# Bachelor Thesis Project

## Vapor-phase Conductive Polymer Coatings on Double Network Hydrogels

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**Abstract**

Fabricating conductive hydrogels (CHs) which is tough, stretchable and electrically conductive at the same time can be challenging. Herein, a double network (DN) hydrogels of different compositions of polyacrylamide (PAAm) and poly (sodium 4-styrenesulfonate) (PSS)/poly (diallyl dimethyl ammonium) (PDADMA) will be freeze-dried and coated with PPy by oxidative chemical vapor deposition (oCVD). The effect of freeze-drying and oCVD PPy coating on the DN hydrogels were studied by conducting ATR spectroscopic analyses, water content analyses and cyclic compression tests. Furthermore, the swelling behaviour of the uncoated DN hydrogels were also performed. The results indicate that freeze-drying does not disrupt the physical and chemical structure of the DN hydrogels and an oCVD PPy coated DN hydrogel with a strong and tough mechanical property was successfully synthesized. The results from the swelling studies shows that DN hydrogels are pH- and salt-sensitive. The DN hydrogels also exhibited pH-swelling reversibility. These characteristics may lead CHs to be a promising material to be used in biomedical applications.

# I  Introduction



**Figure 1.** Pictures of double network hydrogel samples and their polypyrrole coated counterparts (from left to right): Pure PAAm (transparent), PAAm-PSS/PDADMA(10%); PAAm-PPy (transparent); PAAm-PSS/PDADMA(10%)-PPy. Other double network hydrogel samples (coated and uncoated) with different proportions of PSS/PDADMA has similar features with PAAm-PSS/PDADMA(10%)

During the past few decades, conductive hydrogels (CHs) has received great attention due to its novel applications in the biomedical industry such as artificial muscles and cartilage, electronic skin, biosensors and drug delivery systems [1, 2]. The CHs combines the properties of a hydrogel and conductive polymers which allows the CHs to be highly hydrated, flexible, stretchable, biocompatible and electrically conductive at the same time.  Unfortunately, it is not easy to incorporate conductive polymers to the hydrogel network. Hydrogels are a crosslinked network of hydrophilic polymer chains that are characterized by their high water content. On the other hand, conductive polymers such as polypyrrole (PPy) are hydrophobic making it challenging to uniformly distribute the conductive network into the hydrogel and create a well-connected electrical path [1, 3].

To address these challenges, a novel vapor phase deposition technique for conductive polymers called oxidative chemical vapor deposition (oCVD) technique can be used to create a thin conformal coating of PPy on the surface of the hydrogel [4]. OCVD is a solvent free process that is especially advantageous for deposition of monomer with insufficient solubilities such as pyrrole. Furthermore, oCVD allows for the deposition to be performed under mild conditions which prevents the degradation of the sensitive substrates with delicate microstructures. Ultra-thin oCVD PPy coating on the hydrogel surface should keep the underlying mechanical properties of the hydrogel unaffected, while rendering the coated hydrogels electrically conductive.

Since oCVD is performed under vacuum conditions it is imperative to use hydrogel substrates in their dry state. Freeze-drying is a technique to remove water retained in the hydrogel by freezing the water then followed by extraction of ice crystals via sublimation [5].

In this research project, double network (DN) hydrogels of different proportions of polyacrylamide (PAAm) and poly (sodium 4-styrenesulfonate) (PSS)/poly (diallyl dimethyl ammonium) (PDADMA) will be coated with PPy to create conductive hydrogels. As the name suggests, DN hydrogels consist of two interpenetrating networks: one is deformable whereas the other one is stiff [6]. The rationale for creating these DN hydrogels is to improve the mechanical properties of the hydrogels. PAAm is covalently crosslinked with low concentrations (0.1%) of N,N'-methylenebisacrylamide (MBA) which provides the softness and the stretchability of the DN hydrogel [7]. The second network is composed of a polyelectrolytes (PECs), PSS/PDADMA, which is stiff and brittle [8].

The concept of toughness in the DN hydrogels originates from the sacrificial bond principle where the stiff network is fractured in advance of the flexible network [6]. The deformation process allows a large amount of energy to be dissipated due to the reversible breakage and formation of the ionically bonded PSS/PDADMA network. With this strategy, hydrogels have obtained an adequate level of mechanical properties to be used in different applications in the biomedical industry. Furthermore, the integration of PPy into the DN hydrogel matrix will allow the hydrogel material to be a potential candidate in stimuli-responsive biosensors.

The composition of the DN hydrogels used in the research project is tabulated in **Table 1.**

**Table 1.** Sample names and composition of the DN hydrogels used in this project.

|  | DN – 0% | DN – 5% | DN – 10% | DN – 15% | DN – 20% |
|---|---|---|---|---|---|
| Uncoated | Pure PAAm | PAAm-PSS/PDADMA (5%) | PAAm-PSS/PDADMA (10%) | PAAm-PSS/PDADMA (15%) | PAAm-PSS/PDADMA (20%) |
| PPy coated | PAAm-PPy | PAAm-PSS/PDADMA (5%)-PPy | PAAm-PSS/PDADMA (10%)-PPy | PAAm-PSS/PDADMA (15%)-PPy | PAAm-PSS/PDADMA (20%)-PPy |

Herein, oCVD PPy coated DN hydrogels were characterized. In the first section, the chemical composition of the oCVD PPy coated DN hydrogels were characterized by ATR spectroscopic analysis. In the later sections, the effect of freeze-drying on the water content and mechanical properties of the hydrogels were investigated. The effect of the conductive oCVD PPy coatings on the cyclic compressibility of the hydrogels have also been investigated. Finally, the swelling behavior of the uncoated DN hydrogels in media with varying salt concentrations and pH was comprehensively analyzed.

## II   Experimental
### 2.1 Chemical characterization by ATR spectroscopy
The freeze-dried hydrogels listed in **Table 1** and the pure compounds of the hydrogels were characterized by Attenuated Total Reflectance (ATR) spectroscopy. The spectral data was measured using a Shimadzu IRTracer-100 spectrometer in the range of 800 – 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and averaged over 128 scans. The measurements were collected with background as air.

### 2.2 Rehydration of samples
Mechanical tests were performed using rehydrated DN hydrogel samples. The freeze-dried hydrogel samples were soaked in deionized water at room temperature until the hydrogels reached a stable weight, indicating equilibrium. Then, the degree of rehydration of the hydrogels were calculated using Equation 1, where $w_w$ and $w_d$ are the weight of the rehydrated hydrogel and the dry weight of the hydrogel respectively.

$$\frac{w_w - w_d}{w_d} \times 100\%$$
<div align="right">Equation 1</div>

Water content of the rehydrated hydrogels was also analyzed through this experiment and it can be calculated using Equation 2.

$$\frac{w_w - w_d}{w_w} \times 100\%$$
<div align="right">Equation 2</div>

### 2.3 Mechanical testing

Cyclic compression tests for 50% strain were performed on the hydrogels to obtain the mechanical properties of the hydrogel material. The test was done using a Discovery HR20 rheometer with a constant crosshead speed of 50 μm/s at room temperature. Cylindrical samples with diameters of 7 mm and 15 mm were used. The compressive stress ($\sigma$) and the compressive strain ($\varepsilon$) of the hydrogel material were calculated using the following Equations 3 and 4,

$$\sigma = \frac{F}{A}$$
<div align="right">Equation 3</div>

$$\varepsilon = \frac{l_0 - l}{l_0}$$
<div align="right">Equation 4</div>

where, F is the axial force, A is the cross-sectional area of the sample, $l_0$ is the original sample thickness and $l$ is the instantaneous thickness of the sample during compression. The Young's modulus was then calculated based on the slope of initial section of the stress-strain curves (< 5% strain) to determine the elasticity of a material.

### 2.4 Swelling studies

The swelling behavior of the pristine hydrogels (DN-0%, DN-10%, DN-20%) were investigated by soaking oven dried DN hydrogels in solutions of different pHs (3, 7, 11) and sodium chloride (NaCl) in concentrations of 0.45%, 0.9% and 1.8% (by weight). The swelling studies of the hydrogels were done at room temperature until the weight of the hydrogels reached equilibrium. The swelling ratios of the hydrogels can be calculated using Equation 5.

$$\frac{w_w - w_d}{w_d} \times 100\%$$
<div align="right">Equation 5</div>

The reversibility of the swelling behavior of DN-10% in pH 7 solution was further investigated by changing the swelling medium to pH 11 followed by pH 3 and back to pH 7 with 2-hour intervals.

## III  Results and Discussion
### 3.1 Chemical characterization by ATR spectroscopy

**Figure 2.** shows the ATR spectra of the PAAm-PSS/PDADMA DN hydrogel. The ATR spectra of the pure components have been used for comparison. The unique peaks of the pure compounds have been marked with stars in respective colours. The peak assignments of the pure components of the hydrogel are summarized in **Table 2**.
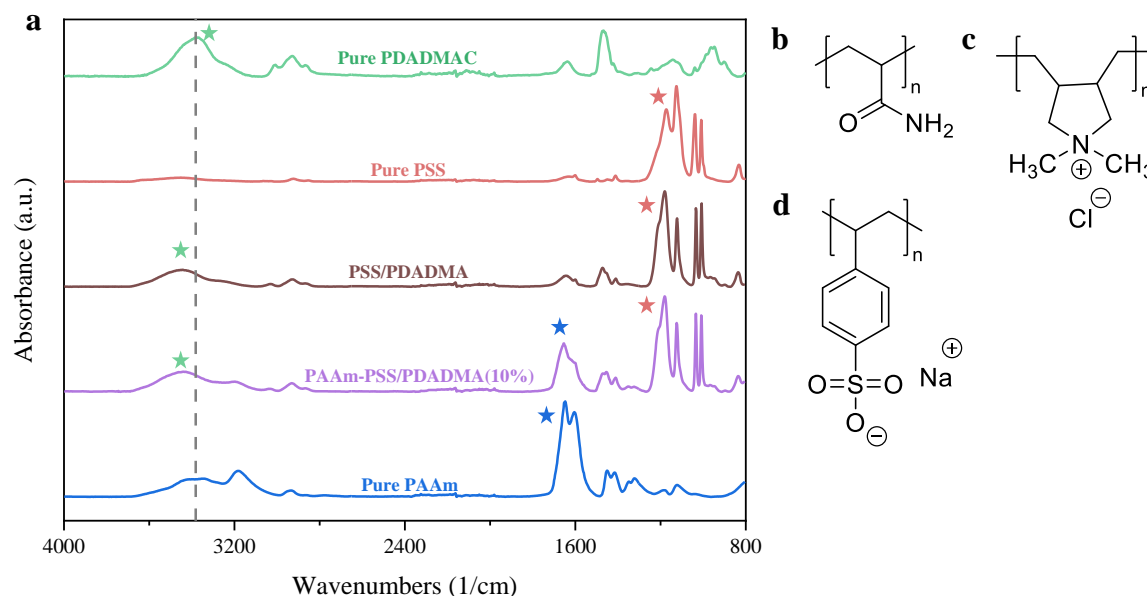
**Figure 2.** (a) ATR spectra of pure PAAm (polyacrylamide), pure PDADMAC (poly(diallyl dimethyl ammonium) chloride), pure PSS (poly (sodium 4-styrenesulfonate)), PSS/PDADMA and PAAm-PSS/PDADMA (10%). (b) chemical structure of PAAm. (c) chemical structure of PDADMAC. (d) chemical structure of PSS.

**Table 2.** ATR peak assignments of pure PDADMAC, pure PSS and pure PAAm.

| Pure PDADMAC | | Pure PSS | | Pure PAAm | |
|---|---|---|---|---|---|
| Peaks (cm$^{-1}$) | Assignment [9] | Peaks (cm$^{-1}$) | Assignment [10] | Peaks (cm$^{-1}$) | Assignment [11] |
| 3373 | -N-H stretch | 1173 | SO$_3$ asymmetric stretch | 3398, 3183 | -N-H asymmetric stretch |
| 2929, 1636 | -C-H stretch | 1122 | Aromatic ring vibration | 2939 | -C-H asymmetric stretch |
| 1468 | Long carbon chain with a high degree of regularity for a linear backbone | 1036 | SO$_3$ symmetric stretch | 1650 | -C=O stretch |
| | | 1012 | -C-H bend of aromatic ring vibration | 1603 | -N-H bend |
| | | 831 | Para substitution of SO$_3$ | 1449, 1334, 1119 | -C-N bend |
| | | | | 1414 | -C-H bend |

The ATR spectrum of PSS/PDADMA exhibits unique peaks from both pure PSS and PDADMAC which confirms successful synthesis of the PSS/PDADMA complexes. It is also seen that the peak assigned to the -N-H stretch of PDADMAC at at 3373 cm$^{-1}$ was shifted to a higher wavenumber in the spectrum of PSS/PDADMA.The shift of the -N-H peak can be attributed to the formation of ionic bond between PSS and PDADMAC. Ionic bonds are capable of forming shorter bonds than other types of molecular interactions due to the larger bond strength. Thus, shifting the chemical band of the -N-H peak to a higher wavenumber [12]. The ATR spectrum of the DN hydrogel (DN-10%) shows the characteristic peaks of pure PAAm as well as the PSS/PDADMA complex. This confirms the successful incorporation of both the polymer networks in the developed double network hydrogel.
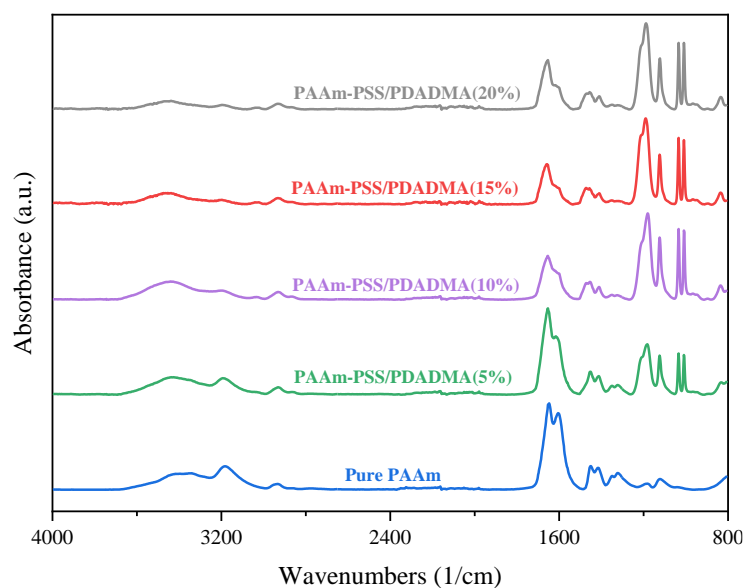
**Figure 3.** ATR spectra of DN hydrogels in different PAAm-PSS/PDADMA compositions; pure PAAm (DN-0%), PAAm-PSS/PDADMA (5%) (DN-5%), PAAm-PSS/PDADMA (10%) (DN-10%), PAAm-PSS/PDADMA(15%) (DN-15%), PAAm-PSS/PDADMA (20%) (DN-20%).

Figure 3 illustrates the ATR spectra of the DN hydrogels with varying proportions of PSS/PDADMA. It can be observed that with increasing PSS/PDADMA content in the DN hydrogel, the contributing peaks becomes more pronounced, whereas the intensity of the PAAm characteristic peaks diminished. Moreover, the -N-H stretch from PDADMAC at around 3300 cm$^{-1}$ underwent an observable shift to a higher wavenumber as the amount of PSS/PDADMA increases in the composition of the DN hydrogel due to the increase of ionic bonds.
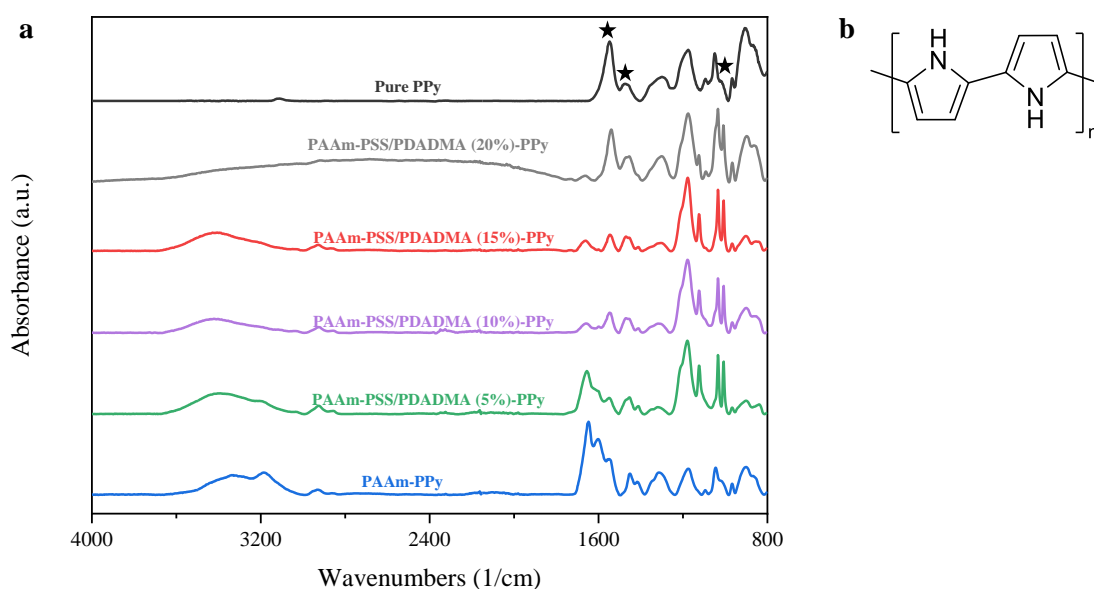


**Figure 4.** (a) ATR spectra of PPy-coated DN hydrogels in different PAAm-PSS/PDADMA compositions; PAAm-PPy (DN-0%), PAAm-PSS/PDADMA (5%)-PPy (DN-5%), PAAm-PSS/PDADMA (10%)-PPy (DN-10%), PAAm-PSS/PDADMA(15%)-PPy (DN-15%), PAAm-PSS/PDADMA (20%)-PPy (DN-20%). (b) chemical structure of PPy.

Figure 4 shows the ATR spectra of the PPy coated DN hydrogels after oCVD. The ATR spectrum for pure PPy is used for comparison. The characteristic peaks of PPy are shown by the peak

at 1549, 1470 and 1019 cm$^{-1}$ and it has been marked with the black stars on **Figure 4**. The peak assignments of pure PPy are summarized in **Table 3.**

**Table 3**. ATR peak assignments of pure PPy.

| Pure PPy | |
|---|---|
| **Peaks (cm$^{-1}$)** | **Assignment [13]** |
| 1549 | C=C/C-C stretch |
| 1470 | C-N stretch |
| 1300, 1409 | In plane bending of C-H |
| 1173 | Pyrrole ring breathing |
| 1096 | C-H in plane vibration |
| 1019 | Deformation in the vibration pane of N-H group |
| 966 | Pyrrole ring deformation |
| 907 | Stretching vibration of polypyrrole (shows polypyrrole is doped with the oxidant) |

The characteristic peaks of PPy were observed in all the oCVD coated DN hydrogel samples which confirms successful polymerization and incorporation of PPy. Similar to the pristine samples, the chemical band from the -N-H stretch shifted to a higher wavenumber as the ratio of PSS/PDADMA increases in the composition of the oCVD PPy coated double network hydrogels. However, this observation was hard to validate from the spectrum of DN-20% due to the broad peak that overlaps the peaks of DN-20% at around 1700-3800 cm$^{-1}$. This broad and featureless peak is a characteristic of PPy in its doped state and is caused by the excitation of free charge carriers from the valence band to the conduction band [14]. The broad peak was initially observed in all the PPy coated DN hydrogel spectra but was omitted in baseline corrected and normalized ATR spectra.

### 3.2 Rehydration of samples
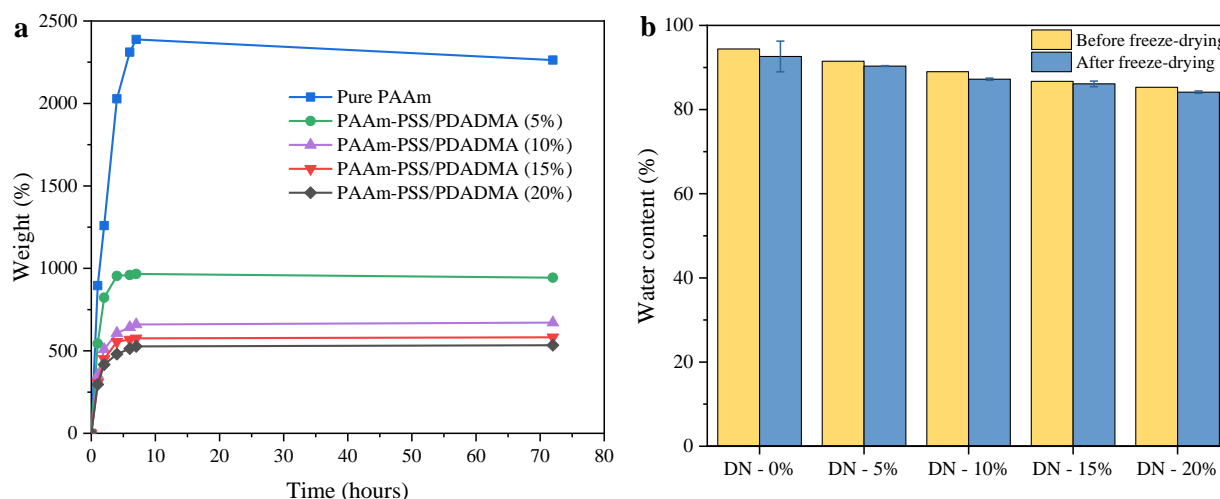3.2.1 Rehydration and water content of DN hydrogels after freeze-drying.



**Figure 5.** (a) Degree of rehydration (%) of the DN hydrogels in respect to time (hours). (b) Water content (%) comparison between the DN hydrogels before and after freeze-drying.

The rehydration curves of the uncoated DN hydrogels after freeze-drying are shown in **Figure 5a.** Based on the graph, a remarkable weight increase of 2263% was observed for pure PAAm. Similar

values of the swelling abilities of PAAm have been obtained in previous studies and therefore PAAm is categorized as a superabsorbent hydrogel [2, 15, 16, 17]. The large weight increase of pure PAAm can be accounted to the high porosity and hydrophilicity of PAAm [2].

Rehydration of the hydrogel decreases with increasing PSS/PDADMA content. PSS/PDADMA exhibits a solid-like characteristic due to its compact structure of its cell walls which causes the material of the DN hydrogels to become denser [8]. This dense structure leads to a more stiff material as well and therefore, the increase of PSS/PDADMA hinders the DN hydrogel to expand as much as the pure PAAm hydrogel.

Moreover, the water content of the DN hydrogel is compared before and after freeze-drying as illustrated in **Figure 5b**. It can be observed that, in both cases, the water content of the hydrogels decreases as PSS/PDADMA increases in the hydrogel. It was expected that the expansion of water after freeze-drying can disrupt the pore walls of the hydrogel [18]. However, it was observed that approximately 98% of the initial water content of the DN hydrogel before freeze-drying was retained after the freeze-drying process. This proves that the structure of the DN hydrogel remains intact after freeze-drying.

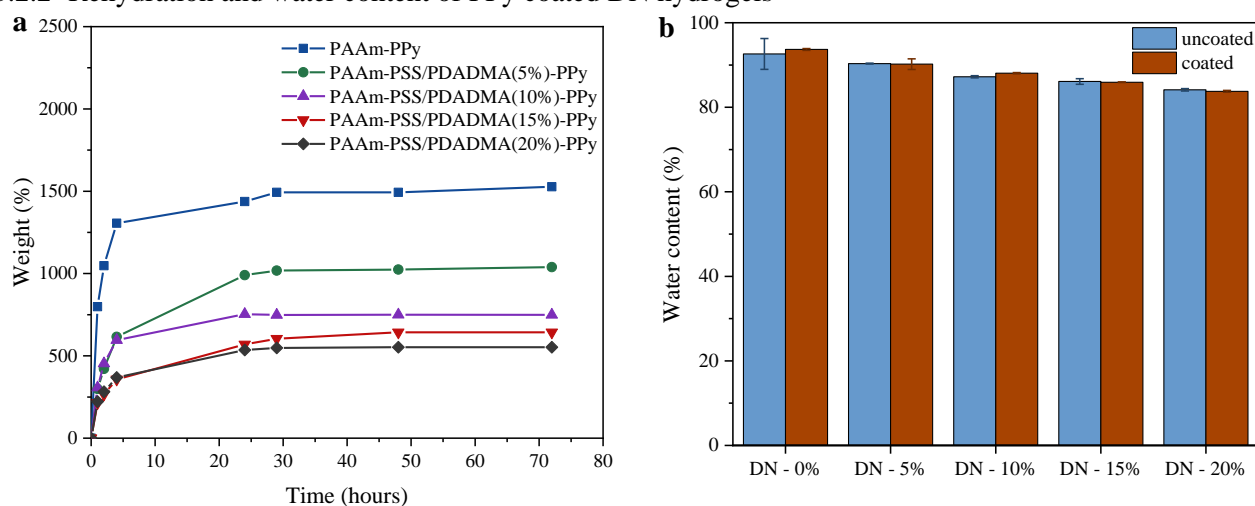### 3.2.2 Rehydration and water content of PPy coated DN hydrogels



**Figure 6**. (a) Degree of rehydration (%) of the PPy coated hydrogels in respect to time (hours). (b) Water content (%) comparison between the hydrogels before and after PPy coating.

**Figure 6a.** shows the rehydration curves of the PPy coated DN hydrogel samples. The most notable change seen on the graph (**Figure 6a**) is the decrease of the equilibrium weight of pure PAAm after the PPy coating. While the uncoated PAAm hydrogel exhibited an increase in weight due to uptake of water up to 2263% after 72 hours, the oCVD PPy coated PAAm hydrogel showed a reduced value of 1527% after the same amount of time. This can be attributed to the hydrophobic polymer configuration (π-π conjugation) of PPy as pyrrole is polymerized during oCVD which hinders the hydration of the hydrogel [2]. Moreover, the hydrophobic PPy restricts the rehydration of the coated PAAm samples as cracks in the coating were observable (see **Figure 1c and d**). This implies that the stiff oCVD PPy coating was not able to keep up with the swelling of the hydrophilic PAAm structure [3].

There was no significant change between the equilibrium weight of the DN hydrogels before and after coating. This might happen due to the thin PPy coating achieved by oCVD. This observation was further supported by the water content of the PPy coated DN hydrogels shown in **Figure 6b**.

**Figure 6b.** shows that the water content of the DN hydrogel before and after the PPy coating are very similar. This implies that although PPy is hydrophobic, this thin coating does not hinder the water retention of the conductive hydrogels compared to the uncoated hydrogel samples.

## 3.3 Mechanical testing
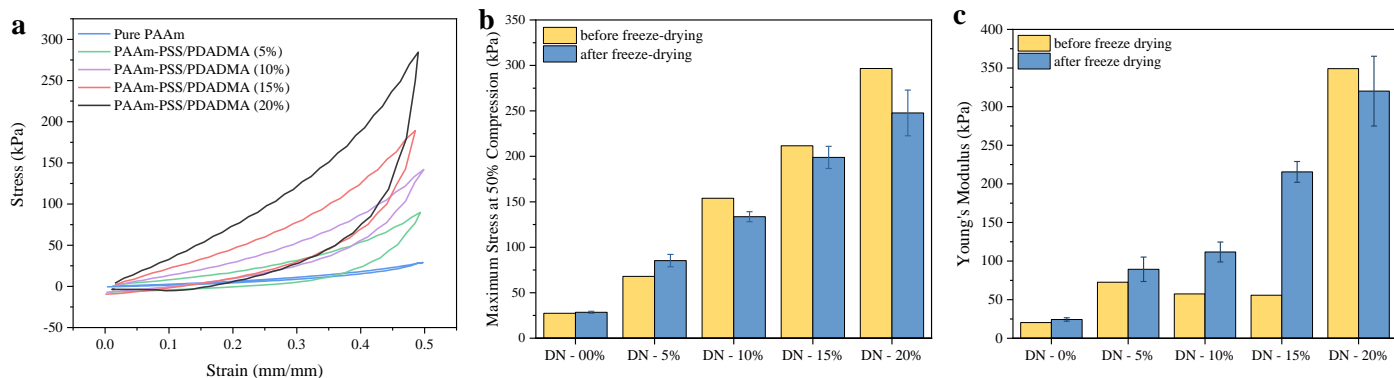### 3.3.1 Mechanical testing of DN hydrogels.



**Figure 7.** (a) Cyclic compression test of hydrogels in different compositions; (b) Comparison of the maximum stress at 50% compression (kPa) of the hydrogels in different PAAm-PSS/PDADMA compositions before and after freeze-drying; (c) Comparison of the Young's modulus (kPa) of the hydrogels in different PAAm-PSS/PDADMA compositions before and after freeze-drying.

The first cycle of the cyclic compression test done on the PPy coated hydrogels were plotted as it is shown in **Figure 7a**. A complete elastic behavior was seen on all the DN hydrogel samples after conducting the cyclic compression test. The increase of hysteresis with increasing PSS/PDADMA in the hydrogel shows that the material of the DN hydrogel was not able to recover simultaneously with the unloading force [19]. The hysteresis loop can also define the amount of energy which was dissipated due to the reversible cleavage and formation of ionic bonds in PSS/PDADMA [20]. This implies that with increasing ionic bonds in the DN hydrogel due to the PSS/PDADMA proportion, DN hydrogels require more time to reform these ionic bonds and hence the DN hydrogel behaves more plastic-like.

Separate graphs to show the elastic recoverability of the material of other compositions of DN hydrogels is shown on **Appendix A**. It is seen from these graphs (**Appendix A**) that the lines which describe the unloading cycle goes to a negative value of stress. This can be accounted to the force of the rheometer which was not controlled enough.

Another noticeable trend from the stress-strain curve (**Figure 7a**) of the DN hydrogel is the maximum stress of the materials after 50% compression which describes the amount of load the material can withstand. The comparison of the maximum stress for the DN hydrogels before and after freeze drying is shown on **Figure 7b**. This graph shows that as more PSS/PDADMA is incorporated in the hydrogel sample, the higher the value is for the maximum stress at 50% compression. This implies that the material becomes more brittle with the increase of PSS/PDADMA. This trend can be seen for both conditions of the samples, before and after freeze-drying.

An irregular trend can be observed while comparing the values of maximum stress at 50% compression, before and after freeze-drying. Therefore, an ANOVA test was performed to verify the significance in the change of values. The results of the ANOVA test shows that there is no significant difference ($p > 0.05$) indicating that the ductility of the DN hydrogels before and after cyclic compression remains the same.

The results of the mechanical testing can be further supported by the analysis of the Young's modulus of the DN hydrogels as shown in **Figure 6c**. It can be observed that the hydrogel becomes more stiff with increasing PSS/PDADMA content which confirms the role of PSS/PDADMA of being the stiff network in the double network hydrogel [8]. This trend is also aligned with the results of the water content analysis on the DN hydrogels which has been described in **section 3.2**.

An inconsistent trend that was observed from comparing the Young's modulus of the hydrogels before-drying. Hence, ANOVA test was also performed to validate the results. The results of the ANOVA test shows that the values of the Young's modulus before and after freeze-drying were not

significantly different (p > 0.05). The results of the mechanical tests on the uncoated DN hydrogels suggests that the mechanical properties before freeze-drying and after freeze-drying were unaffected.

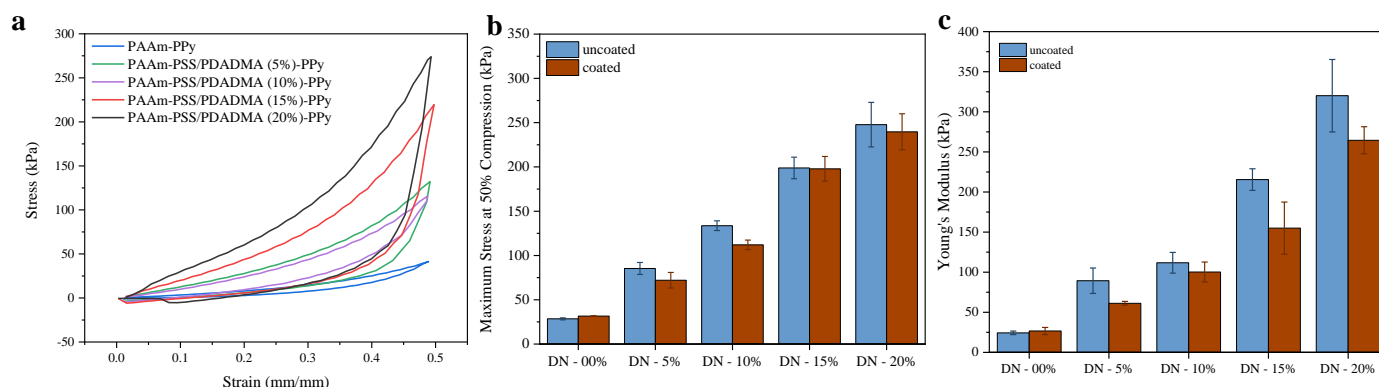### 3.3.2 Mechanical testing of oCVD PPy coated DN hydrogels.



**Figure 8.** (a) Cyclic compression test of PPy coated DN hydrogels. (b) Comparison of the maximum stress at 50% compression (kPa) of the DN hydrogels in before and after PPy coating. (c) Comparison of the Young's modulus (kPa) of the DN hydrogels before and after PPy coating.

**Figure 8a** shows the first cycle from the results of the cyclic compression test done to the oCVD PPy coated DN hydrogel samples. In this graph, similarly to the uncoated DN samples, all the PPy coated hydrogels exerts perfect recoverability as well. This indicates that the addition of PPy into the DN hydrogel matrix does not affect the recoverability of the hydrogels.

The comparison of the hysteresis loop between the pristine samples and the oCVD PPy coated samples are shown in **Appendix A**. For each of the DN hydrogels, a larger hysteresis was seen after the hydrogels were coated with PPy. This implies that with the incorporation of PPy into the DN matrix, the material of the hydrogels behaves more plastically. Elastic behavior of the PPy coated DN hydrogels can be further explained by analyzing the maximum stress at 50% compression and the Young's modulus.

The maximum stress at 50% compression of the oCVD PPy coated DN hydrogels was also compared with their pristine counterparts as illustrated in **Figure 8b**. With the addition of the PPy coating, it is expected that the material will become more brittle. However, the results obtained from the experiment were counterintuitive. It was also verified from the ANOVA test that the maximum stress at 50% compression for the PPy coated DN hydrogels are not significantly different than that of the uncoated DN hydrogels (p > 0.05). Ultra-thin PPy coating on the hydrogel allowed the mechanical properties of the material to be maintained from the uncoated hydrogel sample. This effect was also seen in **Figure 8c** where the PPy coated DN hydrogels has lower Young's modulus value compared to the uncoated hydrogels (p < 0.05).

According to Smirnov et al., who have shown similar results in their research, this phenomena happens due to the effect of an active oxidant that was used to create the PPy coating on the DN hydrogel during oCVD [3]. It is said that crosslink points in PAAm were broken and as a result, the detrimental mechanical properties of the PPy coated hydrogel were observed [2, 3]. This, however, does not mean that the DN hydrogels are negatively affected after PPy coating. The results of the mechanical test implies that the oCVD PPy coated DN hydrogel samples exhibit a strong and tough mechanical property.

### 3.4 Swelling studies
### 3.4.1 Swelling behaviour of DN hydrogels in different pHs

**Figure 9** shows the results of the swelling test which was performed on the pristine DN hydrogels (0%, 10% and 20%). A large weight increase for all the DN hydrogels was observed and this value exceeds the equilibrium weight of the hydrogel which was discussed in **section 3.2**. This can be

accounted to the deprotonation of the -N-H groups of PAAm during the sample preparation stage at high temperatures (105°C). As a result, the osmotic pressure between the hydrogel network and the external solution is increased and there will be a higher tendency of water to penetrate the hydrogel network.

The results of the experiment with DN-0% and DN-10% samples suggest that with increasing pH, the degree of swelling of the hydrogel increased as well. PAAm is capable of being hydrolysed in basic conditions which led to the dissociation of carboxylate groups to the solution, inducing the swelling of the hydrogels [21].

As for the DN-20% sample, it was seen that the hydrogel soaked in pH 3 solution initially had a higher swelling degree and followed by the samples soaked in pH 11 and pH 7 solution subsequently. However, towards the end of the experiment, the hydrogel in pH 11 continued to swell since the hydrolysis of PAAm has not reached its equilibrium. This anomalous trend might be caused by the uncontrolled hydrolysis of PAAm in the hydrogel. Unfortunately, such swelling behaviour of double network hydrogels have not been studied and therefore, further research should be conducted to validate the swelling behaviour of DN-20% in various pHs.
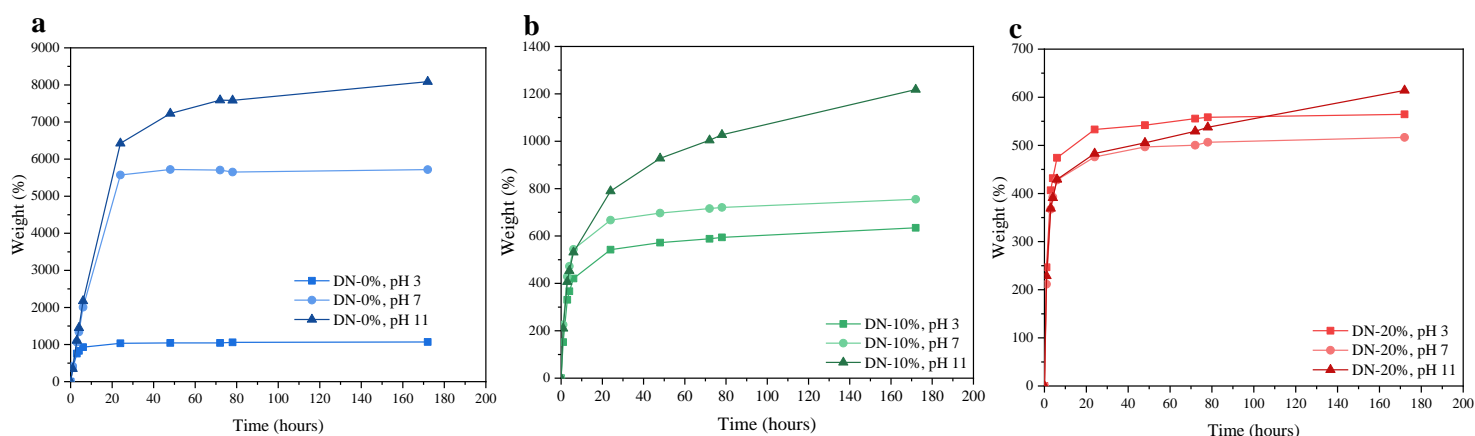


**Figure 9.** (a) Swelling studies of DN-0% (pure PAAm) in pH 3, 7 and 11. (b) Swelling studies of DN-10% (PAAm-PSS/PDADMA(10%)) in pH 3, 7 and 11. (c) Swelling studies of DN-20% (PAAm-PSS/PDADMA(20%)) in pH 3, 7 and 11.

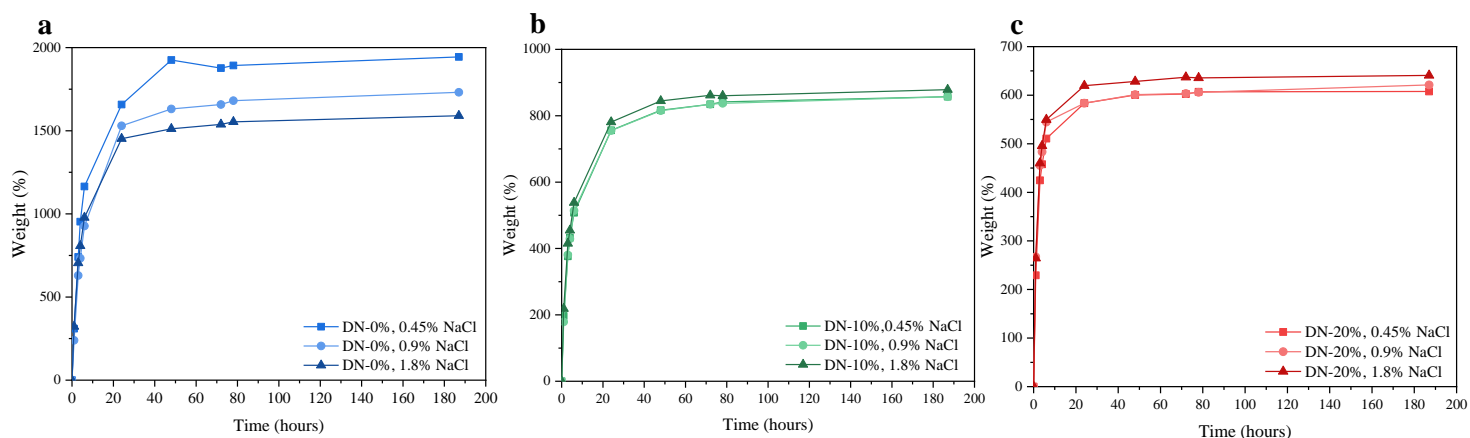3.4.2 Swelling behaviour of DN hydrogels in different salt concentrations.



**Figure 10.** (a) Swelling studies of DN-0% (pure PAAm) in 0.45%, 0.9%, 1.8% NaCl. (b) Swelling studies of DN-10% (PAAm-PSS/PDADMA(10%)) in 0.45%, 0.9%, 1.8% NaCl. (c) Swelling studies of DN-20% (PAAm-PSS/PDADMA(20%)) in 0.45%, 0.9%, 1.8% NaCl.

The results of the swelling studied of the DN-0%, DN-10% DN-20% in different salt concentrations are shown in **Figure 10.** A salt concentration of 0.45%, 0.9% and 1.8% NaCl are selected for this experiment since NaCl is the most common salt that is present in the human body and in normal conditions, the concentration of NaCl in blood in 0.9% (154 mM) [22].

Based on **Figure 10a**. it can be seen that DN-0% exhibits a decreasing degree of swelling as the salt concentration increases. This can be attributed to the increase of ionic strength in the solution which causes a decrease in the osmotic pressure difference between the hydrogel and the solution [23]. Consequently, the tendency of water penetrating the hydrogel network is suppressed.

In contrary to the trend of DN-0%, **Figure 10b and c** shows that DN-10% and DN-20% exhibits the highest swelling ratio in 1.8% NaCl and then followed by the samples soaked in 0.9% and 0.45% NaCl which shows similar degrees of swelling. Such effects happen due to the charge screening effect of the ions in the polymer chains of PSS and PDADMA by the ions present in the solution [24]. Small counterions in the solution ($Na^+$ and $Cl^-$) are capable of weakening the binding between the ion pairs in the macromolecular structure of PSS/PDADMA causing the increase of hydrogel hydration with increasing PSS/PDADMA in the hydrogel [24, 25] . The similar degrees of swelling were obtained between the DN hydrogels in 0.45% and 0.9% NaCl can be accounted to the weak affinity of the NaCl counterions towards the PEC chains and therefore the effect of NaCl towards the DN hydrogels were not noticeable in these concentrations. Other studies with KBr, which has a larger salt "doping" effect on the PEC chains, have shown a more prominent effect when the salt dependency of PECs were studied [25].

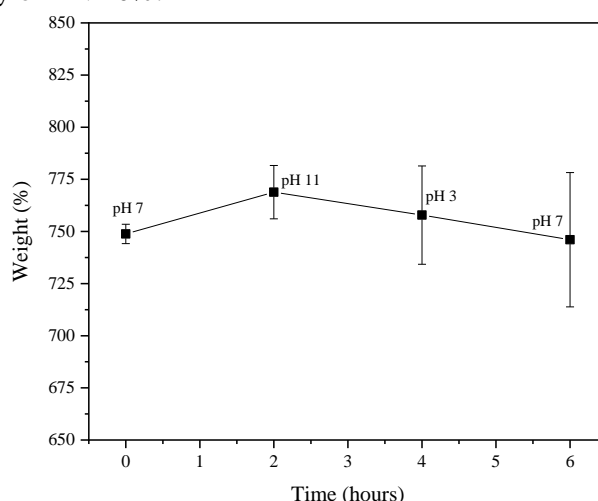### 3.4.3    Swelling reversibility of DN-10%.



**Figure 11.** pH-swelling behaviour of DN-10% (PAAm-PSS/PDADMA (10%)) hydrogel with respect of time (hours)

Previous studies have shown that PAAm is responsive towards pH and hence it is used in drug delivery applications [26]. Herein, the swelling behaviour of the pH dependant PAAm-PSS/PDADMA (10%) DN hydrogel is shown in **Figure 11.** After two hours of soaking the samples in pH 11 solution, it can be seen that there is approximately a 20% weight increase of the samples. This is also supported by the results of the analysis done on the swelling studies of the hydrogels in different pHs where the hydrogel at pH 11 reaches the highest equilibrium weight.

After the samples have been soaked in pH 3 for two hours, it is observed that there is a 10% weight loss from the previous measurement. Based on the analysis done in **section 3.4.1**, it is expected that the weight of the hydrogel in pH 3 would decrease below the weight of the hydrogel in pH 7. However, the results of this experiment do not align with this hypothesis owing to the limited time for reaching equilibrium.

From **section 3.4.1**, it is seen that the DN-10% samples reached equilibrium weight at 48 hours in pH 3 and pH 7, whereas in pH 11 the hydrogel needed 172 hours to reach its equilibrium weight. This implies that due to the slow diffusion rate, the hydrogels weren't able to reach its respective equilibrium weight in the different pHs in a two-hour time frame.

That being said, a pH-swelling reversibility of DN-10% is still possible in a long interval time since the weight of the hydrogel at the end of the experiment was similar to the weight at the beginning of the experiment. The increasing error bar observed on the graph can be attributed to the irregular geometries of samples that was used in this experiment which could experience different rates of water diffusion as well into its respective hydrogel network.

## IV    Conclusion

The results of the experiments conducted in this research project suggests that a hydrophilic, conductive DN hydrogel with a good mechanical property was synthesized using the oCVD technique. ATR spectra of the pure compounds and the DN hydrogels showed that the DN hydrogel was successfully formed and they were successfully coated with PPy after oCVD. The rehydration of the hydrogels indicated that freeze-drying does not disrupt the physical structure of the hydrogels and the ultra-thin PPy coating does not reduce the water absorbency of the hydrogels.

The effect of freeze-drying on the DN hydrogels is also supported by the results of the mechanical testing of the hydrogels which shows that there is no significant difference between the mechanical properties before and after freeze drying. However, after PPy coating of DN hydrogels, the results suggests that a more strong and tough material was achieved.

Furthermore, the results of the swelling studies implies that the DN hydrogels are sensitive towards the change in pH and salt concentrations. The DN hydrogels were also seen to have a pH-swelling reversibility in long time intervals. These behaviors implies that DN hydrogels can be a promising material to be used in drug delivery applications and biosensors.

## V    Further Perspectives

In order to further improve this research project, there are a few aspects worth exploring. Firstly, further research needs to be done on the effect of the antimony pentachloride ($SbCl_5$) oxidant on the chemical and mechanical properties of the PAAm-PSS/PDADMA DN hydrogels. The results of the mechanical testing (**section 3.3**) can be further improved by using a rheometer with a more controlled force and higher sensitivity so that the mechanical properties of the hydrogels can be analyzed in further details.

Further research on the effect of pH on the swelling behavior of DN hydrogels can be conducted using a milder drying method of the hydrogel during the sample preparation stage to prevent pre-experimental deprotonation of PAAm. Swelling studies can also be performed on oCVD PPy coated hydrogels to investigate if the swelling behavior of the hydrogel remains similar after the incorporation of PPy. In addition, further research on the swelling behaviors of the hydrogels can also be done with various physiological fluids and temperatures [21].

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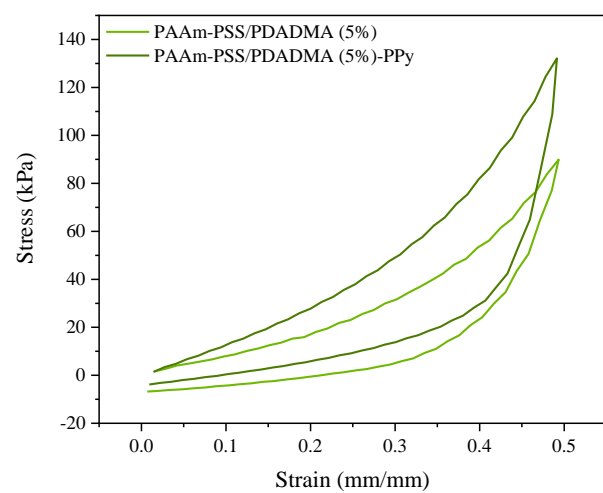
# Appendix A

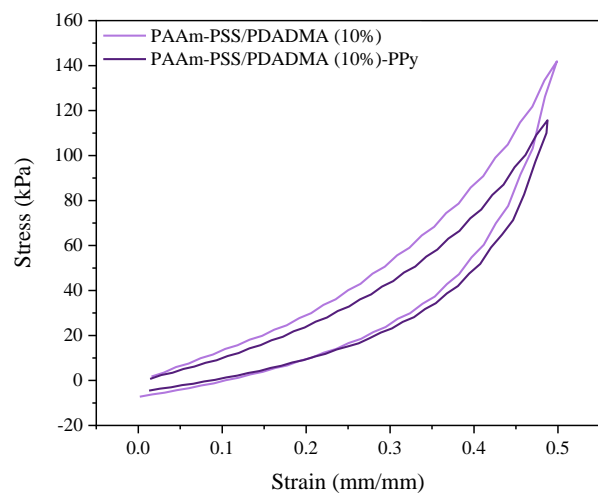Hysteresis comparison between uncoated and oCVD PPy-coated DN hydrogel samples
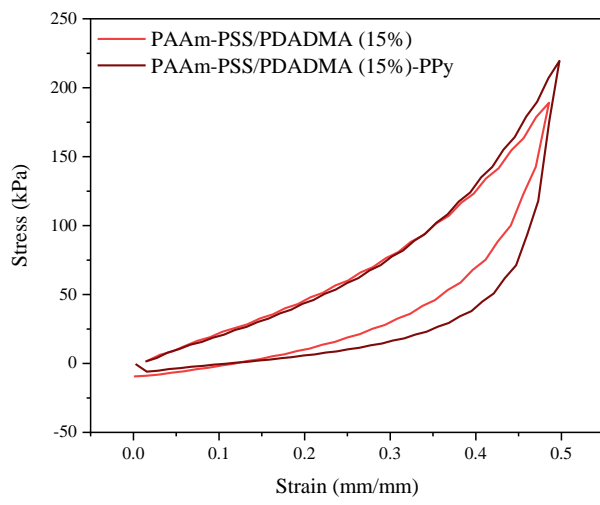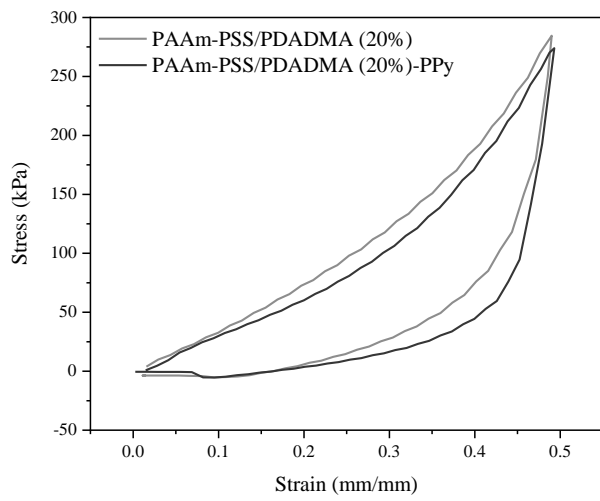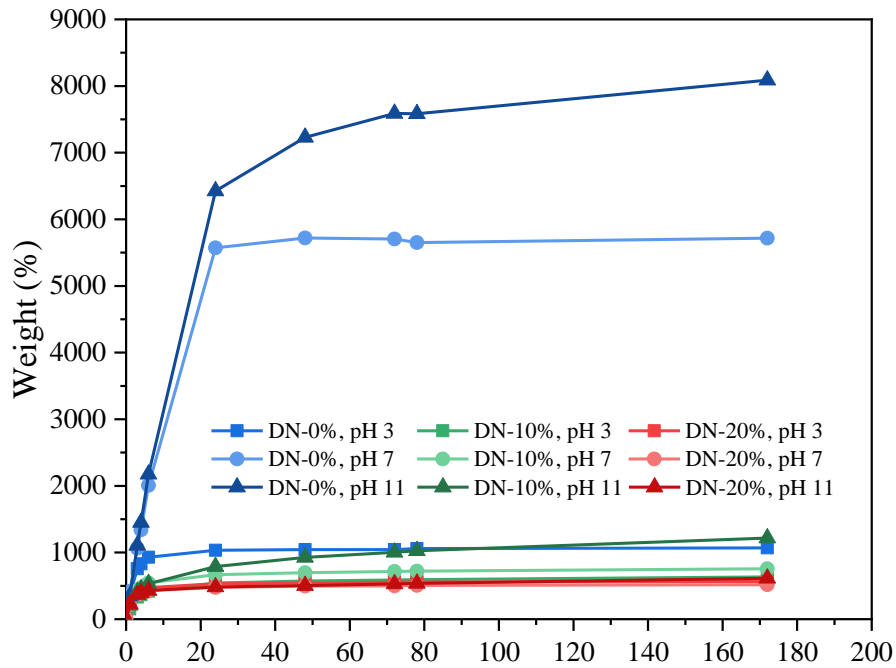
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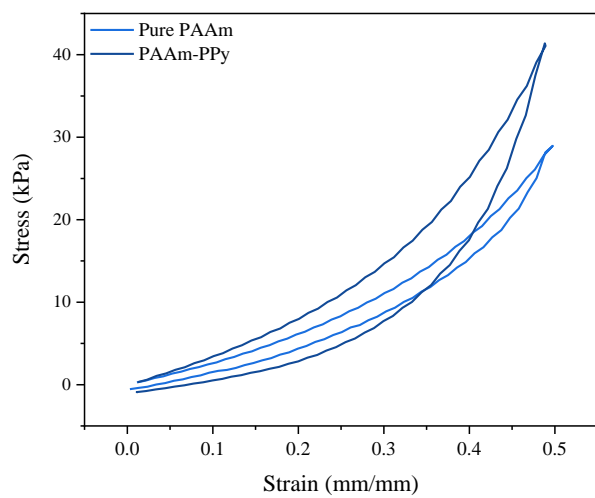


2.  DN-5%



3.  DN-10%

4.    DN-15%



5.    DN-20%

**Appendix B**

Combined graph of swelling studies with DN-0%, DN-10% and DN-20%

1. In pH 3, 7 and 11



2. In salt concentrations of 0.45%, 0.9% and 1.8% NaCl