NE 409 Fourth Year Design Project Final Report

Conformable Heart Sensors using Graphene-Infused Silly Putty

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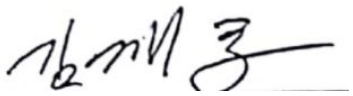
JaeJung Kim 20296471 jj5kim@edu.uwaterloo.ca	
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This report is submitted as the final report requirement of the NE 409 course. It has been written solely by us and has not been submitted for academic credit before (other than appendices A-G) at this or any other academic institution

Executive Summary

Despite recent advancements in microelectronics that have seen sensors become ubiquitous in modern consumer electronics, the way we interact with many sensing technologies remains fundamentally the same. MEMS sensor fabrication techniques are not feasible for many of the wearable and health sensing applications which arguably stand to benefit the most from improvements in sensor technology; the fragile, inflexible nature of MEMS sensors makes them prone to failure under flexure and in other non-ideal environments. Consequently, a robust, human-compatible sensor with the ability to resolve subtle physiological signals without sacrificing the conformability and flexibility of the device and could prove invaluable in health and wellness monitoring.

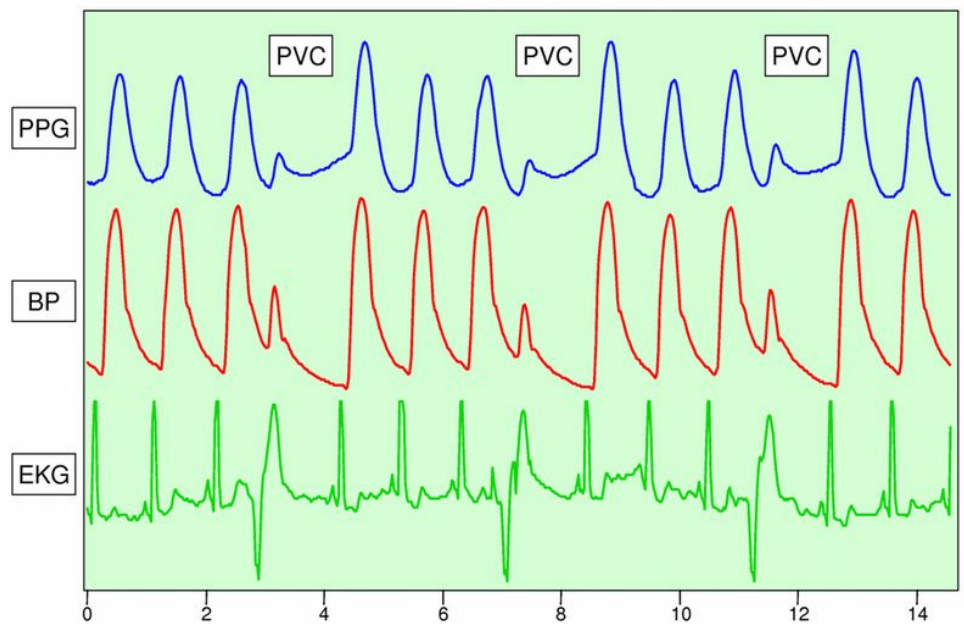
Our prototype sensor takes advantage of the extraordinary properties of graphene polymer nanocomposites to create a robust, ultra-conformable pressure sensor sensitive enough to detect the arterial pressure of the heart. A sensor with the ability to discern pressures as low as **40 mmHg** (approximately half of the typical diastolic pressure in humans) would be able to resolve the arterial pressure waveform associated with the regular palpitation of the heart. This pressure waveform contains valuable information pertaining to the condition of a patient's heart that existing thin/thick-film and piezoresistive pressure sensors cannot resolve due to sensitivity and/or conformability limitations.

Like traditional electrophysiological (ECG) or volumetric oximeter-based techniques (PPG), pressure-based heart sensors can be used to monitor heart rates and detect arrhythmias. A pressure based sensor, however, has the unique advantage of being able to directly measure blood pressure (BP) using only a single sensor. In contrast, BP can only be estimated using PPGs through a process requiring additional reference oximeters. ECGs, which also require multiple electrodes to function, must be used in conjunction with a pulse oximeter or traditional cuff-based pressure monitors to determine a patient’s BP. Given that suboptimal blood pressures are the number one risk factor for death globally[1] a sensor that could accurately measure all of these metrics — particularly one without the complications associated with

[1] Xing, Xiaoman, and Mingshan Sun. "Optical blood pressure estimation with photoplethysmography and FFT-based neural networks." *Biomedical optics express* 7.8 (2016): 3007-3020.

introducing additional reference devices — could prove invaluable in, for example, the diagnosis and treatment of chronic hypertension and heart failure[2].

Our design was motivated by recent research demonstrating that the introduction of nanoscale sheets of graphene into a simple silicone putty renders the resultant nanocomposite electrically conductive and highly sensitive to small deformations thanks to the unique properties of the 2D material. At low strain, the resulting electromechanical sensor was found to have sensitivities, *G*, (where where $G\varepsilon = \Delta R/R_0$) up to 10 times higher than comparable (e.g. carbon black) nanocomposite sensors in literature. We intend to leverage these findings to create a robust health sensor that is both sensitive enough to be used in cardiac monitoring and more user-friendly than current solutions.



Premature Ventricular Contractions (PVCs) can be observed volumetrically from a photoplethysmogram (PPG), from the arterial pressure waveform (BP), or electrically using an electrocardiogram (EKG)

[2] Shaltis, Phillip A., Andrew Reisner, and H. Harry Asada. "Wearable, cuff-less PPG-based blood pressure monitor with novel height sensor." *Engineering in Medicine and Biology Society, 2006. EMBS'06. 28th Annual International Conference of the IEEE*. IEEE, 2006.

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Background

The advancements of sensor manufacturing and microelectronics in general have spurred the growth of the wearable technology industry and opened the door for novel digital health ecosystems. Wearable health and wellness sensors enable seamless and continuous monitoring of key health metrics, often with less effort and at lower costs. As these technologies have continued to advance and become more accessible to people around the world, there has been a fundamental shift in the way we interface with technology and ultimately how the design of device interfaces are approached. Recent advancements have seen tactile sensors, which are characterized by their ability to acquire information upon making contact with their environment become ubiquitous in modern technologies. Given how important humans' sense of touch is with respect to how we interact with the world around us, it is no surprise that many of these sensors are modelled after our own biological sense of touch.

Tuning tactile sensors after our sense of touch has had the added benefit of making technology and interfaces for technology increasingly intuitive and more accessible. In recent decades, we have seen this shift of focus particularly in mobile devices where the technology has moved from button-based interfaces to touchscreen interfaces that leverage large arrays of capacitive sensors. As modern tactile sensors get better at initiating the human body's built-in tactile sensors, and tactile sensing technologies become less expensive and start being implemented in more frequently, the demand for these sensors will only continue to grow.

Despite the growing popularity and demand of current tactile sensing technologies, there remains a persistent demand for robust sensors that are flexible (or otherwise conformable) while also being sensitive and durable. The wearable technology market is a flourishing market, with projected numbers of connected wearable devices across the globe expected to jump from an estimated 325 million devices in 2016 to over 830 million in 2020. Graphene, known for its inherent flexibility and mechanical strength, demonstrates potential as a filler additive in a composite material capable of meeting these design requirements for fabricating robust sensing technologies.

Heart sensors that provide information pertaining to heart health are among the most commonly used health sensor. Motivated by the significant physiological importance and complexity of the heart, focus has been placed in exemplifying an alternative approach to heart sensing that meet the functional requirements of currently existing solutions.

Although modern medicine's detailed understanding of the mechanisms of the heart allows one to extract a lot of useful information from ECG electrodes and related technologies such as capacitive sensors [1], inherent problems associated with resolving very small biopotentials through the skin such as noise, motion artefacts, and complications related to electrode placement and contact are some of the fundamental limitations to the technology.

Using a highly sensitive electromechanical pressure sensor as a heart sensor would enable the measurement of the arterial pressure waveforms generated by the heart rather than the electrical impulses, and consequently circumvent many of the inconveniences associated with current cardiac monitoring techniques.

The arterial pressure waveform obtained through this proposed cardiac electrode still could be used to monitor the activity of the heart, with the added benefit of providing information on the patient's blood pressure. This output waveform could be obtained using a single electrode rather than an array of ten electrodes, making the proposed technology more user-friendly and the outputted data more intuitive and easier to process and interpret. Moreover, the proposed sensor would be reusable and not require the application of a conductive gel to the skin in order make resistive contact, making it more convenient and safer than the existing technology.

Existing Solutions

Tactile sensors typically rely on either strain or pressure gauges that act as transducers to generate a signal as a function of the pressure imposed on them. To accomplish this, materials or devices with electrical properties that change under applied stress form the basis of the vast majority of tactile sensing technologies.

Piezoresistive and capacitive tactile sensors are currently the most common among strain/pressure gauge sensing technologies. Piezoresistive sensors tend to lack the degree of

sensitivity required for effective health and wellness monitoring while capacitive sensors are limited by their lower durability and conformability. Gauge factors of 150 and 0.97 have been demonstrated for piezoresistive and capacitive sensors respectively. These two sensor types have also shown pressure sensitivity at 4.88 kPa^{-1} and 192 kPa^{-1}. Despite the capabilities of current solutions, graphene based nanocomposite sensors have reached gauge factors as high as 1000 and displayed higher pressure sensitivity owing to the inherent properties of graphene.

Nanocomposite Sensors

The unique properties of many materials like graphene at the nanoscale has formed a new class of tactile sensors that in many ways could outperform traditional sensors. Although graphene has been the center of much of the research in nanotechnology and materials science in the last decade, its behaviour in highly viscoelastic polymer matrices is only now beginning to be investigated in earnest. In recent years, there have been extensive efforts to take advantage of the material's extraordinary properties—namely its electrical conductivity and its mechanical robustness—in order to develop robust strain sensors with superior sensitivity by incorporating graphene into various fabrics and rubbers. Although work on these viscoelastic sensing materials has been complemented by progress in the wearable device industry, with fitness watches and monitors quickly becoming ubiquitous in personal electronics as the prices and size of traditional sensors rapidly declines, the lack of sensitivity in these innovative sensors persists as the greatest design challenge [7]

More recently, researchers published their findings on a novel graphene-polymer nanocomposite and briefly demonstrated its potential in different sensing applications, including heart rate and arterial blood pressure detection. They demonstrated that infusing a low viscosity polymer with graphene is a promising approach to overcome the lacking sensitivity observed in current strain sensor technologies. In the resulting paper they detailed the electromechanical behaviour of the novel nanocomposite, looking at its conductivity, stiffness and general rheological properties as a function of the amount of graphene introduced to the polymer matrix.

Using this extraordinary new material we hope to design a more convenient, more accessible sensor that can be used to monitor both cardiac activity and blood pressure while avoiding many of the inherent limitations imposed by electrical sensing cardiac monitoring technologies.

Design Approach

The design of our prototype sensor was inspired by the current lack of robust sensors available for purchase, as identified in the project background. More specifically—although there exists a number of tactile sensors that are extremely sensitive, as well as small number of flexible sensors, and even fewer that sensors are broadly conformable—there are, to our knowledge, currently no commercially available tactile sensors that claim to be sensitive, flexible and conformable all together.

A sensor with these attributes was identified to be in particular demand in the wearable sensing industry, which is currently limited with respect to its ability to make highly personalized devices for individual consumers due to inherent limitations in the largely silicon-based technologies used in the creation of health and wellness sensors today. Given the intrinsic differences between every human's build and physiology, a device that is robust enough to be adaptable to the needs of the individual is the ultimate goal of any wearable technology. To create a sensor robust enough to be considered flexible and conformable without sacrificing its sensitivity we aimed to leverage the extraordinary properties of nanomaterials.

Graphene (the mono-crystalline graphitic film famously isolated by researchers at the University of Manchester in 2004 by manually exfoliating monolayer sheets of the 2D material from bulk graphite using sellotape) is typically described as a 'wonder material'. Despite comprising of just a single layer of sp^2 bonded carbon atoms arranged in a hexagonal 'honeycomb' lattice, graphene is known to be one of the strongest materials known to man. However, of more interest to sensing applications is it's remarkable conductivity. When combined with an inert (typically polymeric) matrix, graphene can render typically insulating materials conductive even in at very low volume fractions.

Although the mechanism through which graphene and other nanomaterials can alter the properties of a polymer matrix are relatively well understood through percolation theory, only recently have researchers began to experiment with highly malleable nanocomposites with mobile conductive networks instead of, for example, composites that leverage graphene's mechanical properties to make a material stronger without significantly changing it's behaviour.

We chose household Silly Putty™ as our polymer matrix because it highly malleable while also being very safe to handle and easy to make.

As the organ responsible for circulating nutrient-rich blood around the body of humans and most other animals, the biological signals produced by the heart contain invaluable information about a human's physiology and overall health. Taking into consideration the importance of metrics related to the heart when it comes to any wearable health sensors, our team aimed to investigate the potential of these highly conformable nanocomposites specifically as a wearable heart sensors. We initially identified five key customer requirements for our novel heart sensor which were used to evaluate the feasibility of our prototype sensor.

1. **Safe to use** (Non-allergenic, non-toxic, not otherwise hazardous). The sensor and any associated elements (housing, hardware, etc.) should not pose any risk - electrical, allergenic, or otherwise - to the end user (including children).
2. **Heart rate** (in BPM) can be derived from output waveform
3. **Blood Pressure** can be derived from the output waveform (after calibration)
4. **Convenience** sensor should be comfortable and user friendly (easily portable, minimal connections)
5. **Arrhythmia detection** can be resolved from the arterial pressure waveforms

In the following sections we will outline the steps that were taken in designing, fabricating, and finally, validating & testing our prototype sensors while justifying any changes in design direction and evaluating the final performance of our prototype sensor.

Design Phases

As outlined in Appendix F, Our team's approach to the creation of the prototype sensor was broadly divided into three separate phases. The first phase (**Phase I**), **sensor design**, in which the graphene nanocomposite was created, formed the basis of the project and was consequently was the most important of the three phases. The completion of this phase was marked by the characterization of the nanocomposite and verification testing & characterization.

In the second and third phases the sensing materials created in the first phase were modified to best fulfill the sensors' desired functionality as wearable sensors. **Phase II** dealt specifically with **electrode design**—that is the shaping and tuning of the nanocomposite material into a form best suited for the designated heart sensing applications—and was marked by the completion of a functional sensor capable of resolving heartbeats. The final phase (**Phase III**) constituted the refinement of the functional sensor created in the second phase and had a final milestone of creating a functional **demo** sensor to be showcased at the Nanotechnology Engineering Symposium.

Phase I: Sensor Design

The creation of a sensing nanocomposite was predicated on

1. The successful exfoliation of nanoscale few-layer graphene from bulk graphite powder
2. The preparation of a 'pristine' viscoelastic PDMS putty
3. The infusion of the exfoliated graphite into the viscoelastic putty

Of these three steps, the first was by far the most problematic and time consuming. Although our initial analysis of the key challenges associated with the project (see Appendix F) included the challenges associated with 'sensor fabrication', in retrospect our team underestimated the time investment required in order to complete the exfoliation.
Unlike mechanical exfoliation which requires the manual stripping of graphene from bulk graphite, liquid-phase exfoliation [6] uses a stabilizing organic solvent such as N-Methyl-2-pyrrolidone (NMP) to stabilize a dispersion of graphite which undergoes ultrasonication using a high-powered tip sonicator.

In our preparation of exfoliated graphite/graphene we started with a 99.9995% graphite powder (Alfa Aesar) with particle sizes under 50 μm. However, limitations with respect to our access to a tip sonicator significantly extended the overall time required to complete the 72hrs of sonication required to obtain sub-micron exfoliated graphite. Using the tip sonicator located at the Velocity garage required we limit our sonication to hours outside of a typical working day in order to avoid being an inconvenience to those working in the lab each day, mostly because of the noise made by the high-powered sonicator and the fume hood space it required. Moreover,

local heating near the tip of the sonicator made the NMP/graphite solution prone to overheating and rapid evaporation.

Rather than using an amplitude of 80 as recommended in the main reference literature [2] we instead used an amplitude of 60. Lowering the amplitude had the effect of reducing the rate evaporation and allowing the the temperature of the solution to reach an equilibrium temperature safe enough that we were comfortable monitoring the sonication occasionally rather than continuously. To partially compensate for the reduced amplitude of sonication we extended the 72hr sonication time by 10-15 hrs. Thanks to concerted efforts from each one of the team members we were able to complete most of the sonication after school and work hours, overnight, and on the weekends to eventually reach ~80 hrs of sonication, but even with these efforts the initial timeline (Appendix B) was delayed by 2-3 weeks simply due to this one essential step.

Next, after sonication of the graphite in NMP, the sonicated dispersion was placed in an ultracentrifuge at 1500 rpm for 90 mins (as outlined in [2]) in preparation for a solvent exchange from the toxic NMP to the less-toxic and more volatile chloroform. However, upon attempting to sonicate the centrifuged dispersions we noticed that the pellet at the bottom of the centrifuge tube seemed to obtain the vast majority of the exfoliated graphene, leaving mostly graphite-free NMP in the supernatant that was filtered. This resulted in very low graphene yields. To prevent the pellet from growing so quickly the centrifuged dispersions were resonicated for 90 - 120 mins before being centrifuged again, this time at 700 rpm for <15 mins. This had the desired effect of forming a pellet with the largest flakes of graphite while leaving behind some exfoliated graphite in the supernatant. The filtered graphite paste was then redispersed in chloroform at a concentration of ~10mg/mL in preparation for mixing with pristine PDMS putty.

At this stage it was possible to begin the first of the validation tests, namely the SEM imaging of the exfoliated graphite. To accomplish this, a droplet of the chloroform/exfoliated graphite dispersion was drop-casted onto a clean silicon wafer and dried overnight to allow the chloroform to evaporate completely before being imaged by SEM. The resulting images (Appendix G) showed that the sonication was successful in producing a normal distribution of sub-micron flakes of exfoliated graphite (graphene), although the mean flake size was a few

hundred nanometers larger than that of the source paper presumably due to the lower sonication amplitude.

This validation also confirmed that we met the first functional engineering specification outlined in our original project proposal: obtaining a size distribution reasonably close to that of the source paper. Note that the size listed for this specification (~200 μm) is actually the lower end of the size distribution observed in the source paper, with their mean flake size being ~400 nm (approximately 200 -300 μm smaller than our mean flake size). With the completion of the sonication, preparation of the putty was started, although in retrospect we realized that starting the putty preparation in the final week of sonication would have potentially saved the team a few days of time.

The next step of the first phase required we prepare samples of ‘pristine’ PDMS putty akin to commercial Silly Putty™ which is also made using PDMS (silicone oil). Starting with ~ 10 mL of Sylgard 184 silicone oil with a viscosity of roughly 4000 mPa.s, 3 g of finely ground boric acid powder was thoroughly mixed into the oil. Heating the oil/boric acid mixture past 150 °C results in the thermal cleavage of the siloxane bonds in the silicone oil, exposing OH groups to the boric acid present in the mixture and eventually undergoing a condensation reaction with the boric acid to form weak, non-permanent crosslinks with a relaxation timescale on the order of a second. Heating the oil required a few attempts by our team due to the uneven heat distribution of the mixture in the beaker when heated using a hotplate. Using a hotplate temperature above 250 °C ensured that the solution remained above the critical temperature for thermal cleavage.

The condensation reaction was evinced by the steam coming from the beaker in which the oil mixture (now a milky white colour) was being stirred. After 20-30 mins of stirring at high heat, the viscosity of the oil had increased significantly to >3000 Pa.s. at which point removal from the beaker with a metal spatula yielded a viscoelastic white putty not unlike commercial Silly Putty™. With the creation of this ‘pristine’ putty, the only remaining step in the first phase was to mix the putty with the exfoliated graphite and validate that the resulting nanocomposite was conductive and pliable.

Upon introducing 2 g of pristine putty to approximately 52 mL of the ~10 mg/mL chloroform/graphene dispersion, the putty was seen to dissolve completely in the volatile

organic solvent. The resulting solution was mixed by stir bar for 2 hrs before being sonicated using a low-power bath sonicator for another 2 hrs for further mixing. After these mixing steps the chloroform was allowed to evaporate from the solution by raising the temperature of the solution to roughly 50 °C for 6+ hrs. After the majority of the chloroform had evaporated, the resulting paste was allowed to dry overnight in the fume hood to get rid of any residual solvent.

The high loading factor of graphene in this dried stock graphene-putty paste (25%) made the putty appear distinctly black. However, despite this seemingly high loading factor, initial resistance measurements using handheld multimeters for validation showed the stock putty to be non-conducting ($R > 60$ MΩ). We saw the same result for the 2 g to 52 mL ratio samples regardless of drying time or extent of mixing, and could not even measure any appreciable current through the stock putty at very high voltages (30+ V) suggesting the resistance of the putties was above the 10 - 100 GΩ range, which certainly was much too high to feasibly meet the first requirement of being safe to use if it required voltages >50V to operate.

To address this problem different ratios of putty to chloroform/graphene were tried. We found that a ratio of ~1 g to 100 mL resulted in a powder-like ‘putty’ that was no longer viscoelastic in nature, but a more conservative ratio of 2 g to ~80 mL had the desired effect of creating a viscoelastic conductive putty. Validation resistance tests on this putty showed it had a resistance in the kΩ - MΩ range as expected, with the resistance changing rapidly when any force was applied to the putty. The final functional specifications for the first phase as outlined in Appendix C mandated that the putty have a fill fraction of ~7% +/- 1% (which, being close to the percolation threshold, was determined to be the ideal volume fraction in the source paper) and be stable (not prone to disintegrating or leaving residue).

Our experiments adjusting the loading factor of graphene by changing the ratio of pristine putty to exfoliated graphite showed that a ratio of approximately 2 g of putty for 80 mL of 10 mg/mL chloroform/graphene solution (~15% fill fraction) yielded a sensor with a resistance in the desired kΩ - MΩ range. We expect that our higher mean filler size and a wider size distribution of graphene flakes was responsible for the higher fill fractions required by our nanocomposite in order to be sufficiently conductive. Thermogravimetric analysis (TGA) was considered as a way of comprehensively determining the volume fraction of graphene in each sample, but was

deemed unnecessary given that the sample with an estimated 15% fill fraction passed the resistance validation as shown in Figure 1.

The final condition for the Phase I milestone required that the nanocomposite be stable and remain intact during use. Our team found that whereas the wet paste containing residual solvent was sticky and prone to disintegrating, the completely dried samples with will fractions <30% all behaved for the most part like normal Silly Putty™ (perhaps slightly more grainy at higher fill fractions). Rolling the composite around in our gloved hands did, however leave behind a light, pencil-like residue at higher fill fractions, almost as though we were handling a pencil lead. After considering the safety concerns associated with graphene making contact with the skin we still considered the composite to have passed the stability specification, although the issue is analysed in more detail in the Safety Considerations section.

Any further validation and characterization such as stiffness and rheometry testing was deemed unnecessary and/or not worth the time given the fact that our composite sensors sample had the desired feel (putty-like, conformable) and behaviour (i.e conductivity) which was the ultimate goal of the Phase I validation tests and specifications.

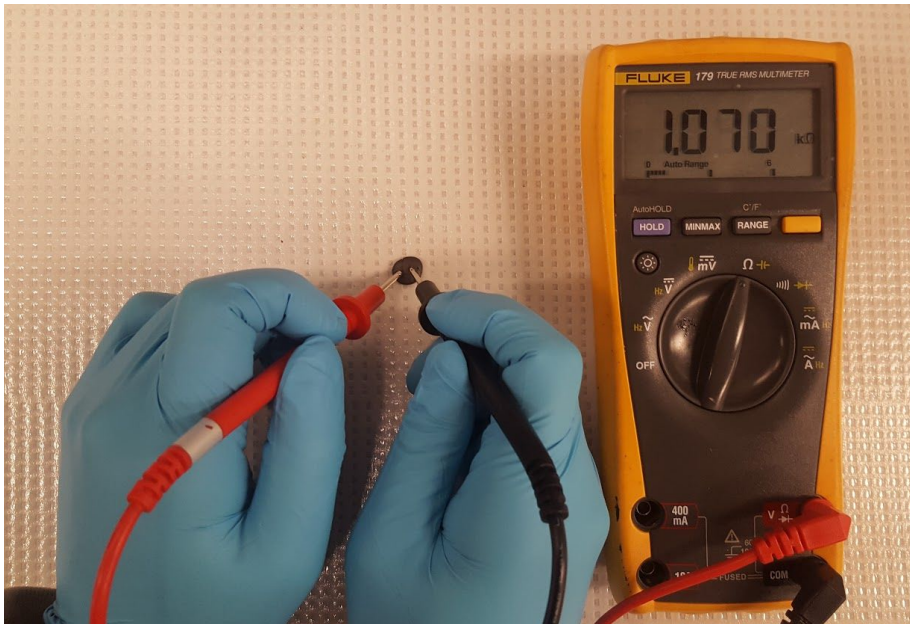

Figure 1: A sensor with a fill fraction of ~15% displaying a bulk resistance in the kΩ range.

Phase II & III: Electrode/Demo Design

With the completion of the fabrication of the conductive viscoelastic putty the last two phases were focused on ensuring that the sensor had its intended functionality. More specifically, the milestones for second phase mandated that the sensor have the necessary resolution and sensitivity to resolve signals from a simulated heartbeat without added inconvenience. The functional specifications for this phase were set quantifiable goals for these milestones. Most importantly the sensor needed to be able to resolve pressures as low as 40 mmHg (half of the average diastolic blood pressure in humans) to demonstrate it was capable of detecting both blood pressures and heart rates. In addition, the sensor needed to be stable over a 30s period and not require additional sensing equipment (e.g. the grounding electrodes for 12-lead ECG) that could pose an inconvenience to the end user.

Starting from the < 2 g of viscoelastic putty created in the first phase, the first step in meeting the specifications for the second phase required that we develop a comprehensive understanding of mechanism behind the change in resistance associated with the application of an applied force. Like any tactile sensor, the overarching goal of the sensor is to transduce an input signal (in this case, an applied force) into a proportional output signal. For the elastoresistive sensor created in phase one, this output signal comes as a result in the change in the resistivity of the putty upon applying a mechanical load.

Typically, less malleable nanocomposite tactile sensors will experience a decrease in resistivity when a (normal) force is applied due to the conductive graphene network being compressed. This compression decreases the distance between neighbouring conductive filler particles, consequently increasing the tunneling current through the bulk material. However, in the case of a 3D sphere of our conductive putty we instead observed an increase in bulk resistance upon applying a force. Moreover the change in sensor shape/volume as a result of the load resulted in a change in resistance associated with the change in geometry which competed with the change in resistance from network deformation making it difficult to receive consistent output signals. This behaviour (the increase in resistivity) was likely a result of the graphene network deforming under load more than being compressed. To limit this competing behaviour we reshaped a small area of the putty into a thin (<1 mm) circular disk. In this shape, applying a

load while measuring the current at a constant 5V resulted in an increase current corresponding with the expected drop in bulk resistance.

At this point the putty sensor was ready for testing with simulated heartbeats. To accomplish this load tests were performed using a piezoelectric load cell capable of reliably applying pressures as low as 40 mmHg. The current through the sensor for a constant 5 V was measured using a precision DMM, with the probes making contact with the sensor at opposite sides of the active sensing area. When combined with a custom LabVIEW virtual instrument capable of recording and saving both the input (force) and output (current) data in realtime we were able to compare the performance of our graphene-infused putty sensor to the aforementioned functional engineering specifications. The overall setup is pictured in Figure 2.

To evaluate whether the flat putty sensors passed the heart rate/blood pressure resolution requirements, the force required to apply a uniform pressure onto the active sensing area (circular diameter: 1 cm) was calculated and found to be ~0.2 lbf for a pressure of 40 mmHg. Applying a ‘hard’ normal force of 1 lbf (roughly 7x the force required to actuate the typical keyboard switch) and a ‘soft’ normal force of 0.2 lbf ensured that the two conditions related to resolving heart rate (relatively hard) and blood pressure (soft) were checked. This test was combined with the main prototype test outlined in Appendix E which compared the response of a commercial flexible piezoresistive pressure sensor (Flexiforce) to that of our prototype putty sensor for both the hard and soft loads.

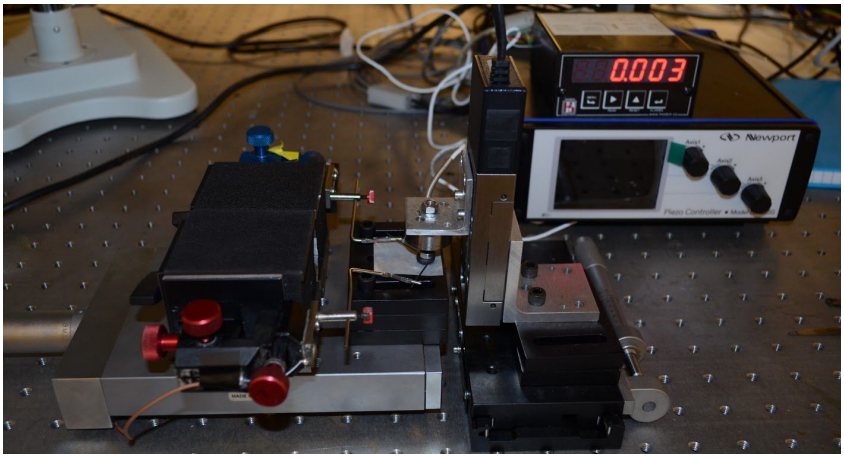

Figure 2: The setup used to measure and record the response of the putty sensor under load.

As we had initially hoped, the putty sensor was able to resolve both the ‘hard’ and ‘soft’ normal forces and thus met the key functional requirements of the second phase. On the other hand, although the flexible (but not particularly conformable) commercial Flexiforce sensor successfully resolved the ‘hard’ applied load, it failed to produce a detectable current response under the ‘soft’ applied load that corresponded with the diastolic blood pressure. The data from these measurements is available in Appendix H. The sample putty sensor also met the reusability and convenience requirements outlined in the Phase II functional specifications by not require multiple electrodes, being reusable, and using a minimal number of connections/leads.

By passing these key functional requirements our team reached a major milestone in our project by demonstrating the potential for these nanocomposite sensors in heart sensing applications. However, the final stability functional requirement for the second phase presented a number of challenges with our prototype putty. Although our prototype successfully could resolve ‘soft’ input loads over periods of ~30s as specified in the functional specification, timescales beyond this were prone to significant output signal drift as a result of the relaxation of the viscoelastic putty and its embedded conductive network. This is a natural consequence of the short relaxation timescales for the reversible PDMS crosslinks which allows the sensor to display remarkable malleability and conformability, but also results in the gradual reformation of the conductive network over timescales on the order of ~1 min making it difficult to resolve small output signal underneath the superimposed resistance relaxation/drift.

Moreover, the extreme sensitivity of the putty sensor made it prone to motion artefacts, although these artefacts would be relatively easy to address with straightforward and well-established digital signal processing (DSP) filtering techniques. However, the difficulties associated with subtracting a variable relaxation/drift baseline from a signal are not as easy to address, which unfortunately rendered most of the remaining functional requirements for Phase III (related to having a simple demonstration of heart signal capturing for the symposium demonstration) **infeasible** given the time restraints and the inherent complexity of the signal processing required to stabilize the signal over the periods required for arrhythmia detection (the last functional specification of Phase II), for example.

Overall, the major milestones associated with the second and third phases were still completed, just not to the extent planned in the interim plans and functional specifications. This is mainly a result of the aforementioned drift problems, the time constraints, and the potential safety concerns associated with the use of graphene in the sensor (analysed in more detail in the following section). Rather than demonstrating heart sensing functionality at the symposium as initially planned for the Phase II milestone, a small mass of sensing putty was placed between two glass slides and connected to a handheld multimeter to demonstrate the working principle behind the sensor (change in resistance for small applied force) and compared beside the commercial sensor hooked up to a second handheld DMM.

Summary & Future Outlook

Overall we were successful in meeting our main goal of creating a robust sensor that was flexible, conformable, and also sensitive. The prototype sensor passed the key tests (outlined in Appendix E) designed to confirm its potential as a wearable cardiac sensor. More specifically, it successfully resolved normal pressures as low as the 40 mmHg threshold specified as the target sensitivity threshold without sacrificing the flexibility and conformability of the sensor. Comparing our sensor to the traditional sensing technologies our prototype sensor demonstrates sensitivities significantly higher than traditional sensing technologies even for relatively low fill fractions (which allows the composite to retain the viscoelastic properties of the PDMS putty matrix). Table 1 provides a brief comparison of the sensitivity performance of other composite sensors from literature whereas Appendix I provides a more comprehensive comparison of the properties of traditional tactile sensing technologies.

According to the source paper the gauge factor is on the order of 100 - 500 for viscoelastic nanocomposite graphene sensors (depending on the strain amplitude), which is orders of magnitude higher than traditional strain gauges. Based on our estimations the gauge factor of our prototype was in this range although without access to dedicated strain testing equipment it is difficult to measure the low strain amplitudes we saw for our flat disc prototypes. Unlike most other nanocomposites our prototype can also sustain strain amplitudes well over 100% as compared to other nanocomposites that typically operate in the <10% range. The response time of our sensor was also well within in the range of being effective for our desired application (<100 ms).

However, the tradeoff for the high malleability of our prototype was the long-term stability of the sensor. Although the prototype exhibited linearity and cyclic stability for the <30s measurement periods used in our prototype tests, the ~1s relaxation timescale of the reversible cross links that give the PDMS putty its remarkable conformability caused the stability of the output signal to drift over timescales >1 min due to relaxation. This limitation and others are summarized in the following section.

Table 1: Brief comparison of nanocomposite sensitivities using selected literature values

Sensor type	**Publication**	**Vol. Frac. (%)**	**Gauge Factor**
Metallic foil gauge (low strain amplitudes)	-	-	2
TPU + Graphene (low strain amplitudes)	H. Liu, Y. Li, K. Dai, G. Zheng, C. Liu, C. Shen, X. Yan, J. Guo and Z. Guo, "**Electrically conductive thermoplastic elastomer nanocomposites at ultralow graphene loading levels for strain sensor applications**", Journal of Materials Chemistry C, vol. 4, no. 1, pp. 157-166, 2016.	0.011	5.4
Latex + Graphene (30% strain amp.)	Y. Lin, X. Dong, S. Liu, S. Chen, Y. Wei and L. Liu, "**Graphene–Elastomer Composites with Segregated Nanostructured Network for Liquid and Strain Sensing Application**", ACS Applied Materials & Interfaces, vol. 8, no. 36, pp. 24143-24151, 2016.	0.42	6.9
NR + Graphene (>30% strain amp.)	C. Boland, U. Khan, C. Backes, A. O'Neill, J. McCauley, S. Duane, R. Shanker, Y. Liu, I. Jurewicz, A. Dalton and J. Coleman, "**Sensitive, High-Strain, High-Rate Bodily Motion Sensors Based on Graphene–Rubber Composites**", ACS Nano, vol. 8, no. 9, pp. 8819-8830, 2014.	0.67	35
Our prototype (estimated values)	-	~15%	~100
PDMS + Graphene	C. S. Boland, U. . Khan, G. . Ryan, S. . Barwich, R. . Charifou, A. . Harvey, C. . Backes, Z. . Li, M. S. Ferreira, M. E. Möbius, R. J. Young and J. N. Coleman, "**Sensitive electromechanical sensors using viscoelastic graphene-polymer nanocomposites**," Science, vol. 354, no. 6317, p. , 2016.	6.76	500

Limitations

As it was previously shown, the prototype sensor successfully resolved ‘soft’ (<40 mmHg) and ‘hard’ loads for short periods. However, long periods (over about 30 seconds) are subject to output signal drifts/shifts and can be challenging to resolve. This drift is simply a result of the relaxation of the putty due to its viscoelasticity which also what gives the sensor its conformability. The inevitable reformation of the conductive network makes it challenging to resolve small output signals underneath the superimposed resistance relaxation without a dedicated signal processing efforts.

Since heart health usually requires long term monitoring, we would need to use digital signal processing that would filter out such drifts. Our proposed approach for the necessary signal processing would use the Fast Fourier Transform (fft) that would transform a short time signal from its original domain (time) to the frequency domain. Extracting the fundamental frequencies and amplitudes of this short time series would allow us to reconstruct a periodic signal free of drift. However, even with a perfect reconstruction of the signal from a few seconds of data, information related to anomalies in the signal (i.e arrhythmias) is lost in reconstruction meaning any implementation of a DSP algorithm for our prototype sensor would need to be dynamic enough to adjust and update on the fly. A schematic of our proposed DSP approach is pictured in Figure 3.

Another limitation is the sensitivity/conformability tradeoff that exists in any composite sensor. The sensitivity of our sensor could be controlled by tuning the filler-to-matrix ratio. Adding more of the graphene (conductive filler) would increase the sensitivity of the sensor, however this would come with the cost of it being less flexible/conformable. Fortunately, one of the advantages of using a nanomaterial as a conductive filler is that the sensitivity can be adjusted with very small changes to the already low fill fraction meaning that the overall composite for the most part maintains its intrinsic properties even after being infiltrated with a conductive filler.

Another limitation would be reproducibility which is tied to the problems with scaling up the technology. Due to the extreme sensitivity of the nanocomposite and the dependence of its performance on the fabrication method and morphology it would be difficult. Moreover, because

extracting graphene sheets from graphite is very time-intensive and sensitive to changes in preparation, attempts to reproduce sensor behaviour and could result in sheets with different flake sizes as shown from our results. This would thus result in sensitivity variations for different putties even with the same morphology and fill fraction.

Figure 3: Schematic of proposed signal processing framework

Environmental Concerns

Due to the relative recency of the development of nanotechnology we are only now beginning to understand the potential risks associated with engineered nanomaterials. These concerns extend to the use of graphene nanosheets in our project.

Whereas engineered nanoparticles are produced intentionally, ultra-fine particles usually refer to an incidental byproduct of some process (e.g. vaporization, combustion). However, according to the recently published report ‘Approaches to Safe Nanotechnology’ from the Centers for Disease Control and Prevention, the reported effects of ultra-fine particles such as particulate matter from exhausts serve as a good proxy for the expected effects of engineered nanoparticles of the same scale. More specifically they found that ‘if engineered nanoparticles have the same physicochemical characteristics that are associated with reported effects from ultrafine particles, they may pose the same health concerns’ [7], with inhalation being the most common route of exposure.

The same report also found that ‘surface area and activity and particle number’ appeared to be better predictors the of potential hazards associated with a nanoparticle that its than mass. Animal inhalation studies looking at the effect of graphene analogues such as carbon nanotubes (CNTs) suggest that high-surface area nanoparticles can be particularly damaging to lung tissue, resulting in inflammation, a decrease in pulmonary function, and early onset of interstitial fibrosis among other symptoms (Figure 4). Given that the size distribution of the graphene

nanosheets required for our products also results in engineered nanoparticles with extremely high surface areas, extra care must be taken during the preparation of the graphene nanosheets for our viscoelastic sensors.

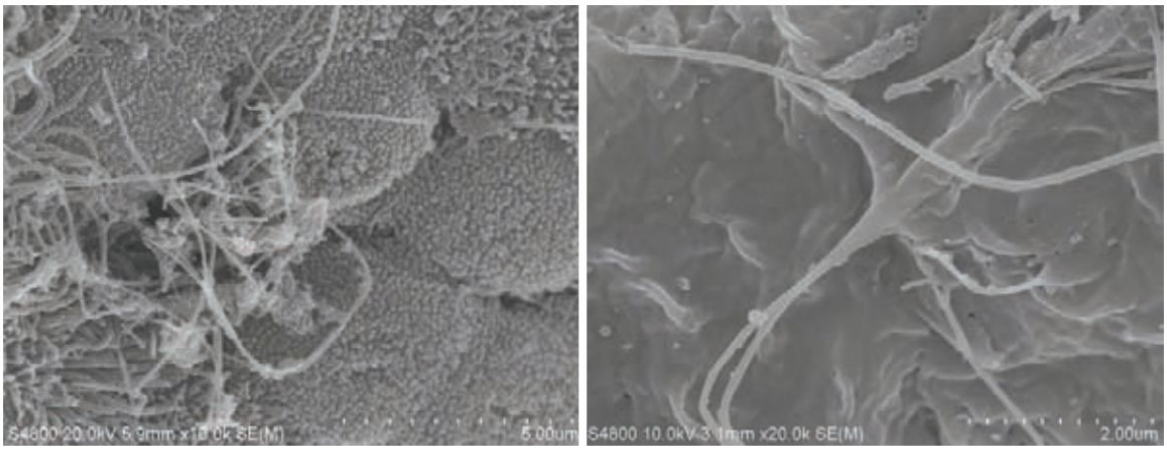

Figure 4. Deposition (left) and clearance (right) of MWCNTs from the conducting airways of mice following inhalation exposure [7]

Fortunately, the liquid phase exfoliation technique used to prepare the graphene nanosheets from the graphite powder minimizes the risk of the graphene nanosheets becoming airborne at any point during the preparation of the sensors as the graphene remains suspended in a solvent throughout the exfoliation. The only fabrication step with a risk of the graphene becoming airborne is the vacuum filtration of the graphene in NMP before being re-dispersed in chloroform. This step will be performed in a fume hood outfitted for use with nanomaterials to ensure that no airborne particles are introduced to the working environment. Because the polymer matrix is stable, inert, and safe enough to be handled by young children, the risks associated with inhalation are miniscule during fabrication and for the eventual end-user.

Although inhalation risks are minimal, there are still some risks associated with ingestion of the small chunks of the putty with or without the graphene nanosheets. Commercial silly putty itself is completely non-toxic when ingested or inhaled, but the introduction of the exfoliated graphite will potentially introduce some risks associated with the ingestion of the putty. The size of the

sensors could also potentially pose a choking hazard if a small child were able to detach the sensor, but both of these concerns can be addressed in the design of the sensor housing.

Biocompatibility Concerns

Another consideration is the interaction between the graphene-functionalized putty and the skin. Because the graphene is stably dispersed in a polymer matrix, we do not expect there not be any adverse effects, especially at low concentrations/fill fractions. Graphene has also been used in epidermal sensors and tattoos (Figure 5) for medical sensing. Based on these studies the graphene will not permeate or irritate the skin.

However, there are still many contrasting opinions on the toxicity of graphene and graphene-like materials. Some recent studies suggested that graphene-based materials might be hazardous to our health, while some other in vitro and in vivo studies indicated no toxicity. In order to address this inconsistency, various studies have been done to understand the intrinsic toxicity of graphene using pristine graphene to examine its biocompatibility. By definition, pristine graphene is referred to monolayer graphene produced by processes such as CVD, or few-layer submicron-sized graphene sheets produced by liquid exfoliation process. These graphenes are free of oxides, defects, or any non-carbon functionalities.

A group of researchers conducted a multimodal biohazard assessment on pristine graphene to examine the potential biological effect on human body cells by using A549 cell line as to imitate for the inhalation exposure and skin contact. A549 cells were planted on pristine graphene film and on glass as a baseline. After 24 hours of exposure, the two samples were compared to observe any noticeable difference in the gross structure of the cytoskeletal proteins actin, tublin or the morphology of cells [12]. However, the aforementioned cellular structures of both samples did not change, or no nuclear abnormalities were observed. The result indicates that pristine graphene sheets are biocompatible in the lung. Further experiment was conducted similarly but using ultrafine carbon black as controls. This experiment differentiated the concentration of both graphene nanosheets and ultrafine carbon black from 1 to 5 ug/mL. The result showed that non-toxic responses for graphene nanosheets, while a cytotoxic responses were observed for ultrafine carbon black at 5 ug/mL. Additional experiments using the similar concepts but using different measuring techniques or devices, such as live cell-based electrical impedance sensing,

automated fluorescence microscopy, or automated image acquisition and multi-parametric analysis [12], were done and indicated that pristine graphene sheets are non-toxic to our human body. In other words, pristine graphene flakes or thin films are biocompatible at the concentration range of 1 to 5 ug/mL, therefore can be used in many biotechnological, electrical, medical applications.

Given the relatively low fill fraction of graphene in our sensors we do not expect irritation or allergic reactions to be an issue. Moreover, even at low fill fractions the high resistance of the putty is high enough to ensure that very low currents will be required in order to derive a signal from the sensor. At such low currents there is little risk of electrical shock.

Figure 5. Recent studies take advantage of graphene's extraordinary properties in medical epidermal sensors. Pictured is a graphene arm tatoo used for health sensing [10]

Acknowledgements

Our group would like to send our acknowledgements to the following people and facilities that enabled the pursuit and development of this project.

1. Professor Vivek Maheshwari, our project consultant for lending his expertise and offering us his laboratory space, access to all necessary testing and characterization equipment. His continuous support and project guidance has been a great deal of assistance in exploring this project to this degree.

2. Velocity Science for allowing us to use their laboratory facility and equipment. As the high-powered tip sonicator was a crucial aspect in our material synthesis process, consistent and reliable access to said equipment has afforded us both cost and time efficiency.

3. Dr. Coleman and his team at Trinity College Dublin for being the first to demonstrate the potential for this material and providing guidance when needed. Their willingness and enthusiasm to answer our questions has been a great deal of support particularly in reaching the current timeline in our project.

Glossary

The following is a list of the acronyms used throughout the report with a brief description of the items.

MEMS Microelectromechanical System. *A form of technology defined by miniaturized mechanical and electro-mechanical elements specifically structures and devices that are made using microfabrication techniques.*

ECG Electrocardiography. *A process that utilizes electrodes placed on the skin to record the electrical activity of the heart over an extended time period.*

PPG Photoplethysmogram. *An optically resolved plethysmogram that takes the volumetric measurement of an organ by illuminating the skin to measure changing light absorption.*

BP Blood Pressure. *The pressure measurement of circulating blood against the walls of blood vessels.*

BPM Beats Per Minute. *The total number of detected heartbeats in a one minute time frame.*

PDMS Polydimethylsiloxane. *An inert, non-toxic and optically clear silicone based organic polymer used as one of the main ingredients for Silly Putty synthesis.*

TGA Thermogravimetric Analysis. *A material characterization tool that measures the temperature changes in conjunction with the mass change of a sample over time.*

NMP N-Methyl-2-Pyrrolidone. *An organic solvent used as a stabilizing and dispersion agent for exfoliated graphene sheets.*

SEM Scanning Electron Microscope. *A material characterization tool that utilizes an electron gun to generate images by scanning the sample surface with a focused electron beam.*

DSP Digital Signal Processing. *The use of digital processing to perform various signal processing operations.*

FFT Fast Fourier Transform. *An algorithm that converts a sample's signal over the time domain and divides it into components in the frequency domain and vice versa.*

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Appendix A: Interim Customer Requirements

The main customer requirements we've identified are what we consider to be feasible improvements to the end-user experience for existing cardiac sensors, which our team has worked with and experienced first hand.

Each requirement is tied to a quantitative specification detailed in the Engineering Specification section for each phase.

Primary

The following requirements are the main requirements of the proposed sensor from the perspective of the prospective end-user. The requirements are listed (roughly) in order of their priority.

6. **Safe to use** (Non-allergenic, non-toxic, not otherwise hazardous). The sensor and any associated elements (housing, hardware, etc.) should not pose any risk - electrical, allergenic, or otherwise - to the end user (including children).
7. **Heart rate** (in BPM) can be derived from output waveform
8. **Blood Pressure** can be derived from the output waveform (after calibration)
9. **Convenience** sensor should be comfortable and user friendly (easily portable, minimal connections)
10. **Arrhythmia detection** can be resolved from the arterial pressure waveforms

Stretch Goals

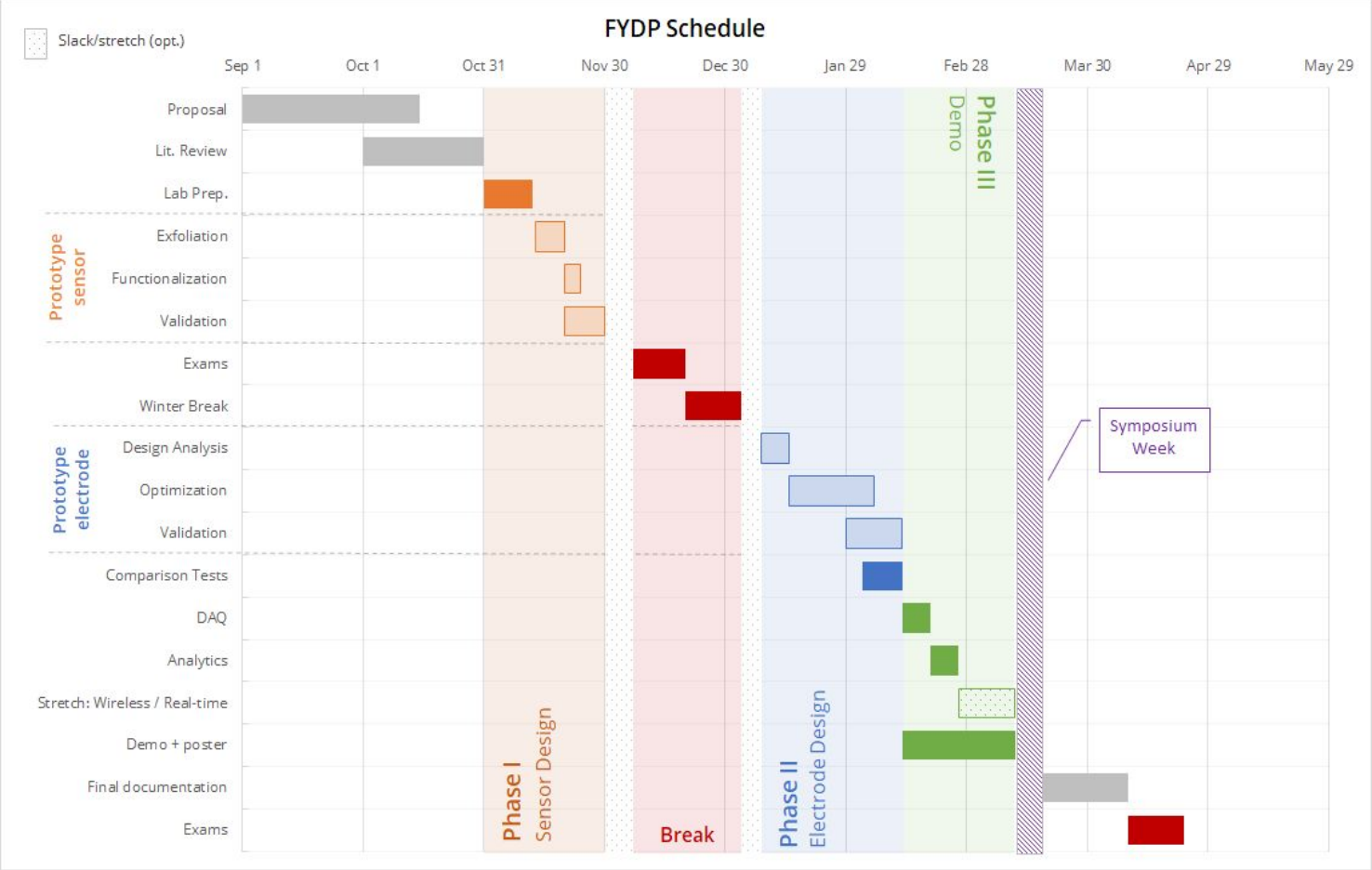
The following customer requirements are optional stretch goals that we are unlikely to pursue unless ahead of schedule due to the difficulty associated with the implementation of some of these features. In the case that there is time to add these features, they will mostly likely be implemented in the order that they are listed

1. **Wireless capabilities** and communication; real-time interface
2. **Reporting functionality** that can alert patient's family doctor when dangerous arrhythmia is detected for immediate patient care
3. **Motion detection/active filtering**

Appendix B: Interim Project Plan and Milestones

The key milestones of the project are depicted in the following preliminary Gantt chart. These timings are subject to change as the project develops and are specifically designed with slack/contingency time built in.

Even with delays accounted for, the timeline is subject to change as the project develops. The schedule is designed such that the majority of the work will be done the month before the symposium allowing the team time to prepare sufficiently for the demonstration and final documentation.



The main lab space will be provided by Prof. Vivek Maheshwari. The required safety trainings are as follows:

1. **Workplace Violence Awareness** – SO1081
2. **Employee Safety Orientation** – SO1001
3. **WHIMIS** 2015 – SO2017
4. **Laboratory Safety** – SO1010

All the listed trainings are accesible through the University of Waterloo website (https://uwaterloo.ca/safety-office/training/training-programs). All group members completed the required training and are well equipped to work with the materials and solvents from training and past experience.

Required equipment includes:

1. Centrifuge
2. Vacuum Line
3. Hot Plate
4. Fume hood with nano-filter
5. Sonicator
6. Piezoelectric Load Tester
7. Electrical Test Equipment
8. General lab equipment (glass vials, stir bars, etc.).

A recent tour of the lab space confirmed it was appropriately equipped for the project. One additional equipment that is essential for the project is an ultrasonic tip-sonicator. This will be provided to us free by the Velocity Science lab in Downtown Kitchener.

The majority of the chemicals required to prepare the sensor will be purchased using the assigned budget (see below)

Material	Min. Quantity	Cost (CAD)	Supplier
Sensor Preparation			
99.99% Graphite	28 g	$59.99	Alfa Aesar
N-methyl-pyrrolidone (solvent)	2 L	$290.50	Sigma-Aldrich
25mm PTFE filter (0.1µm)	1 box	$275.37	Sterlitech
Carbon Black	5 g	$155.50	Sigma-Aldrich
Silicone Oil (polymer)	1 L	$110.00/ 2L	UW Chem Store
Boric Acid	1 kg	$80.30/kg	Sigma-Aldrich
Chloroform	2 L	$37.28	UW Chem Store
Equipment Testing & Validation			
Electrical Test Leads	5 Ft	$15.75	uGem/ Amazon
Adhesive Bandage	1 box	$45.75	CANMedDirect.ca
Vacuum Filtration	Provided		-
Centrifuge	Provided		-
Piezoelectric Load Cell	Provided		-
Voltage Source, DMM	Provided		-
Tip Sonicator	Provided		Velocity Science
Bath Sonicator	Provided		Velocity Science
SEM	Provided		University of Waterloo
Polarized Raman Spectroscopy	Provided		University of Waterloo
Rheometer	2	$25/hr	University of Waterloo

(continued next page)

Totals			
Subtotal*	-	$1120.44	
Shipping/Taxes*	23%	$257.70	
Contingency	10%	$112.04	
Total	-	**$1490.18**	

Note: The $600 currently allocated to our group does not cover the cost of the minimum orders for *Sensor Preparation*. Requesting samples and using carbon black/graphite purchased by the lab has allowed us to operate so far, but the cost of the solvent and 0.1 µm filters alone eliminates most of our budget and forces us to depend on the generosity of other labs. Please consider re-evaluating our budget.

Having consulted with our faculty supervisor, the following budget proposal has accounted for all materials and equipment required for this project. There is a 10% contingency cost included to factor in any additional supplies that may be required in the future.

The "*Sensor Preparation"* section shown in the table above includes the key chemicals required for our material synthesis, refer to detailed procedure in Appendix A.

The "*Equipment Testing & Validation"* section of the table includes all the required equipment for sensor fabrication and material characterization. The majority of testing equipment required is made available to us through Prof. Maheshwari. We expect a relatively high cost for material characterization as SEM requires the completion of user training and further supervision from lab manager's and equipment operators.

As we are purchasing a number of our materials from suppliers outside of Canada, the percentage of shipping costs and taxes have been calculated referring to quotes received from external suppliers.

Our Team

Chris Williams *Team Lead*

Chris has worked extensively with health sensors and shares a patent with the President of the Canadian Royal Academy of Science for technology using novel signal processing methods for extracting metrics from health sensors. He has also co-authored papers with groups at MIT & Harvard related to graphene & microfiltration membranes respectively.

JaeJung Kim *Verification & Testing Lead*

Jae's industry experience as a process engineer and his deep understanding of the impact of different experimental parameters on the efficacy of sensitive cleanroom processes makes him well suited to the role of characterization & testing lead. In the past he has also researched the effect of annealing on novel nanoscale pillars.

Justin Ahn *R&D Lead - Materials*

Justin has worked with industry companies to solve material scalability challenges and their integration into processes. Justin's extensive experience with designing experiments for electrochemical material synthesis and in testing of novel nanoscale battery electrode materials lends itself to his role as a research and development lead.

Ahmed El-Madkhoum *Product Lead*

Having recently been diagnosed with an arrhythmia of his own, Ahmed has had first-hand experience with current cardiac monitoring technology. Discovering these palpitations spurred him to develop a detailed understanding of the diagnosis and mechanism of his own arrhythmia and others that will help him create a product with the customer in mind.

Dr. Vivek Maheshwari *Faculty Supervisor*

Prof. Maheshwari's years of expertise in researching polymer rheologies and recent research developing novel dynamic sensors using nanoscale viscoelasticity makes him a valuable addition to our team.

Appendix C: Interim Functional Specs

Phase I Engineering Specifications

This section outlines the quantitative goals we've set for the first verification phase in our design plan. These specifications are in agreement with parameter values that were identified to be optimal for a sensor with our desired sensitivity. The Verification & Testing section details the equipment that will be used to measure these parameters.

Nanosheet Dimension: ~200 μm

Creating graphene with approximately the same size distribution as outlined in the seminal paper ensures that the conductivity and sensitivity of the sensor (a function of the number density of connections) are similar to the unprecedented values measured in the source paper.

Graphene Fill Fraction: 7% (+/- 1%)

Based on the nanocomposite material parameters (namely conductivity and stiffness) outlined in the source paper, a fill fraction of ~7% should work the best for our purpose. The target **conductivity** can also be defined as it is a function of this fraction.

Composite Stability: Infused putty should not disintegrate or leave any visible residue on paper or skin at normal operating temperatures. No appreciable mass loss from repeatedly adhering putty to surface (+ **safety**)

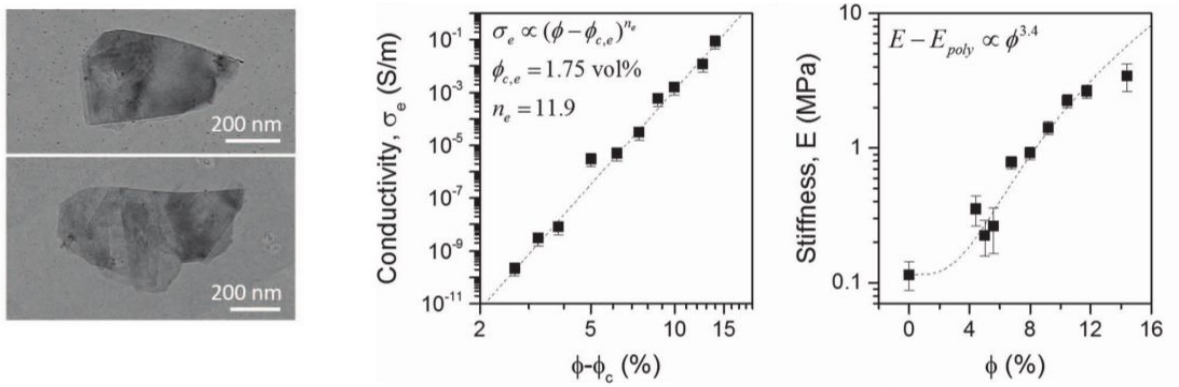


Figure 2: *(Left)* TEM images of exfoliated graphene nanosheets with the desired dimensions *(Right)* Plot of the conductivity of the functionalized putty as a function of reduced graphene volume fraction, $\phi - \phi c$, where ϕ is the volume fraction and ϕc is the electrical percolation threshold [1]

Phase II Engineering Specifications

This section outlines the quantitative goals we've set for the second verification phase in our design plan. The engineering specifications associated with this stage is focused around setting quantitative targets that define whether or not a sensor design is 'functional' or not.

Heart Rate: The sensor should be able to resolve heart rates between 60 bpm and 120 bpm. This range covers heart rates above and below the average resting heart rate (RHR: ~70 BPM)

Pressure Resolution: At least 40 mmHg (0.5x typical diastolic pressure in humans). Resolving this pressure should enable the computation of the blood pressure from the output signal (+ **capabilities**)

Continuous signal: A heart rate should be able to be resolved in under 30 seconds (throughout relaxation). In comparison, a typical 12-lead ECG requires 10 electrodes and ~10 seconds (+ **convenience**).

# of Electrodes: Clear output signal should not require multiple electrodes, should be reusable, and should use minimal connections/leads. Single electrodes should have intuitive placement so that the average person could obtain a useful output signal (+ **reusability & convenience**)

Phase III Engineering Specifications

This section outlines the quantitative goals we've set for the final verification phase in our design plan. The engineering metrics set for this phase are related to the development of the interface of the functional demo.

Signal to noise ratio: Stationary: Resolvable without processing (by eye)
Signal to noise ratio: Walking: Resolvable with basic signal filtering

Simulated/Real Pulse:
(Software can identify simple arrhythmia from pressure waveforms with 60% accuracy)

Layman test: A person not involved with the project should be able to set up, place, and operate the sensor with minimal assistance such that their heart rate can be measured

Appendix D: Interim Verification Plans

The preparation of the viscoelastic graphene-polymer nanocomposite as outlined in the Boland et. al's seminal paper [2] uses liquid-phase exfoliation of graphite in an organic solvent to create a stable dispersion of conductive graphene nanosheets. These solution phase methods are commonly used to produce suspensions of almost entirely few-layer sheets of graphene [8]. This dispersion is then mixed in solution-phase with a silicon polymer matrix where the solvent is allowed to evaporate. The resulting nanocomposite putty retains some of graphene's extraordinary properties—namely its conductivity—due to the presence of the nanosheets now embedded throughout the soft polymer matrix. This conductivity is evident as there is a linear increase in the DC (direct current) electrical conductivity of the composite material as a function of the conductive graphene 'filling' the polymer matrix (see Figure 2).

In practice, the graphene forms a vast network of partially-connected conductive paths throughout the polymer matrix [9], as pictured in Figure 1. The deformation induced by strain causes pseudo-magnetic fields throughout the matrix that leads to significant changes in conductivity [8], allowing the resulting matrix to be used as a highly sensitive electromechanical sensor. As it stands, the quality of nanofiller dispersion in the polymer matrix directly correlated to its effectiveness for improving the electrical and mechanical properties. In addition, the aspect ratio of the material and the surface-to-volume ratio of the filler are crucial optimization parameters outlined in detail in the engineering specifications. Fortunately, in order to render the insulating polymer matrix conductive, only a small fraction of the matrix needs to be filled with the highly conductive nanosheets. Due to the low fill fraction of graphene in the polymer substrate, there remains a possibility to introduce additional additives to our sensors for additional functionality should the opportunity arise. For a detailed breakdown of the procedure refer to Appendix A.

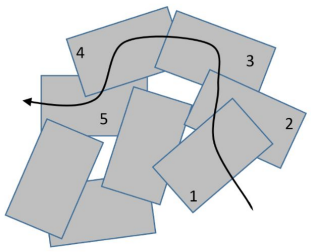


Figure 1: An example of a possible electron path through the graphene sheet network [1]

Apart from the obvious **resistance-based measurements using a DMM** to test the sensor conductivity, the graphene nanocomposite will be characterized in more detail in order to compare the performance of our sensor with that reported in the source paper. Initial characterization efforts will use **SEM to gain insight into the size distribution of the exfoliated graphite/graphene**. Given the dependence of the sensor conductivity/resistivity on the number density of graphene nanosheet connections (see Figures 1 & 2), characterization of the sheet size is important. Measurements of the **sensitivity and operating range of the graphene nanocomposite sensor for different fill fractions** will also aid in the optimization of the sensor for our desired health sensing application. More advanced quantitative characterization techniques (e.g. rheological measurements) are not a priority as qualitative measurements of properties such as stiffness are more relevant for practical applications.

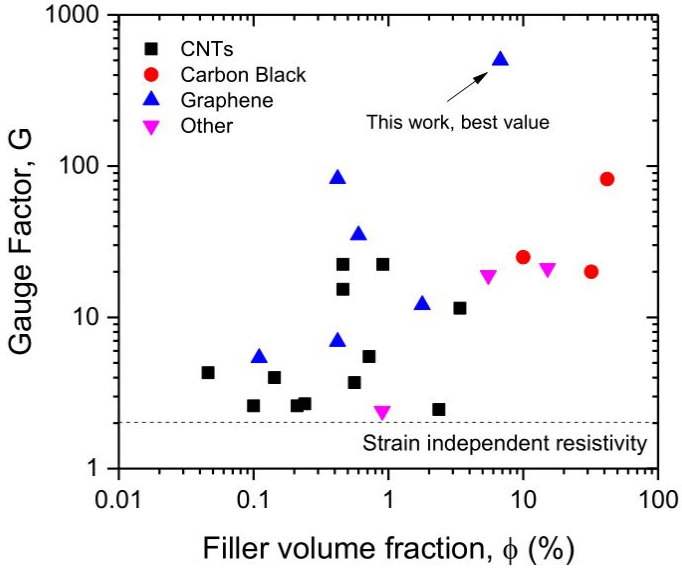


Figure 4. Graph of Gauge Factor vs. Filler Volume Fraction

Appendix E: Interim Prototype Test Plans

The final stage of testing will compare the proposed graphene nanocomposite sensor to the two previous sensors using the same op-amp circuit with the deformable viscoelastic sensor serving as the variable resistor. Based on the results of the measurements in the source paper we expect to see an exponential decay in resistance shortly after the initial force is applied that corresponds with the relaxation of the polymer matrix. Data related to the shape and consistency of this relaxation will likely be useful later in the project where data analysis is required.

Comparing the performance of existing pressure sensors and nanocomposite (i.e carbon black and graphene-based) sensors in Phase I is a very important part of the validation and verification of the feasibility of our proposed sensor - testing in later phases is described in the appropriate engineering specifications sections. Given that the utility of our proposed sensor is centered around its ability to resolve arterial pressure waveforms with an amplitude in the 10 - 100 mmHg range (a pressure of 40 mmHg corresponds with half of the typical ‘resting’ diastolic pressure in humans), the main parameters with which we are concerned is the sensitivity and operating ranges of the sensor.

Given the relative rarity of nanocomposite sensors, an evaluation of the performance of commercially available conformable sensors serves as a baseline for our sensor validation. The commercial sensor we chose for our comparison is TekScan’s FlexiForce sensor. Although it is not particularly stretchable, it is considered a printable/flexible/stretchable a (P/F/S) sensor which uses thin-film force sensors to detect the relative change in force. Its basic operation mechanism is the same as strain gauges; as force is applied to the active surface the resistance of the device will increase.

A simple op-amp circuit (Figure 3) where the output voltage is a function of the input resistance can be used to measure the sensitivity and linear operating range of the device, with the FlexiForce serving as the variable resistor at the inverting input terminal. A piezoelectric load cell can be used to ensure that the force applied to the active surface of the sensor is consistent and repeatable. An exhaustive summary of existing tactile sensors is available in Appendix B - Tactile Sensor Comparison.

A similar comparison can be made using a carbon black based nanocomposite sensor which, like P/F/S sensors are flexible and stretchable (but not printed) variable resistors. A carbon black nanocomposite was chosen due to the fundamental similarities between the carbon black and graphene as a filler. Figure 4 shows a comparison of the gauge factor (sensitivity) for different nanocomposites reported in literature, including three carbon black nanocomposites. A comparison using the same basic op-amp measurement setup should allow us to further

distinguish the two nanocomposites, highlight the advantages of using graphene over carbon black, and investigate the feasibility of a carbon black nanocomposite as an alternative.

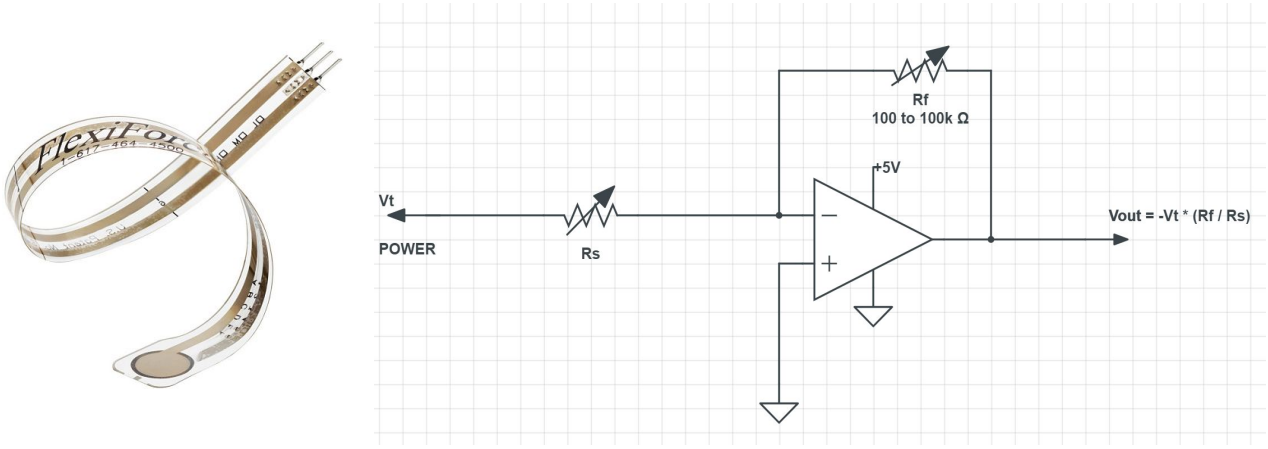


Figure 3. (Left) Constructed of a pressure-sensitive ink and two layers of substrate, the FlexiForce is thin & flexible. (Right) A simple op-amp circuit can be used to measure the sensitivity and operating range of the device.

Appendix F: Interim Design Specifications

The design planning phase of our project consists of three major phases: successfully infusing a viscoelastic polymer with graphene to make a nanocomposite sensor, designing a functional sensor, and processing the output.

Our group has allocated the beginning of the 4A term to oversee the logistics associated with starting the project and the transition into the development phases of the project. More specifically a formal project proposal document has been completed for overall organization, all standard operating procedures (SOP) for material synthesis and electrical testing have been documented, the necessary chemicals for graphene synthesis are currently on-hand and the orders for the remaining supplies have been placed.

The remaining time in the 4A term will be focused on the fabrication of a functional viscoelastic sensor whereas the 4B term will be focused on the sensor design and data processing.

Phase I: Sensor Design

In Phase I the focus is on successfully executing a synthesis protocol for producing graphene using liquid-phase exfoliation. An integral aspect of this preliminary design phase is in the consistency of our procedure and the resulting yield. Due to the sensitivity of graphene with respect to contaminations or changes in procedure, it is crucial that the graphene quality is consistent to achieve reliable testing data. To verify the consistency in material synthesis, various stages of material characterization will be performed, focusing on the material's morphology and purity.

Phase I also includes the task of incorporating the graphene into a viscoelastic polymer substrate to form a homogenous composite material. Procedures for this stage will be based on the aforementioned source paper, that used polysilicone (silly putty) for the polymer matrix. If required, alternative polymer matrixes such as polystyrene and commercial putty materials are feasible alternative polymer matrices.

A comparison analysis between existing pressure sensors and nanocomposite sensors (i.e carbon black and graphene-based viscoelastic sensors) is one of the main objectives of the first phase. This will help us determine the feasibility of the idea and gives us a standard by which we can evaluate the performance of the sensors we create, enabling the team to make informed engineering decisions throughout the project. The validation method for the comparison analysis will be discussed in detail in the 'Verification & Test Plans' section.

Phase 1 will be concluded with further validation of the nanocomposite properties, particularly those that are a function of the graphene fill factor relationship and the material's response to deformation. The rheological and electromechanical properties of the material, namely its

conductivity and stiffness, will be optimized such that the measured parameters correspond with the target values (based on the source paper).

Phase II: Electrode Design

The secondary phase focuses on transforming the optimized sensor material into a functional cardiac sensor able to resolve signals from the heart. This entails deciding on the sensor size, placement, and housing among other design parameters.

In Phase II, the sensor is further characterized in order to validate the feasibility of the sensor design. An important aspect of this phase will be the preliminary analysis of output waveforms to determine sensitivity and resolution thresholds. The putty's response to physical deformations will be also be investigated in more detail during this phase, with a focus on correlating output signal with applied pressures and understanding the impact of the polymer relaxation on the output signal. Several parameters will be considered for ongoing optimization and validation. With the reliability of the procedure validated in Phase I, the previously mentioned pseudo-optimized parameters such as the graphene content and fill fraction may be revisited as a means of achieving the target specifications.

Of course, a functional sensor must be able to clearly and continuously resolve cardiac signals. As a result this phase will also involve extensive load tests to simulate heart beats, as well as measurements of our own heartbeats with the designed sensor and a traditional ECG sensor (for reference).

Phase III: Demo

The final stage of our proposed project involves preparing a simple demonstration of the functional cardiac sensor. In order to demonstrate its functionality a basic front-end for the sensor's output must be designed in this phase. This entails creating basic data acquisition and analysis software. As a stretch goal, the software could also be able to identify basic arrhythmias.

The task of preparing the demo is closely related to the final documentation of the results of our project in the forms of a symposium poster and final report which will also be completed in this phase. A fully functional demo prototype should be a qualitative, user-friendly tool used to correlate arterial pressures with the corresponding pulses from heartbeats and potentially characterize specific cardiac patterns such as arrhythmias. As such, the main objective of this stage is to allow the output of our optimized sensor to be interpreted without the need for a complex load testing setup. The aim is for the device to represent a non-invasive and user-friendly approach to cardiac monitoring and to showcase the feasibility of our sensor being in real-world usage cases.

Key Design Challenges (Interim)

1. **Sensor fabrication** (sensor stiffness & conductivity, stiffness, temperature dependence)

   The most important aspect of the project is to create a functional electromechanical sensor using a viscoelastic graphene-polymer nanocomposite. Instead of attempting to recreate the material from scratch, using the recently published study as a guide will allow us to achieve this within the allotted time. The team will also need to characterize the resulting composite to confirm that the produced sensor putties have the desired properties (see Engineering Specifications).

2. **Form factor** (housing, sensor size, placement, etc.)

   Because the viscoelastic composite sensors are easily moldable, we are afforded a lot of freedom when it comes to experimenting with different form factors. However, given the strict time constraints, it is imperative that the project not stall in this design phase. As the team's main focus is to apply the material to a person's body for cardiac monitoring, focusing on a few key parameters such as the graphene filling fraction (which controls the stiffness and conductivity of the sensor), sensor placement, and sensor size should help maximize the efficiency of the design process.

3. **Interpreting arterial pressure waveform** (resolving heart rate, pressure, arrhythmias)

   Although there is no scarcity of pathological resources detailing the fundamental physics[3] behind arterial pressure waveforms and diagnoses using said waveforms[4,5] the team will need to make a concerted effort into understanding the differences between arterial pressure and electrical heart signals, especially as they pertain to diagnosis.

4. **Hardware** (battery size & life, compatibility, safety, communication, signal integrity)

   In order to make a device more user friendly than existing cardiac monitoring technologies, design choices related to the hardware used to create and capture the signal must be made carefully. One example decision would be related to the tradeoff between device compactness and device robustness.

5. **Software** (ease of use, real-time, signal processing, noise handling)
   Since the signal obtained through the sensor is arterial pressure waveforms, generic software used for measuring ECG signals would at least need to be modified. Thus, a new, simple software is required to detect the heart rate obtained by the sensor for demonstrative purposes. An example of a difficulty that will need to be addressed by the software would be handling the relaxation of the polymer matrix since it will be reflected in the signal output. The software would also have to be adaptive so that it is not prone to artefacts and can operate in non-ideal conditions.

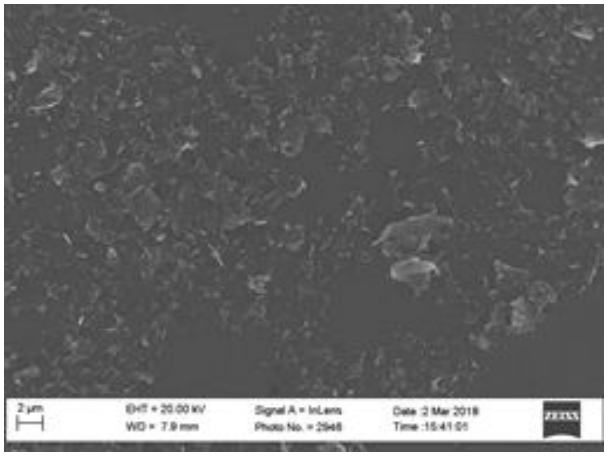
Appendix G: Verification Data

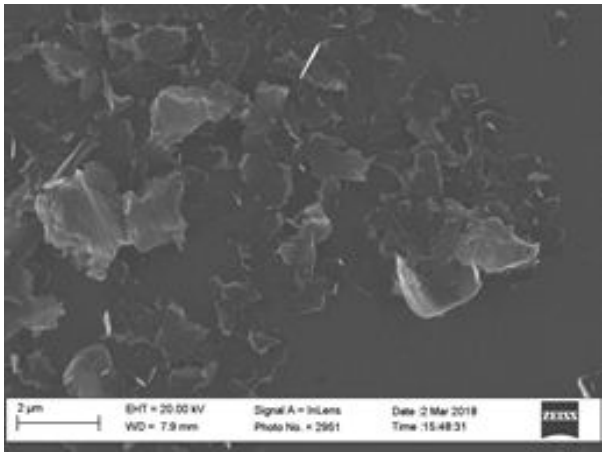
Reference

Putty

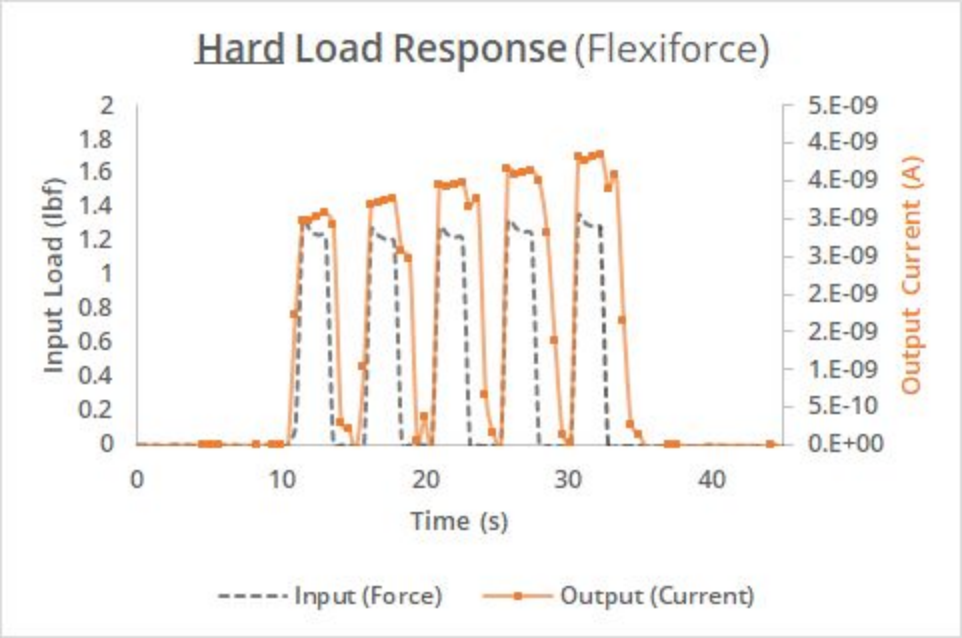
G-Putty (sample 1)

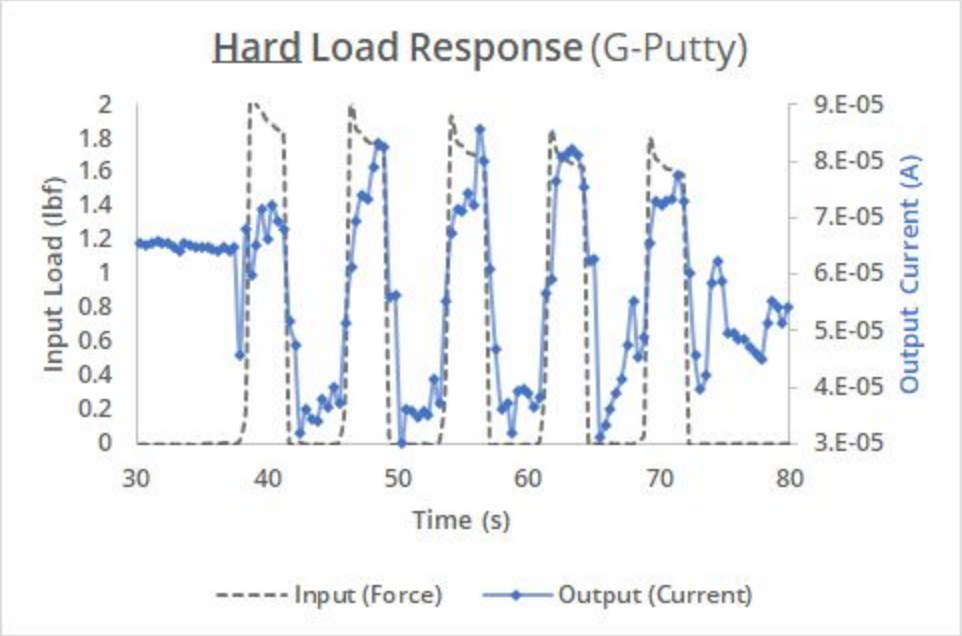
G-Putty (sample 2)

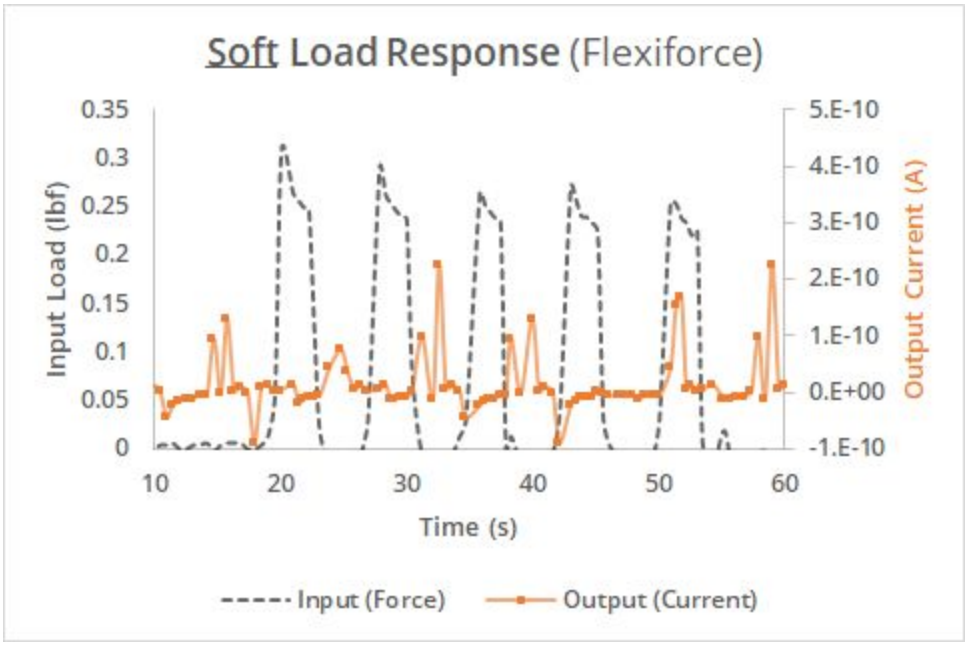


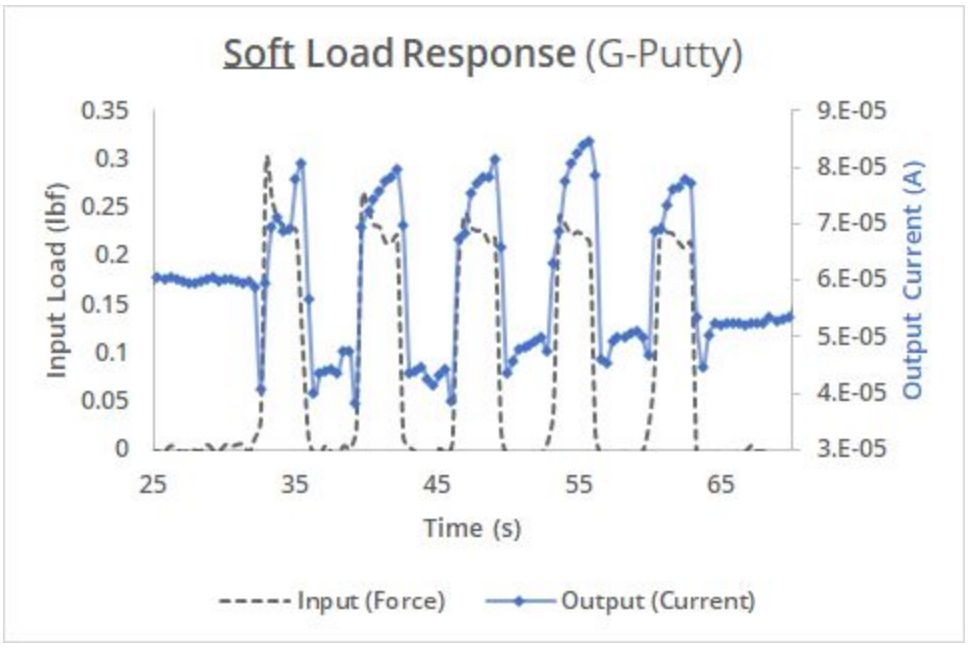


Appendix H: Prototype Test Data






Soft Load Response (Flexiforce)
Input Load (lbf)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Output Current (A)
5.E-10
4.E-10
3.E-10
2.E-10
1.E-10
0.E+00
-1.E-10
10
20
30
40
50
60
Time (s)
Input (Force)
Output (Current)


Soft Load Response (G-Putty)
Input Load (lbf)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Output Current (A)
9.E-05
8.E-05
7.E-05
6.E-05
5.E-05
4.E-05
3.E-05
25
35
45
55
65
Time (s)
Input (Force)
Output (Current)

Appendix I: Tactile Sensor Comparison[3]

Transduction principles	Advantages/ disadvantages	Sensed mechanical component	Key materials	Sensitivity (GF)	Range	Linearity	Response time	Cyclic stability	Ref.
Piezoresistivity	✓ High sensitivity ✓ Large measuring range ✓ Simple structures and fabrication techniques ✓ Low cost × Poor stability × Hysteresis effect × Temperature dependent	Strain	Percolative graphene films	150	0–2%	Approximately linear	No	4000 cycles (0–0.5%)	[148]
			Graphene woven fabrics	500 ($0<\varepsilon<2\%$) 10,000 ($\varepsilon>8\%$)	0–10%	Nonlinear	10–30 ms	1000 cycles (0–2%)	[145]
			Aligned carbon nanotube thin film	0.82 ($0<\varepsilon<40\%$) 0.06 ($60<\varepsilon<200\%$)	0–280%	Two consecutive linearity region	14 ms	10,000 cycles (0–150%)	[77]
		Pressure	Conductive elastomeric composite on a micropyramid array	4.88 kPa^{-1} (0.37 kPa < P < 5.9 kPa)	0–8 kPa	Two consecutive linearity region	0.2 s	Not known	[70]
			Conducting polymer film with hollow-sphere microstructure	133.1 kPa^{-1} ($P<30$ Pa) GF < 0.4 kPa^{-1} ($P>1$ kPa)	0–100 kPa	Nonlinear	50 ms	8000 cycles (0–5 kPa)	[172]
			Patterned PDMS conducting thin films	1.8 kPa^{-1} ($P<300$ Pa)	0–1150 Pa	Nonlinear	10 ms	67,500 cycles (0–1 kPa)	[202]
		Shear	Reversible interlocking of nanofibers	0.75	0–5%	Linear	Not known	Not known	[201]
		Strain vibration	Au thin film with channel cracks	200 ($\varepsilon<0.5\%$) 1000 ($0.5\%<\varepsilon<0.7\%$) >5000 ($0.7\%<\varepsilon<1\%$)	0–1%, 0–966 Hz	Nonlinear	Not known	1000 cycles (0–0.5%)	[17]
Capacitance	✓ High sensitivity ✓ Temperature independent ✓ Well established fabrication techniques ✓ Low power consumption × Highly susceptible to parasitic influence and electromagnetic interference × Complex circuitry × Crosstalk between sensing unit	Strain	Carbon nanotube	0.97	0–300%	Linear	100 ms	10,000 cycles (0–100%)	[209]
			Carbon nanotube forests	1	0–150%	Linear	Not known	Not known	[303]
		Pressure	Flexible suspended gate OTFT	192 kPa^{-1}	0–5 kPa	Approximately linear	10 ms	100,000 cycles (0–1 kPa)	[92]
			OTFT with micro-structured PDMS	8.4 kPa^{-1} ($P<8$ kPa)	0–60 kPa	Nonlinear	10 ms	15,000 cycles (0–3 kPa)	[93]
			Ionic conductor	0.01 kPa^{-1}	0–40 kPa	Approximately linear	Not known	1000 cycles (0-2.5KPa)	[74]
		Elasticity (Young's moduli)	PDMS embedded with a pair of air gap	0.002 kPa^{-1} (Young's moduli <500 kPa)	100–500 kPa	Nonlinear	Not known	Not known	[246]
Piezoelectricity	✓ High sensitivity ✓ Good dynamic response ✓ Low-power-consumption or self-power ability × Not suitable for static sensing × Susceptibility to temperature × Drift of sensor output over time	Strain	Piezopotential-powered graphene transistors	389 ($\varepsilon<0.15\%$) 69 ($0<\varepsilon<0.3\%$)	0–0.3%	Two consecutive linearity region	Not known	3000 cycles (0–0.2%)	[304]
			Individual ZnO piezoelectric fine-wires	700 ($0<\varepsilon<0.5\%$) 1250 ($0.5\%<\varepsilon<1\%$)	0–1.5%	Nonlinear	10 ms	Not known	[99]
		Pressure	ZnO nanowire piezotronic transistors	2.1 μS kPa^{-1} (0 kPa < P < 10 kPa)	0–30 kPa	Nonlinear	0.15 s	1000 cycles (curvature radius = 15 mm)	[100]
		Pressure vibration	Interlocked microdome	35 mA Pa^{-1} ($P<2.45$ kPa)	0–17.15 kPa, 0–20,000 Hz	Nonlinear	Not known	Not known	[32]
			PVDF/1 wt% rGO	5 mA Pa^{-1} (2.45 kPa < P < 17.15 kPa) Load frequency = 0.5 Hz					

[3] Yang, Tingting, et al. "Recent advances in wearable tactile sensors: Materials, sensing mechanisms, and device performance." *Materials Science and Engineering: R: Reports* 115 (2017): 1-37.

Appendix J: Detailed Recipe[4]

Graphene Preparation:

1. The graphene dispersion process is required in order to turn graphite into a form of graphene nanosheet. This is done by the ultrasonic tip-sonication of graphite in N-methyl-pyrrolidine at 100 mg/mL with the total volume of around 300 mL for 72 hours at 80% amplitude .
2. Unexfoliated aggregates and large nanosheets are removed by mild centrifugation at 1500 rpm for 90 minutes.
3. Using a 0.1 μm pore size polyester membrane, vacuum filter the graphene dispersion to form thick nanosheet films.
4. Re-disperse the film at high concentration (~10 mg/mL) by ultrasonic tip-sonication in chloroform for 1.5 hours.
5. The resulting nanosheet should have average length of 500 nm.

Silly Putty Preparation:

1. Mix boric acid with silicone oil at 300 mg/mL in a vial.
2. Gently stir the mixture on a hot plate. Start the hot plate at room temperature and slowly increase the temperature up to 190℃. Once the temperature is reached, leave the mixture for 1 hour with constant stirring speed.
3. The final mixture should look like a homogeneous solution with a milky appearance.
4. After an hour, let the mixture cool down.

Nanocomposite Preparation:

1. 2 g of putty and 52 mL of the graphene/chloroform dispersion is put together.
2. Stir the mixture for 2 hours.
3. Sonicate the mixture in a low-power sonic bath (Branson 1510 model 42 kHz) for 2 hours. This is required to dissolve the putty in the chloroform.
4. The mixture is then placed on a hot plate at 45℃ for 6 hours. Evaporation of the solvent occurs in this process. The resulting mixture should look like a dark grey paste.
5. The paste is then left to rest in the fume hood for 12 hours to evaporate any remaining solvent.
6. The composite putty was removed from its container. It is then mixed further by repeatedly folding on a hot plate at 40℃ for 45 minutes.
7. Mix pristine putty with portion of the stock composite putty to acquire various samples with varying graphene content

[4] Boland, Conor S., et al. "Sensitive electromechanical sensors using viscoelastic graphene-polymer nanocomposites." *Science* 354.6317 (2016): 1257-1260.