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Electrical Stimulated Polyvinyl Alcohol-Borax-Graphene Hydrogel for Drug Releasing and Delivery

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Abstract. Polyvinyl Alcohol hydrogel has promising applications in numerous biomedical, biomaterial, and tissue engineering. However, it has poor conductive properties, restraining its development within huge fields such as bio-signals acquisition systems, thermal stability, and drug delivery. Adding Graphene as a nanofiller will produce PVA/Borax/Graphene nanocomposite hydrogel, which is an excellent procedure to significantly improve the conductive properties of PVA. The toxicity will not affect the nanocomposite while very well-dispersed graphene will significantly improve the thermal and conductivity stability of the nanocomposite. In this study, we investigated the performance of a newly prepared conductive hydrogel gel using the freezing/thawing method.

Keywords: Polyvinyl Alcohol, Polyvinyl Acetate, PolyvinylAlcohol /Borax / Graphene, Graphite Oxide, Micro Electrical Mechanical Systems.

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Электростимулированный гидрогель (поливиниловый спирт-бура-графен) для высвобождения и доставки лекарств

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Аннотация. Гидрогель из поливинилового спирта (ПВС) применяется во многих областях биомедицины, биоматериалов и тканевой инженерии. Однако он обладает слабыми проводящими свойствами, что сдерживает его развитие в таких областях, как системы сбора биосигналов или доставка лекарств. Добавление графена в качестве нанонаполнителя позволит получить нанокompозитный гидрогель (ПВС / бура / графен), что значительно улучшит проводящие свойства ПВС. Нанокompозит не токсичен, а хорошо диспергированный графен обеспечит термическую стабильность и проводимость. В данном исследовании мы показали эффективность проводящего гидрогеля с использованием метода замораживания / оттаивания.

Ключевые слова: поливиниловый спирт, поливинилацетат, нанокompозит «поливиниловый спирт – бура – графен», оксид графита, микроэлектромеханические системы.

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Introduction

In several biomedical and pharmaceutical application, hydrogels are massively applied for biomedical engineering, biomaterial, and tissue engineering studies, because of their biodegradability, biocompatibility, non-toxicity, high water content, and other desired attributes [1]. The increasing usage of hydrogels in electrical applications, leads to studies that focus on the poor conductive properties of hydrogels. The uses and applications of hydrogels are limited because they are typically non-conductive and cannot be controlled using electrical stimulation. Enhancing the conductive properties of hydrogels are applicable by providing additives with high conductive characteristics such as metallic nanoparticles, different formations of carbon, and conductive hydrogels [2]. These additives contribute by embedding physically

into aqueous gel solutions in order to form new propagation for these components as electrical paths within the hydrogel network.

Graphene has been vastly utilized to improve the electrical conductivity of hydrogels, while additionally improving thermal, stiffness, and mechanical properties [2, 3]. Specific mechanisms to fabricate a graphene-based polymer are still unclear, however, conductive hydrogel composite requires the construction of a three-dimensional network of interconnected graphene that can improve the electrical conductivity of hydrogel [3]. Two main obstacles for graphene-based hydrogel are, the difficulty of well-dispersion of graphene within hydrogel network because of the strong intermolecular interactions between the two-dimensional sheets of graphene, and large specific surface area of polymeric hydrogel networks. And a percolation limitation occurs at low filler content and polymer chains surround graphene sheets stopping them from reaching to mixture percolation limits [2, 3].

This study introduces an experiment to fabricate Polyvinyl Alcohol/Borax/Graphene (PVA/B/G) hydrogel using freezing/thawing method and testing its conductivity. PVA hydrogels are viscoelastic, semi-solid, soft, cross-linked three-dimensional networks containing hydrophilic chains capable of holding large quantities of water [1]. PVA can form chemical and physical cross-linked networks because its repeating molecular unit possesses hydroxyl groups [1], [4]. The freezing/thawing method avoids the use of chemical additives and any modification of bioactivity or toxicity agents [5]. This method is responsible for physical crosslinking in PVA hydrogel networks and allows for more control of the degree of crystallization by increasing cycling numbers. Using Borax as a crosslinker improves the intermolecular hydrogen bonding between hydroxyl groups in PVA chains [1, 4, 6].

The best way to describe the crystalline structure of PVA (Bunn investigated in detail the crystalline structure of PVA) on the molecular scale is to visualize PVA's crystallin as a double layered structure. These layers are held together by Van der Waals interactions. The double layers within the PVA's crystalline itself are held together by the formation of acetal bridges between the hydroxyl groups [1], [7]. Additionally, PVA chains have amorphous matrixes that give it overall shape, but the PVA crystallites are ordered randomly in small regions. Freezing/thawing method is a Physical crosslinking method because it avoids chemical additives and any modification of bioactive agent and the toxicity [6]. A study was done by Lawrence et al, shows borate ions formed after dissolving Borax in water have high potential to bond chemically with PVA chains and form crosslinked PVA-Borax hydrogel [6, 8]. Borax as a crosslinker, assists the submitting of negative charge that supports the intermolecular hydrogen bonding between the hydroxyl groups on the PVA matrices [8, 9]. At appropriate concentrations, Borax dissociates into boric acid and borate ions according to the equation:



The bond between PVA and Borax is formed between two diols units, one from PVA and one borate ion from Borax, and this cross-linking between PVA and the cross-linker is called di-diol complexation [2], [10]. The PVA/Borax reaction can be simplified into two main reactions; mono-dial complexation and cross-link di-diol complexation. Mono-dial complexation causes the cross-link di-diol complexation to behave as a polyelectrolyte (Fig. 1). The intramolecular structure of PVA/Borax hydrogel relies on balance of interactions between polymer-polymer and polymer-solvent units and the concentration of PVA and Borate ions [11]. Specifically, the existence of cross-link di-diol complexation

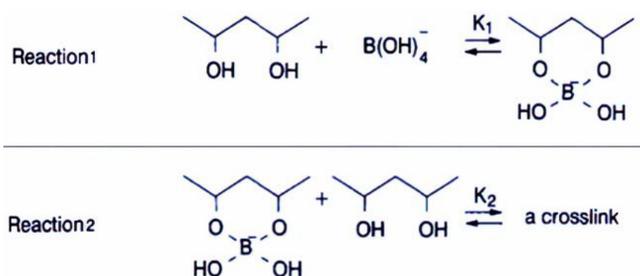


Fig. 1. Gelation mechanism in PVA/Borax hydrogels

reduces the chain dimensions, and the existence of electrostatic charge forms repulsive force between mono-diol units increasing the chain deformation [8, 12]. According to Leibler et al, the structure of PVA-Borax hydrogels depend on these five factors [11]; (1) the excluded volume effect of polymer chain, (2) the charge repulsion among crosslink sites, (3) the intermolecular crosslinking reactions of PVA with borate ions, (4) the intramolecular crosslinking interactions of PVA with borate ions, and (5) the electrostatic screening effect exerted by free Na^+ ions on the negative charged crosslink regions. The 1st and 2nd factors increase the polymer chain size while 4th and 5th factors decrease the polymer chain size [14].

Graphene is a crystalline allotrope with a two-dimensional single layer sheet, one carbon atom thick, sp^2 orbital hybridization, possessing hexagonal lattice, and the specific surface area of $2360 \text{ m}^2\text{g}^{-1}$. Graphene consists of two different bonds, σ and π -bond, σ -bond with three neighbors and one π -bond which is oriented out the plane. The distance between the atoms is about 1.42 \AA . Graphene has extremely high conductivity due to its zero-overlap semimetal, which means both atoms and holes work as charge carriers [15]. In order to reach the optimal degree of enhancement for polymers using Graphene, there are two main factors; (1) well-dispersion of Graphene and strong intermolecular interactions of Graphene with polymeric matrix and (2) high filler content is required [2]. When comparing to the dispersion of Graphite Oxide (GO), GO is easier to be dispersed and exfoliated because GO is functionalized with oxygen, which chemically interacts stronger to the PVA matrix. In other cases, Graphene is more difficult to be dispersed and exfoliated because of Van der Waals interactions, which allow Graphene to re-agglomeration effortlessly [2]. Boa et al investigated PVA nanocomposites focused on GO and Graphene and their enhancement properties. One of the strategies to improve the Graphene dispersion in the PVA matrix is using molecular functionalization. These functional groups easily bond with the hydroxyl groups of the PVA matrix and improve the dispersion of Graphene [15]. However, this strategy disrupts the formation of electrical connections between Graphene sheets. Thus, undesirably impacting the conductivity of PVA hydrogels. Another alternative and more suitable strategy would be to disperse Graphene in a favorable solvent before mixing Graphene with PVA. Hydrogen bond is mainly responsible for the enhancement of specific surface area and load transfers between the PVA matrix and Graphene or GO. Figure 2 shows rich oxygenated functional groups in GO, which are responsible for good formation of well-dispersion and strong hydrogen bonding within the PVA matrix. According to the previous facts, GO is supposed to improve PVA hydrogel properties, but the same study has shown opposite results. The better enhancement accrued to nanocomposites based on dispersed Graphene, especially for mechanical properties [15].

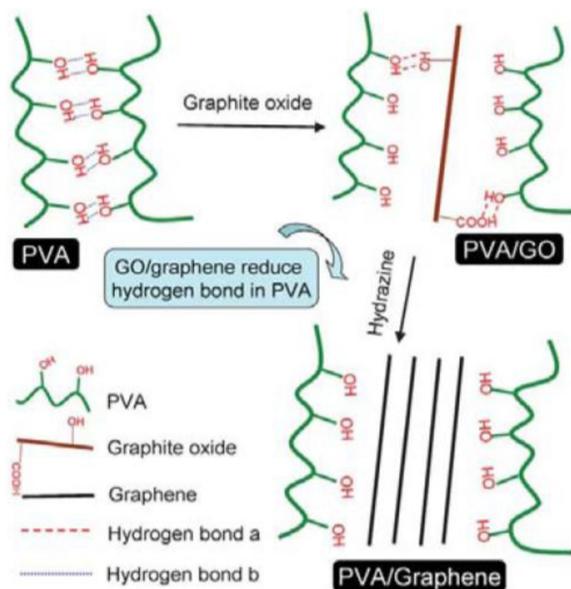


Fig. 2. Schematic illustration for GO/Graphene dispersion with PVA hydrogel [15]

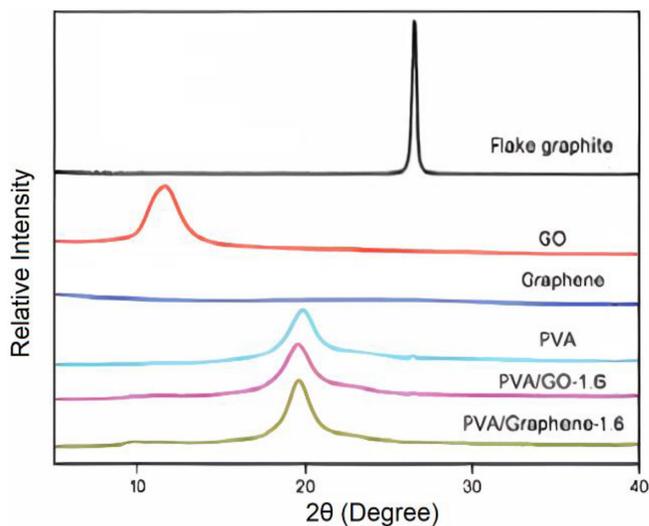


Fig. 3. XRD traces of GO, Graphene, and PVA nanocomposites

Figure 3 shows the XRD examination for Flake graphite, GO, Graphene, PVA, PVA/GO-1.6, and PVA/Graphene-1.6. There is an obvious sharp peak of the Graphite trace, showing diffraction of (001). Below that, on the GO trace, the sharp peak location disappeared, and another peak appears at a different position, which indicates the increasing of interlayer spacing of GO. The Graphene trace shows no peaks, which indicate the long-range disorder of Graphene. The PVA, PVA/GO-1.6, and PVA/Graphene-1.6 traces show the same peak positions with pure PVA after the incorporation of GO and Graphene, which indicates that PVA polymers maintain their local network structures. The disappearance of the GO peak after incorporation with PVA indicates the exfoliation of GO into the

PVA matrix. The PVA/Graphene-1.6 trace shows a sharper and higher peak than PVA and PVA/GO-1.6. The higher and sharper peak represents the stronger enhancement of PVA crystallinity compared to the enhancements of PVA and PVA/GO-1.6, overall, a greater improvement of PVA properties.

Figure 4 shows the TEM examination of (a) PVA/GO-1.6, and (b) PVA/Graphene-1.6 to assess the dispersion and exfoliation of GO and Graphene nanosheets within the PVA matrix. The lines in the figure represent the side views of GO and Graphene nanosheets. The well-dispersion of GO and Graphene in PVA structures are evident to observe, but partially homogenous dispersion is best observed in magnified images. In figure 4, the thickness of the observed lines, indicates the number of layers of GO and Graphene. The thickness of GO lines is between 2–4 nm, which indicates that the line contains 1 to 3 nanosheets. The thickness of Graphene lines is between 17–40 nm, which indicates that the re-agglomeration of Graphene occurred. In the small nanosheet scale, the re-agglomeration occurs because of the strong Van der Waals interaction between Graphene nanosheets. Because of the absence of functionalized groups in Graphene such as epoxy, hydroxyl and carboxyl, the formation of hydrogen bonding between Graphene nanosheets and PVA matrix is insufficient to balance Van der Waals interaction between Graphene nanosheets. However, in case of GO dispersion, oxygenated functionality is rich, thus there are more formations of hydrogen bonding. Van der Waals interactions are balanced and form better exfoliation and dispersion [15].

Essentially, there are five factors that impact the improvement of mechanical properties for PVA nanocomposites [15,16]. First, (1) the hydrogen bonding between the GO/Graphene nanosheets and the PVA matrix, and (2) the hydrogen bonding between the PVA chains. These first two factors are particularly important for PVA nanocomposites and the enhancement of mechanical properties. Due to the hydrogen barrier effect, the hydrogen bonding between the PVA chains will reduce in PVA nanocomposites. Additionally, the hydrogen bond reduction effect will occur in PVA nanocomposites, because of increasing hydrogen bonding between the PVA matrix and GO/Graphene. The remaining factors are (3) the crystallinity of PVA, (4) the mechanical strength of GO/Graphene nanosheets, and (5) the dispersion of GO/Graphene nanosheets in PVA hydrogels. Indeed, these five factors are used to tradeoff between mechanical enhancements in PVA hydrogels, depending on how the GO/Graphene nanosheets are utilized. The electrical conductivity of PVA nanocomposites were investigated using a high resistance meter. The conductive behavior of PVA/GO/Graphene nanocomposites are shown in Figure 5. According to the study, enhancement of conductivity has been achieved by increasing 7 orders in PVA/Graphene-1.6. The improvements

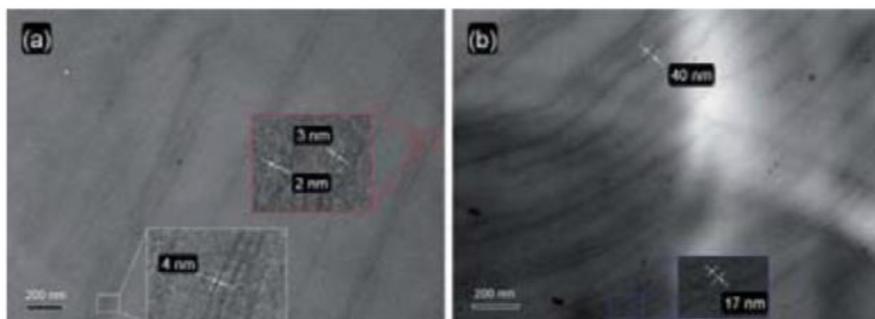


Fig. 4. TEM examination of (a) PVA/GO hydrogel, and (b) PVA/Graphene hydrogel [15]

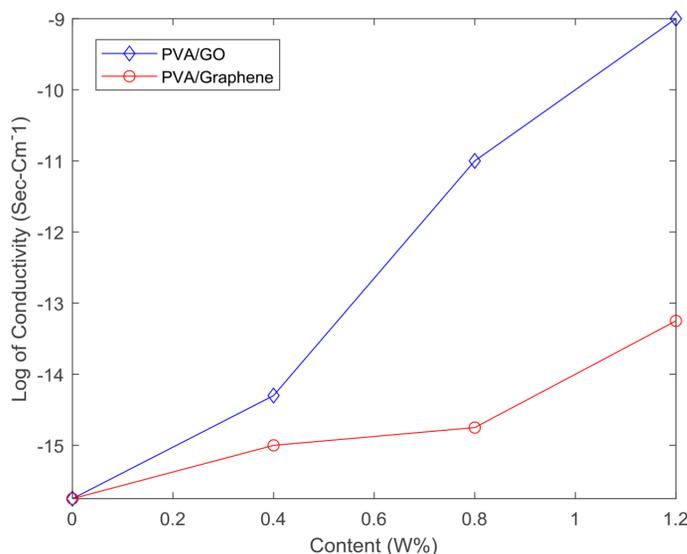


Fig. 5. The conductive behavior of PVA/GO/Graphene nanocomposites

are related to the conducting co-network formed by Graphene dispersion. Figure 5 shows less improved conductivity for dispersed GO, this is related to the damage caused by the functional oxygenation of GO for the disrupted conjunction and lattice.

Materials

Polyvinyl Alcohol was purchased from SIGMA-ALDRICH company. White powder form, ranges between 85,000–124,000 $g\ mol^{-1}$, 99+% hydrolyzed [17]. Borax was purchased from CAROLAINA company. White powder form is 381.42 $g\ mol^{-1}$, and the Formula is $[Na_2B_4O_7 \cdot 10H_2O]$ [18]. Graphene Nanoplatelets were purchased from SIGMA-ALDRICH company. Dark black powder form is 12.01 $g\ mol^{-1}$, 10 (+/-5) Ωsq^{-1} (for a 25 μm film) [19, 20]. All the chemicals were analytical grade and used as received.

Preparation of Graphene Borax suspensions

Ultimately, for this experiment, a total of nine 50mL PVA/B/G sample were prepared. All 9 sample were made with constant concentrations of Borax. Then divided into 3 sets, where there were 3 different concentrations of PVA (2 wt%, 3 wt%, and 4 wt%). And within each set of PVA concentration, there were 3 different concentrations of Graphene (none, 0.005 wt%, and 0.025 wt%). See table 1.

Due to the difficulty of handling small amounts of Graphene, the samples with Graphene concentrations were prepared first, as aqueous Borax/Graphene solutions. Two separate solutions were prepared, one Borax/Graphene solution for each Graphene concentration (0.005 wt%, and 0.025 wt%). For example, in the case of the 50 mL-sample with 0.005 wt% of Graphene, the required Graphene weight would be 2.5 mg. In addition to being extremely difficult to weigh, most of the 2.5 mg of weighted Graphene would adhere to the plastic sample container. To resolve the adhesion issue and for easier handling, a 10x larger-volume aqueous Borax/Graphene solution was prepared with a proportional concentration of Graphene. In the same example, preparing a 250 mL aqueous Borax/

Graphene solution would require 25 mg of Graphene. And 25 mg of Graphene can be more precisely measured and more easily handled, than 2.5 mg. Then taking 25 mL from the 250 mL solution would yield the desired Borax and Graphene concentrations, ultimately need for the 50 mL PVA/B/G sample. This methodology was used for both Graphene concentrations. Two 250 mL aqueous Borax/Graphene solutions were prepared as follows: (1) Borax-0.6 wt%/Graphene-0.01 wt% sample, 250 mL water + 1.5 g Borax + 25 mg Graphene. (2) Borax-0.6 wt%/Graphene-0.05 wt% sample, 250 mL water + 1.5 g Borax + 125 mg Graphene.

Each 250mL Borax/Graphene sample was placed on a magnetic stirrer hotplate for 20 minutes and kept at a temperature of 50 °C (see Fig. 6).

As an added benefit, this method ensures a homogeneous Borax/Graphene solution without the possibility of Graphene sedimentation.

Fabrication of PVA-B-G hydrogels

Each 250mL-PVA/B/G sample was placed on a magnetic stirrer hotplate for 4 h and continuously stirred at a rate of 600 rpm and a temperature between 75 and 80 °C. Each sample was sonicated for 30 minutes at 50 °C. Then the samples were poured into cylinder-shaped molds (65 mm diameter, 17 mm high). Each sample was subjected to five freezing/thawing cycles, freezing for 24 h at a

Table 1. Parameters of PVA/B/G samples in order based on variable concentrations of PVA, Borax, and graphene

Sample	PVA	Borax	Graphene
PVA-2.0/B-0.3	2wt%(1.0 g)	3wt% (0.15 g)	0
PVA-3.0/B-0.3	3wt% (1.5 g)	3wt%(0.15 g)	0
PVA-4.0/B-0.3	4wt%(2.0 g)	3wt% (0.15 g)	0
PVA-2.0/B-0.3/G-0.005	2wt%(1.0 g)	3wt% (0.15 g)	0.005wt%(2.5 mg)
PVA-3.0/B-0.3/G-0.005	3wt%(1.5 g)	3wt% (0.15 g)	0.005wt%(2.5 mg)
PVA-4.0/B-0.3/G-0.005	4wt%(2.0 g)	3wt% (0.15 g)	0.005wt%(2.5 mg)
PVA-2.0/B-0.3/G-0.025	2wt%(1.0 g)	3wt%(0.15 g)	0.025wt%(25 mg)
PVA-3.0/B-0.3/G-0.025	3wt%(1.5 g)	3wt%(0.15 g)	0.025wt% (25 mg)
PVA-4.0/B-0.3/G-0.025	4wt%(2.0 g)	3wt%(0.15 g)	0.025wt% (25 mg)

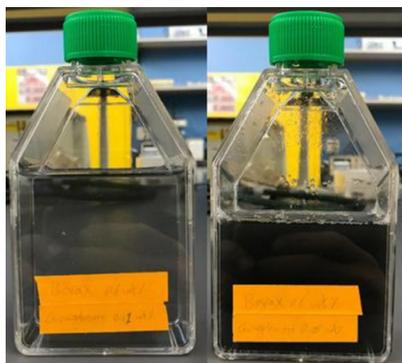


Fig. 6. Borax-0.6/Graphene-0.01 sample (Left), and Borax-0.6/Graphene-0.05 sample (Right)

temperature of $-20\text{ }^{\circ}\text{C}$ and then thawing for 3 h at room temperature. All samples eventually reached the desired sample volume of 50mL to begin the test portion of the experiment.

Electrical Examination

A digital multimeter was used to measure the resistances of all the PVA/B/G hydrogel composites. The PVA/B/G hydrogels were connected within built electrical circuits, through which electrical currents were passed to observe the breakdown of the PVA/B/G hydrogels. As the voltage increased up to 64 V, a digital multimeter was used to monitor the values of the electrical currents.

Results and discussion

Results were documented with photographs during various stages of the experiment. Freezing and thawing states of the hydrogels, the application of electrical voltage, and the meter readings of the resistances of the hydrogels. Figure 7 shows the final freezing cycle of the PVA/B/G hydrogels. The morphology of the PVA/B/G hydrogel was observed with the increasing PVA concentration, as shown by the increased density of the lines passing through the samples. Samples #1, #2, and #3 show the results of increasing PVA concentrations. These samples contained no Graphene and thus the changes in morphology can be attributed to the increasing of PVA concentrations. Additionally, freezing cycles were beneficial in that they reduced air bubbles in all samples.

Figures 8 show the PVA/B/G hydrogel samples in thawed states after five freezing/thawing cycles. Each frame contains an aerial view with a side view pictured below. The side is used to best view and evaluate the existence of air bubbles. Compared to the other samples, samples #3, #6, and #9 contained more air bubbles due to their having the highest PVA concentrations. The high PVA concentrations of these samples made them more difficult to stir as volume decreased and more difficult to rid of air bubbles.

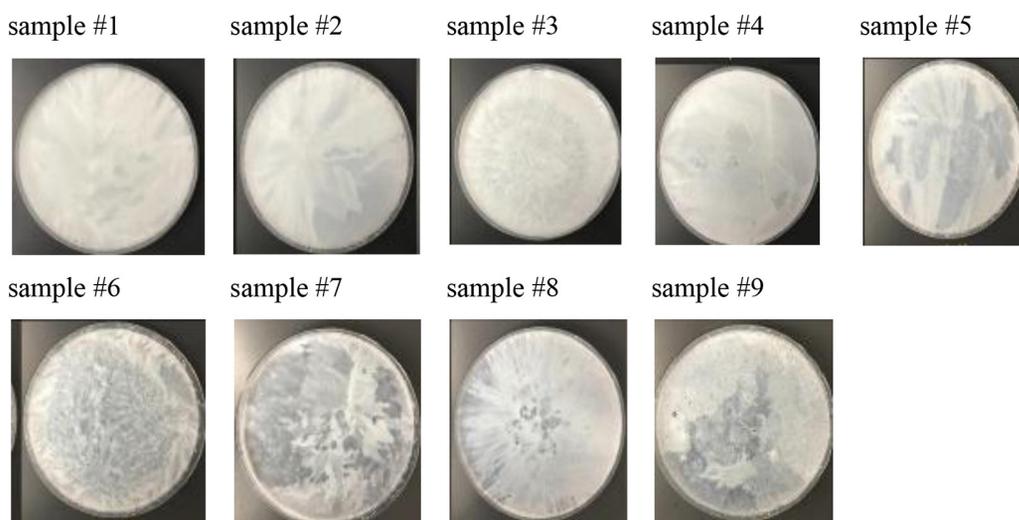


Fig. 7. Last freezing cycle of PVA/B/G hydrogels; sample #1: PVA-2/Borax-0.3, sample #2: PVA-3/Borax-0.3, sample #3: PVA-4/Borax-0.3. Sample #4: PVA-2/Borax-0.3/Graphene-0.005, sample #5: PVA-3/Borax-0.3/Graphene-0.005, sample #6: PVA-4/Borax-0.3/Graphene-0.005, sample #7: PVA-2/Borax-0.3/Graphene-0.025, sample #8: PVA-3/Borax-0.3/Graphene-0.025, and sample #9: PVA-4/Borax-0.3/Graphene-0.025

Figure 9 shows the resistance readings of two different hydrogel samples, one without dispersed Graphene (Figure 9, left) and one with dispersed Graphene (Figure 9, right)., When comparing the resistances of the two hydrogels, the PVA/B/G hydrogel resistance reduced by approximately 1:23 compared to the PVA/B hydrogel resistance. This indicates that the dispersion of Graphene into PVA/B hydrogel enhanced the electrical conductivity of the hydrogel. The incorporation of Graphene into the

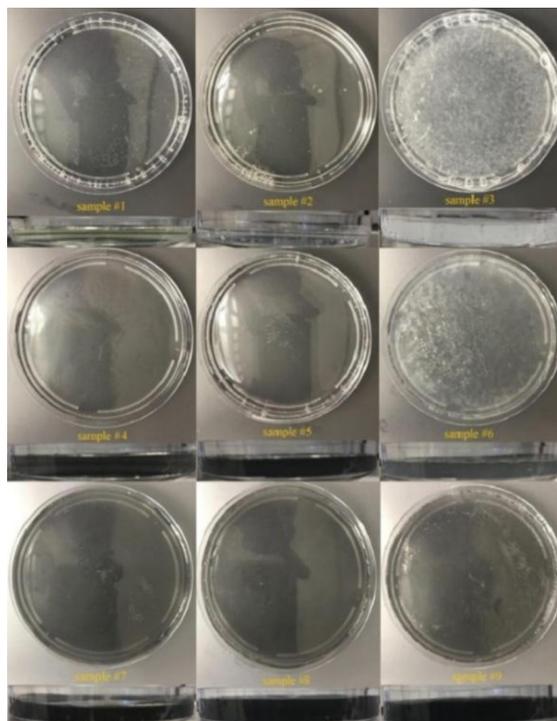


Fig. 8. PVA/B/G hydrogels in the thawed state after five freezing/thawing cycles; sample #1: PVA-2/Borax-0.3, sample #2: PVA-3/Borax-0.3, sample #3: PVA-4/Borax-0.3. Sample #4: PVA-2/Borax-0.3/Graphene-0.005, sample #5: PVA-3/Borax-0.3/Graphene-0.005, sample #6: PVA-4/Borax-0.3/Graphene-0.005, sample #7: PVA-2/Borax-0.3/Graphene-0.025, sample #8: PVA-3/Borax-0.3/Graphene-0.025, and sample #9: PVA-4/Borax-0.3/Graphene-0.025



Fig. 9: measuring PVA/Borax hydrogel resistance (Left) and PVA/B/G hydrogel resistance (Right)

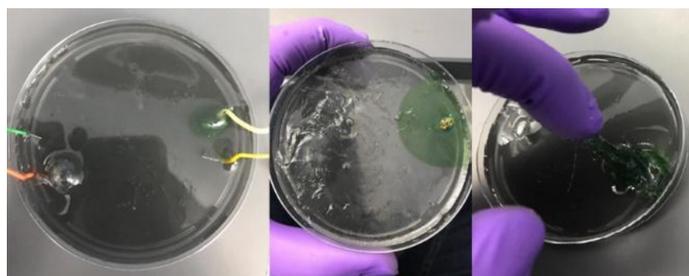


Fig. 10. Photographic picture shows the breaking of hydrogel after the applied electrical stimulation

PVA/B hydrogel formed new electrical paths throughout the hydrogel. When connecting the PVA/B/G hydrogels to the test electrical circuit, the hydrogels generated a measurable electrical current starting at approximately 5V of applied electrical voltage. There was no detectable current for applied voltages less than 5V. When applying the maximum electrical voltage of 64V, the generated electrical current was approximate 15 mA

When applying the electrical voltage, there was noticeable physical breaking in the PVA/B/G hydrogels. The formation of air bubbles on one side (negative side), which indicate the increasing of the thermal energy in the PVA/B/G hydrogels. And the propagation of green color throughout the PVA/B/G hydrogels, starting from the positive side to the negative side (Fig. 10 center). The occurrence of the green color was an anticipated result of the Copper wire being dissolved in the PVA/B/G hydrogel. Therefore, in figure 12 right, we can see the occurred breaking by electrical voltage on the hydrogel.

Conclusions

By incorporating polymeric hydrogels with certain types of electrical nanoparticles, some nanocomposites can be enhanced electrically and mechanically. Researchers have reported in many studies the improvements of these hydrogels and the novel fields they can be applied to, especially drug-releasing and delivery. This experiment introduced an improved novel conductive hydrogel for drug delivery, using Polyvinyl Alcohol (PVA), Borax, and Graphene nanoplatelets. All these additive materials are biodegradable, biocompatible, and hydrophilic, which makes them ideal candidates for nanocomposites providing a perfect enhancement of conductivity. On a test electrical circuit, the combination of these ideal nanocomposites plus utilizing the freezing/thawing cycle method showed that PVA/B/G hydrogels support well-dispersed Graphene. And well-dispersed Graphene creates good electrical electron paths with the hydrogel. The dispersion of Graphene significantly reduces the resistance of PVA/B hydrogels.

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