingly, GO reduction resulted in an increase in the I_D/I_G ratio. The I_D/I_G ratios of GO/PAAm and GO/PAAm/alginate increased from 1.140 ± 0.015 to 1.193 ± 0.001 and from 1.113 ± 0.001 to 1.185 ± 0.011 , respectively, after chemical reduction. The results indicated that the incubation of GO-containing hydrogels (GO/PAAm and GO/SA/PAAm) in ascorbic acid solution led to a distinct reduction in the GO components. No significant differences in the I_D/I_G ratios of r(GO/PAAm) and r(GO/SA/PAAm) were observed, suggesting that the double network structure did not interfere with the reduction reaction (Fig. 3(b)).

3. Electrical and Electrochemical Properties of Conductive DN Hydrogels

The electrical and electrochemical properties of various hydrogel samples prepared with a monomer: crosslinker ratio of 29:1 were investigated (Fig. 4). Interestingly, incorporating alginate into PAAm increased the electrical conductivity, which might be due

to the increase in the ionic polymer content in the composites and/or the presence of calcium ions in the composites (Fig. 4(b)). GO-containing hydrogels (GO/PAAm and GO/SA/PAAm) had higher conductivity than GO-free hydrogels (PAAm and SA/PAAm). The conductivity of the GO-containing hydrogels significantly increased owing to their chemical reduction. Therefore, the DN formation using alginate, incorporation of GO, and subsequent chemical reduction synergistically promoted the electrical properties of the composite hydrogels. Consequently, the conductive DN hydrogel (i.e., r(GO/SA/PAAm)) had the highest electrical conductivity. For example, GO/SA/PAAm DN hydrogels displayed higher conductivity ($6.2 \times 10^{-4} \pm 0.3 \times 10^{-4}$ S/cm) than SA/PAAm ($3.6 \times 10^{-4} \pm 0.1 \times 10^{-4}$ S/cm), and the conductivity was further increased to $2.0 \times 10^{-3} \pm 0.4 \times 10^{-4}$ S/cm by reduction (r(GO/SA/PAAm)). The increased conductivity of the reduced composites can be attributed to the formation of a well-dispersed conductive rGO network. The EIS analyses of these samples demonstrated trends similar to those of conductivity (Fig. 4(c)). PAAm showed a higher impedance in the low-frequency region than the others. GO incorporation and reduction significantly lowered the impedance. However, the effect of alginate incorporation on impedance was not significant, and the results differed from those for electrical conductivity (Fig. 4(d)).

We also investigated the effects of crosslinking density and reduction time on the electrical and electrochemical properties of r(GO/SA/PAAm) (Fig. 5). The crosslinking density was varied by different monomer: crosslinker (AAM:MBA) ratios. The reduction times were 6 h, 12 h, and 24 h. Crosslinking density did not significantly affect the conductivity of the hydrogels (Fig. 5(a)). Importantly, the conductivity continuously increased as the reduction time increased regardless of the crosslinking density. The conductivity of r(GO/SA/PAAm) after reducing 24 h was 3- to 5-fold higher than that of the unreduced sample (GO/SA/PAAm). Meanwhile, both crosslinking density and reduction time influenced the EIS results (Fig. 5(b), (c)). A lower crosslinking density and longer reduction time resulted in lower impedance. For example, the impedance values at 1 Hz gradually decreased as the crosslinking density decreased

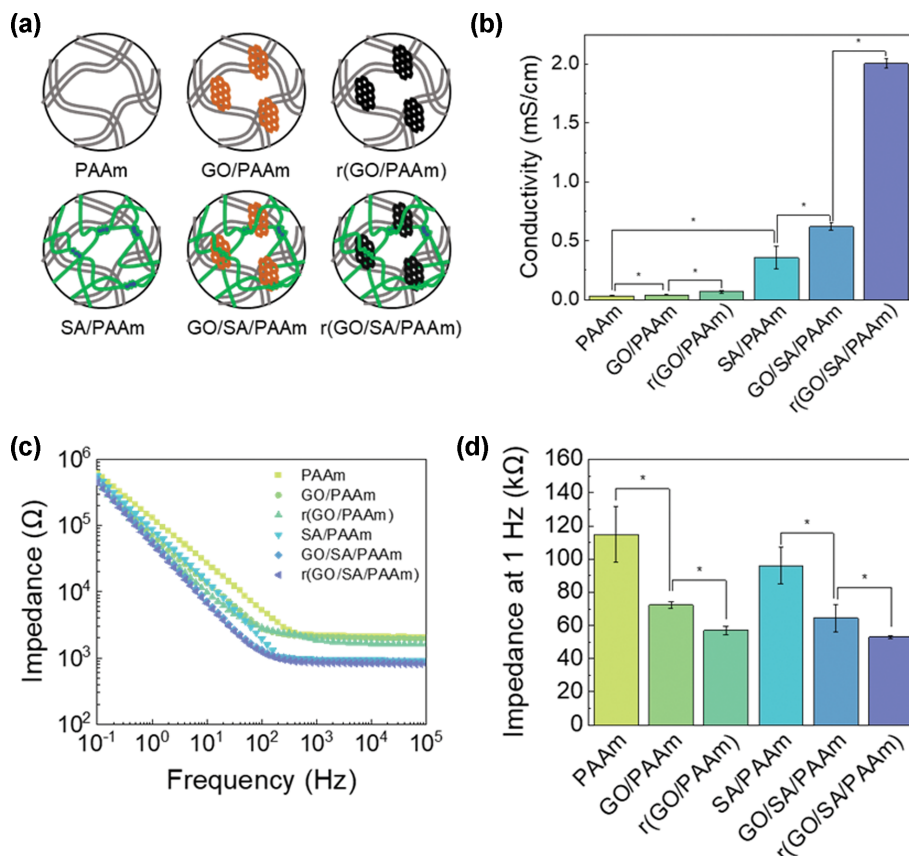


Fig. 4. Electrical and electrochemical properties of various hydrogels - PAAm, GO/PAAm, r(GO/PAAm), SA/PAAm, GO/SA/PAAm, and r(GO/SA/PAAm). (a) Schematic illustration of each hydrogel group. (b) Conductivity and (c) Bode plots of EIS of various hydrogels. (d) Impedance at 1 Hz of the hydrogels. The hydrogels were prepared at a ratio of monomer : crosslinker as 29 : 1. r(GO/PAAm) and r(GO/SA/PAAm) were prepared by the reduction for 24 h from GO/PAAm and GO/SA/PAAm, respectively.

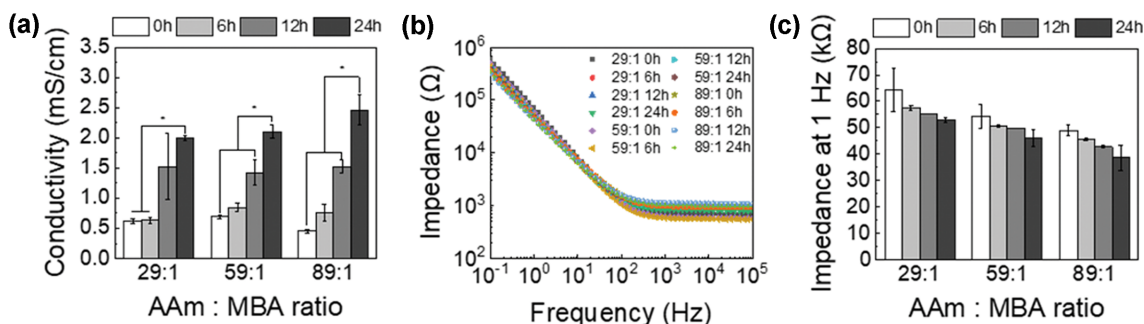


Fig. 5. Electrical and electrochemical properties of r(GO/SA/PAAm) hydrogels prepared with various crosslinking densities and reduction times. (a) Electrical conductivity. (b) Bode plots of EIS spectra. (c) Impedance at 1 Hz.

and the reduction time increased. Highly crosslinked hydrogels may prohibit ionic movement within hydrogel matrices, resulting in an increase in impedance. A high reduction degree of GO (longer reduction time) implies a high electrical conductivity, resulting in a decrease in impedance.

4. Mechanical Properties of Conductive DN Hydrogels

In this study, we aimed to improve the mechanical properties, such as toughness, of rGO-containing conductive hydrogels by creating a DN. To this end, the tensile strength, fracture strain, fracture energy, and Young's modulus of the individual hydrogel samples

were analyzed and compared (Fig. 6). Note that these samples were prepared with a 29 : 1 molar ratio of AAm and MBA and a 24 h reduction time (for the reduced samples, r(GO/PAAm) and r(GO/SA/PAAm)). The tensile strength significantly increased with the incorporation of GO and was not affected by chemical reduction (Fig. 6(b)). Interestingly, the contribution of SA to tensile strength was minimal in the presence of GO or rGO in the gel. In contrast, the fracture strain was substantially improved by SA treatment (Fig. 6(c)). Neither GO incorporation nor chemical reduction affected fracture strain. As shown in Fig. 6(d), both SA and GO compo-

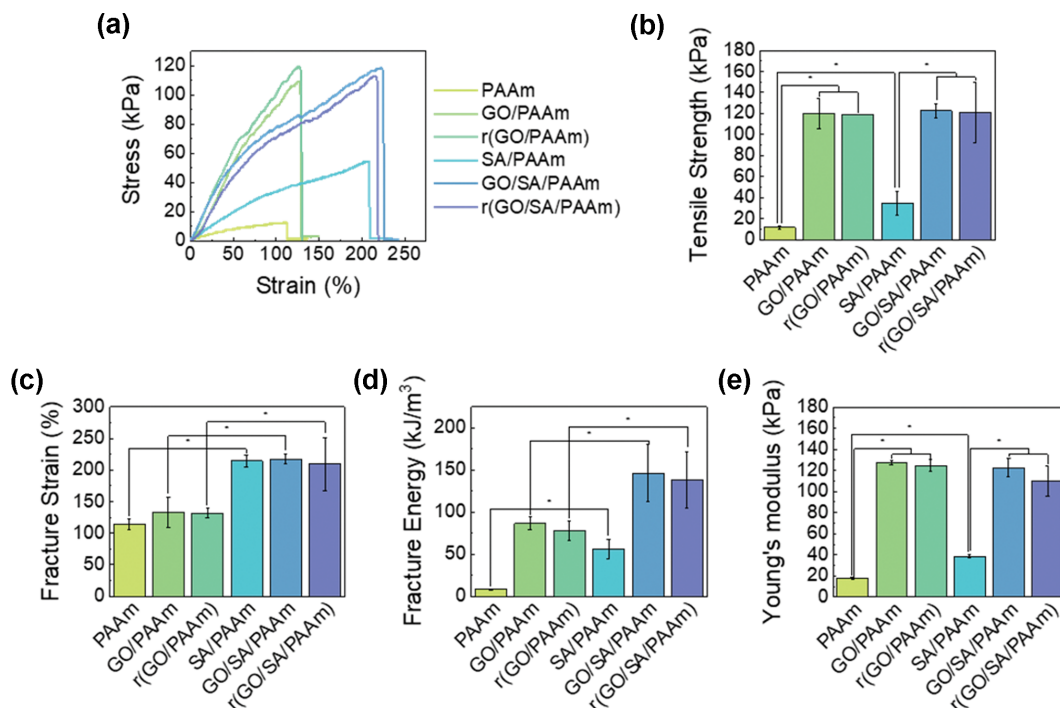


Fig. 6. Mechanical properties of various hydrogel - (a) Strain-stress curves. (b) Tensile strength. (c) Fracture strain. (d) Fracture energy. (e) Young's modulus. The hydrogels were prepared at a ratio of monomer : crosslinker of 29 : 1. r(GO/PAAm) and r(GO/SA/PAAm) were prepared by the reduction for 24 h from GO/PAAm and GO/SA/PAAm, respectively.

nents in the composites significantly increased the fracture energy. Chemical reduction did not influence the fracture energy. Young's moduli of the samples exhibited trends similar to those of the tensile strength (Fig. 6(e)). Combined, the SA network mainly contributed to the enhancement of ductility, while GO enhanced the strength of the network and provided additional physical bonds with the matrices. SA forms ionic crosslinks that can serve as the first network to dissipate external stress [33]. GO strongly interacts with various macromolecules via hydrogen bonding, ionic interaction, and van der Waals interaction, which can increase the strength of the composites [34,35]. Recent studies have demonstrated that crosslinked GO networks can be formed inside alginate hydrogels with multivalent ions such as Ca^{2+} [36-38] as GO also has many oxygen-containing functional groups that can interact with each other through Ca ions [39]. No significant differences in tensile strength and Young's modulus were found between the single-network hydrogel group (PAAm, GO/PAAm, r(GO/PAAm)) and the DN hydrogel group (SA/PAAm, GO/SA/PAAm, r(GO/SA/PAAm)). However, the toughness (e.g., fracture energy) was 1.5- to 2-times higher for the DN hydrogel group than the single network hydrogel group. Particularly, r(GO/SA/PAAm) showed a 1.6-fold higher fracture strain and 1.8-fold higher fracture energy than r(GO/PAAm), while demonstrating a similar tensile strength and stiffness (Young's modulus). When the DN hydrogel was deformed, the weak physical bonds were sacrificed first, dissipating the energy, and improving the toughness of the hydrogel. Therefore, we could greatly improve the mechanical properties of rGO-based conductive hydrogels by employing DN with alginate, which would be beneficial for various biomedical applications.

We further investigated the effects of crosslinking density on the mechanical properties by varying the AAm:MBA ratio (Fig. 7). The mechanical properties of all the samples were improved by GO addition, regardless of the crosslinker ratio (29 : 1, 59 : 1, and 89 : 1). Additionally, chemical reduction did not change the mechanical properties of the 29 : 1 and 59 : 1 groups. In contrast, for the 89 : 1 group, chemical reduction slightly lowered the tensile strength, fracture energy, and Young's modulus. It was speculated that the DN hydrogels prepared with a low crosslinking density might not effectively prevent the aggregation of rGO components within the matrix, and/or rGO-chain interactions might be reduced. For the r(GO/SA/PAAm) hydrogel group, the hydrogel with a 59 : 1 ratio exhibited the highest fracture energy. The high fracture strain and fracture energy of the hydrogels prepared with 59 : 1 and 89 : 1 ratios were attributed to the first network of SA. The crosslinking density of the PAAm networks of the hydrogel with 59 : 1 and 89 : 1 ratios was lower and more porous compared to the hydrogel with a 29 : 1 ratio, which might have effectively sacrificed the SA network first prior to the breakage of the PAAm network under stress conditions. Moreover, the aggregation of rGO components might be prevented more effectively in the hydrogel with a 59 : 1 ratio than that with an 89 : 1 ratio. The r(GO/SA/PAAm) DN hydrogel with an AAm:MBA ratio of 59 : 1 exhibited the highest fracture energy (toughness). Based on the electrical and mechanical properties, the r(GO/SA/PAAm) DN hydrogel prepared with an AAm:MBA ratio of 59 : 1 and 24 h of reduction was determined to be optimal. It displayed $2.1 \times 10^{-3} \pm 1.1 \times 10^{-4}$ S/cm of electrical conductivity, 106 ± 16 kPa of tensile strength, $345 \pm 51\%$ of fracture strain, and 220 ± 39 kJ/m³ of fracture energy. These conductive DN hy-

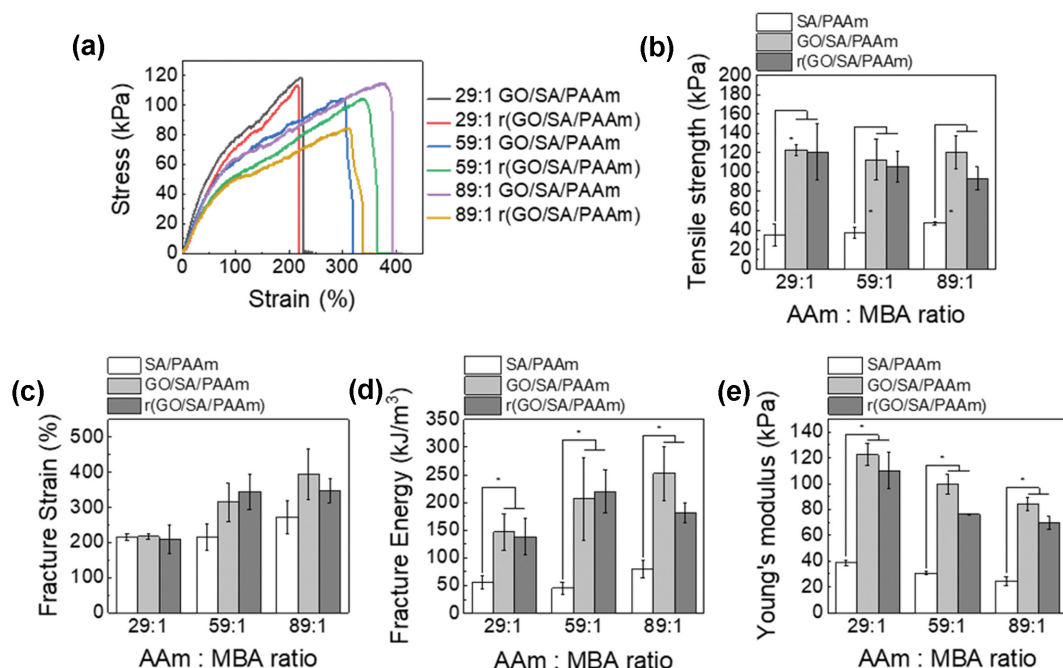


Fig. 7. Mechanical properties of various hydrogels prepared with various crosslinking densities. (a) Strain-stress curves. (b) Tensile strength. (c) Fracture strain. (d) Fracture energy. (e) Young's modulus. The reduction time is 24 h. r(GO/SA/PAAm) was prepared by the reduction for 24 h from GO/SA/PAAm.

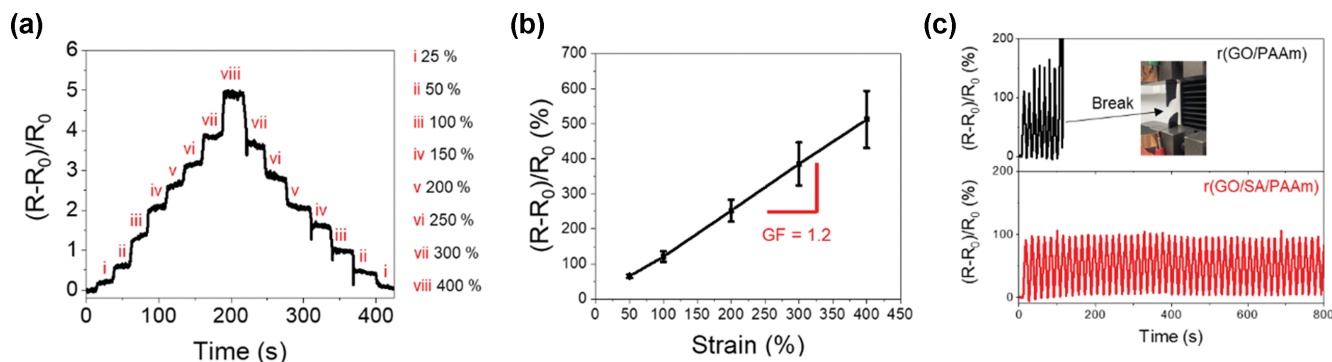


Fig. 8. Strain sensor application of the r(GO/SA/PAAm) hydrogel. (a) Resistance changes with different strains. Roman number indicates the strain. (b) Gauge factor under different strain. (c) Repeat test of resistance change value with 100% strain of strain sensor.

drogels can address the limitations of existing conductive hydrogels (e.g., poor mechanical and electrical properties) and offer great potential for various applications.

5. Strain Sensor Applications

We attempted to demonstrate the potential applications of r(GO/SA/PAAm) hydrogels as strain sensors. We measured the changes in resistance of the r(GO/SA/PAAm) at various strains (25–400%) (Fig. 8(a)). Increases in strain from the static state resulted in proportional increases in resistance likely due to increases in the distances between the dispersed rGO flakes within the matrix. dispersed in the hydrogel matrix increased. The strain was increased up to 400% and gradually decreased to 0%, while the resistance was monitored during elongation. Interestingly, resistance values were similar at the increasing strains and the decreasing strains. Results indicated that r(GO/SA/PAAm) possessed good recovery of the

electrical and mechanical properties. The corresponding gauge factor was 1.2 ± 0.18 , indicating that the r(GO/SA/PAAm) hydrogel had a good strain sensitivity (Fig. 8(b)). Liu et al. assembled κ -carrageenan/PAAm DN hydrogel strain sensor and found that the gauge factor was 0.23–0.63 at a strain of 100–1,000% [31]. Li et al. reported that agar/AAC-Fe³⁺ DN hydrogel had a gauge factor of 0.46–0.83 at a strain of 100–1,000% [32]. Compared with other hydrogel-based strain sensors, our r(GO/SA/PAAm) hydrogel exhibited a relatively high gauge factor, indicating that the r(GO/SA/PAAm) hydrogel is useful as a strain sensor. For repeated uses of the strain sensor, appropriate tensile fatigue resistance is required. In this regard, tough DN hydrogel is beneficial owing to its general fatigue resistance. Our r(GO/SA/PAAm) could be repeatedly used as a strain sensor with 100% strain (Fig. 8(c)). Even after 50 cycles of stretching, r(GO/SA/PAAm) showed minimal changes in

resistance. In contrast, for the single network hydrogel (i.e., r(GO/PAAm)), its resistance increased with the repetition and was completely broken after 100 cycles, indicating that the structure of a single network hydrogel can be easily damaged by tensile fracture.

CONCLUSION

We fabricated conductive DN hydrogels with appropriate electrical conductivity and mechanical toughness. We prepared r(GO/SA/PAAm) by the polymerization of PAAm and alginate with GO and subsequent chemical reduction, in which rGO, SA, and PAAm served as the conductive component, first network, and second network, respectively. The prepared r(GO/SA/PAAm) hydrogel displayed good electrical conductivity ($2.1 \times 10^{-3} \pm 1.1 \times 10^{-4}$ S/cm), which was 3- to 5-fold higher than that of the unreduced GO/SA/PAAm hydrogel. Moreover, further optimization with a monomer : crosslinker ratio (59:1) and reduction time (24 h) significantly improved the mechanical properties with 105.9 ± 15.9 kPa tensile strength, $344.6 \pm 50.6\%$ failure strain, and 219.7 ± 38.9 kJ/m³ fracture energy. These properties were significantly better than those of the rGO-containing homopolymer hydrogel (i.e., r(GO/PAAm)). Finally, we demonstrated that the r(GO/SA/PAAm) hydrogels can be used as strain sensors. Our electrically conductive and mechanically tough conductive DN hydrogels have potential application in various biomedical applications, such as bioelectrodes, tissue engineering scaffolds, and biosensors.

CRedit AUTHORSHIP CONTRIBUTION STATEMENT

Byongyeon Kim: Methodology, Investigation, Data curation, Writing - original draft, Formal analysis. **Jungeon Park:** Methodology, Investigation. **Jae Young Lee:** Conceptualization, Supervision, Writing - review & editing.

CONFLICT OF INTEREST STATEMENT

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2021R1A4A3025206) and a grant from the Korea Health Technology R&D Project through the Korea Health Industry Development Institute (KHIDI), funded by the Ministry of Health & Welfare (HI14C3484).

REFERENCES

1. M. Bahram, N. Mohseni and M. Moghtader, *An introduction to hydrogels and some recent applications*, IntechOpen (2016).
2. E. M. Ahmed, *J. Adv. Res.*, **6**, 105 (2015).
3. Q. Chai, Y. Jiao and X. Yu, *Gels*, **3**, 1 (2017).
4. H. Jeong, D. Y. Lee, D. H. Yang and Y. S. Song, *Macromol. Res.*, **30**, 223 (2022).
5. K. Liu, S. Wei, L. Song, H. Liu and T. Wang, *J. Agric. Food Chem.*, **68**, 7269 (2020).
6. J. Ren, X. Wang, A. Zhang, L. Zhang, L. Zhao, Y. Li and W. Yang, *Macromol. Res.*, **28**, 1253 (2020).
7. W. Zhang, P. Feng, J. Chen, Z. Sun and B. Zhao, *Prog. Polym. Sci.*, **88**, 220 (2019).
8. R. Kour, S. Arya, S. J. Young, V. Gupta, P. Bandharia and A. Khosla, *J. Electrochem. Soc.*, **167**, 037555 (2020).
9. D. S. L. Abergel, V. Apalkov, J. Berashevich, K. Ziegler and Tapash Chakraborty, *Adv. Phys.*, **59**, 261 (2010).
10. A. Raslan, L. Saenz del Burgo, J. Ciriza and J. L. Pedraz, *Int. J. Pharm.*, **580**, 119226 (2020).
11. R. K. Singh, R. Kumar and D. P. Singh, *RSC Adv.*, **6**, 64993 (2016).
12. S. C. Ray, *Applications of graphene and graphene-oxide based nanomaterials*, William Andrew Publishing, Oxford (2015).
13. R. Yue, Y. Liu, S. Xia, S. Xu and S. Cao, *Macromol. Res.*, **30**, 477 (2022).
14. K. Raidongia, A. T. L. Tan and J. Huang, in *Carbon nanotubes and graphene* (Second Edition), K. Tanaka and S. Iijima Eds., Elsevier, Oxford (2014).
15. M. S. Kang, S. J. Jeong, S. H. Lee, B. Kim, S. W. Hong, J. H. Lee and D.-W. Han, *Biomater. Res.*, **25**, 4 (2021).
16. H. Jo, M. Sim, S. Kim, S. Yang, Y. Yoo, J.-H. Park, T. H. Yoon, M.-G. Kim and J. Y. Lee, *Acta Biomater.*, **48**, 100 (2017).
17. L. H. Sperling, *Interpenetrating polymer networks: An overview*, In D. Klemperer, L. H. Sperling and L. A. Utracki (Eds.), *Interpenetrating Polymer Networks*, American Chemical Society (1994).
18. A. Lohani, G. Singh, S. S. Bhattacharya and A. Verma, *J. Drug Deliv.*, **2014**, 1 (2014).
19. S. Naficy, S. Kawakami, S. Sadegholvaad, M. Wakisaka and G. M. Spinks, *J. Appl. Polym. Sci.*, **130**, 2504 (2013).
20. T. Nakajima and J. P. Gong, in *Encyclopedia of polymeric nanomaterials*, S. Kobayashi and K. Müllen Eds., Springer, Berlin, Heidelberg (2015).
21. J.-S. O and E.-J. Lee, *Macromol. Res.*, **29**, 383 (2021).
22. S. Damiati, *Macromol. Res.*, **28**, 1046 (2020).
23. Q. Chen, H. Chen, L. Zhu and J. Zheng, *J. Mater. Chem. B*, **3**, 3654 (2015).
24. X. Jiang, N. Xiang, H. Zhang, Y. Sun, Z. Lin and L. Hou, *Carbohydr. Polym.*, **186**, 377 (2018).
25. R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio and M. S. Dresselhaus, *Adv. Phys.*, **60**, 413 (2011).
26. M. M. Lucchese, F. Stavale, E. H. Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete and A. Jorio, *Carbon*, **48**, 1592 (2010).
27. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, **45**, 1558 (2007).
28. I. Childres, L. A. Jauregui, W. Park, H. Cao and Y. P. Chen, *New Dev. Photon Mater. Res.*, **1**, 403 (2013).
29. W. R. Runyan, *Semiconductor measurements and instrumentation*, McGraw-Hill, New York (1975).
30. M. Naftaly, S. Das, J. Gallop, K. Pan, F. Alkhalil, D. Kariyapperuma, S. Constant, C. Ramsdale and L. Hao, *Electronics*, **10**, 960 (2021).
31. S. Liu and L. Li, *ACS Appl. Mater. Interfaces*, **9**, 26429 (2017).
32. H. Li, H. Zheng, Y. J. Tan, S. B. Tor and K. Zhou, *ACS Appl. Mater. Interfaces*, **13**, 12814 (2021).

33. X. Qi, S. Simsek, B. Chen and J. Rao, *Int. J. Biol. Macromol.*, **165**, 1675 (2020).
34. S. Lee, I. S. Jeon and J. Y. Jho, *Macromol. Res.*, **30**, 295 (2022).
35. H. Shin, M.-Y. Lim, S. Kong, S. Kim, S. W. Lee, Y. Lee and J.-C. Lee, *Macromol. Res.*, **29**, 487 (2021).
36. R. Sabater i Serra, J. Molina-Mateo, C. Torregrosa-Cabanilles, A. Andrio-Balado, J. M. Meseguer Dueñas and Á. Serrano-Aroca, *Polymers*, **12**, 702 (2020).
37. Á. Serrano-Aroca, L. Iskandar and S. Deb, *Eur. Polym. J.*, **103**, 198 (2018).
38. H. Zheng, J. Yang and S. Han, *J. Appl. Polym. Sci.*, **133**, 43616 (2016).
39. S. Park, K. Lee, G. Bozoklu, W. Cai, S. T. Nguyen and R. S. Ruoff, *ACS Nano*, **2**, 572 (2008).