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Amine-functionalized interpenetrating Polymer networks for CO2 capture

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Honors Project Final Report
2021-2022

Amine-functionalized interpenetrating Polymer networks for CO2 capture

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I affirm that this report represents work performed by me and I assume full responsibility for originality, comprehension, and accuracy of all aspects of the report.

Student Name: **James Wills**

Signature:_______________

Date: 4/1/2022

Executive Summary

The exponential rise of CO2 concentration in the atmosphere over the last several decades along with the rapidly changing severe weather patterns has caused great concern among the scientific community. In recent years, the global CO_2 concentration has increased from 270 to 400 ppm and continues to grow.[1] An arms race to determine the best possible cost-effective solution for CO_2 capture has begun. Prior to the full adoption of renewable energy, a viable CO_2 capture process will allow for the continual use of fossil fuels as a zero-emission process. A process to efficiently produce >99% purity CO_2 to be sequestered or recycled is paramount in combating worldwide climate change.

The utilization of amines to capture CO_2 is a leading approach that many groups are studying. Polymer based sorbents have begun to be utilized to strengthen the amines' ability to adsorb and desorb CO_2. Utilizing a polymer allows for the amine to be crosslinked and suspended on the surface of the polymer matrix. A porous polymer increases the surface area for amine to react with CO_2. The addition of a polymer also decreases the amine density. A low-density amine has been found to be beneficial in the desorption of CO_2. A mixture with a high amine density will increase the intermolecular forces, mainly hydrogen bonding, and increase the required energy for the desorption of CO2 off of the sorbent.

Testing to determine the proper polymer-amine combination for Vacuum Swing Adsorption (VSA) was conducted. Various samples were created and ran through physical testing to determine the efficacy in capturing CO_2 and provide an experimental basis for large scale processes. Qualitative testing was utilized to determine whether the samples could withstand the cyclic process of adsorption/desorption in VSA. Tests including contact angle and water uptake were run to determine the effects of hydrophilic/hydrophobic natures of the polymer-amine mixtures on the adsorption/desorption behaviors for VSA. Various substrates such as Potassium Chloride (KCl) were studied to determine if they aided in the creation of a porous polymer support. The created solutions of Polypropylene Glycol Diglycidyl Ether (PPGDE) and Polyethyleneimine (PEI) were found to be the most favorable of the polymer-amine mixtures studied. Porous structures were easier to create, and the mixtures polymerized more easily. PEI was able to be isolated and believed to create the desired primary amine sites. Further testing will need to be conducted to determine the optimal composition of this mixture. The solutions were exposed to CO_2 and their IR spectra were obtained using Raman. Raman testing provides a full spectrum of the specific vibrations of the particular bonds on a molecule. Raman is less sensitive to water than FTIR and therefore helped determine the best sample to use for CO_2 adsorption. The spectra collected for the PPGDE-PEI mixtures provided verification that they were able to absorb CO_2 under ambient conditions. This provides an experimental basis to continue to investigate PPGDE-PEI as a suitable option for CO_2 adsorption in VSA.

Moving forward, further testing of polymer-amine sorbents is recommended to help create a proper vehicle for CO_2 adsorption. Once the optimal composition is selected, the scale up process can begin. The complexities of small-scale testing will only increase as the process is scaled to industrial applications. In future studies, there is a need for further investigation into the best adsorption conditions for this process. Vacuum assisted thermal swing adsorption is currently the leading candidate for scale up. It allows for a lower sorbent regeneration temperature to decrease the rate of sorbent degradation while also producing CO2 with the desired purity.

The tedious process of determining the proper combination of solvent, solute, and substrate gave insight into the complexities of this worldwide issue. CO2 capture is a developing science with an influx of funding and interest but it is still in its infancy. Continual testing and prototypes must be created to eventually provide a viable process. As these processes develop, a zero-emission fossil-fuel source becomes more and more tangible.

Introduction

With growing concerns about climate change and an increase of Carbon Dioxide (CO_2) in the atmosphere, there has been a strong push to provide a solution to the CO_2 problem. CO_2 is the main component of the majority of greenhouse gases produced. In recent years, the global CO_2 concentration has increased from 270 to 400 ppm and continues to grow.[1] This is expected to have detrimental effects on weather patterns, sea levels, and global wildlife. This has caused many companies to make pledges to reduce emissions with no specific plan or technology described. Bill Gates has recently raised more than $1 billion for direct air CO_2 capture and for supporting other clean energy start-up companies.[2] A race to provide a viable solution to CO_2 removal/storage has begun among researchers and investors alike.

There are many ways companies are going about this research. After air capture was investigated to address increasing anthropogenic CO_2 emissions. This led to the exploration of CO_2 absorption from ambient air using aqueous alkaline solutions for industry specific applications.[3,4] Unfortunately, the energy and temperature required for regenerating these solutions is high and scaling-up would be inefficient. The utilization of amines to adsorb CO_2 from the air has been explored in recent years. Many amines degrade easily, corrode instruments, and require high amounts of energy to be regenerated as a solvent. Therefore, polymer based porous sorbents have begun to be utilized to strengthen the amines effectiveness. In this paper, we will explore the creation of an amine-glycol interpenetrating polymer network for Vacuum Swing Adsorption (VSA) CO_2 capture. A desirable sorbent should have two key features: (i) high surface area for immobilizing amine functional groups which serve as CO_2 adsorption sites and (ii) the low heat of CO_2 adsorption. The former should provide high CO_2 capture; the latter offers low temperature for sorbent regeneration – the most energy intensive step in the thermal swing CO_2 capture process.

In prior years, a temperature swing approach was used to adsorb/desorb CO_2 from the polymer-amine sorbent. This study will utilize a new approach using vacuum swing technology. It is being explored to see if it can become more energy efficient than the temperature swing process. VSA hopes to aid in the regeneration and prevent degradation by lowering the thermal changes required in the adsorption/desorption process. This new technology must be able to create a high purity (~99.9%) CO_2 product for sequestration or recycling, once scaled up to an industrial level. The goal of this project will be to provide a viable sorbent for the CO_2 adsorption to take place in VSA. The sorbents properties were tested qualitative and quantitatively. Texture examinations, contact angles and swelling ratio tests, among others, were utilized to discern potential sorbents. FTIR Spectroscopy is a useful tool in analyzing the adsorption of CO_2. Monitoring how the peaks of the IR spectra change between adsorption cycles gives insight into whether or not the CO_2 has changed the bonds and been weakly adsorbed into the mixture. Developing a reusable efficient sorbent will be key in the battle against rising global CO_2 levels.

Background

Prior to the eventual adoption of renewable energy, capturing CO_2 from stationary sources allows for the continual use of fossil fuels as zero-emission technology. Capturing CO_2 from the atmosphere, a negative emission technology, allows for the offsetting of CO_2 emissions from gasoline/diesel-driven transportation. Capturing CO_2 from fossil fuel-driven vehicles is not economically feasible. The addition of a CO_2 capture device to these vehicles would increase the curb weight of the vehicles which drastically decreases their fuel efficiency. **Table 1** illustrates the relative emission coefficients of various compounds found in fossil fuel energy sources.[11]

Table 1. Emission coefficients of CO_2

Emission Coefficient of CO_2 by Fuel					
Fuel	Gasoline	Coal	Natural Gas	Diesel	Atmosphere
lb CO_2/Btu[a)]	148.54	211.06	116.65	163.45	-
Emission	Gasoline[c)]	Coal	Natural Gas	Diesel	Atmosphere
CO_2	18 vol %	13.6 vol %[e)]	4 - 9.1 vol %[e)]	12 %[f)]	420 ppm
CO	0.85 vol %	-	-	5-1500 ppm[b)]	100 ppb
NO_x	0.08 vol %	-	0.64[d)]	20-2500 ppm[b)]	-
O_2	0.7 vol %	4.2 vol %[e)]	3.3 vol %[e)]	30000-200,000 ppm[b)]	21%

[a)] Carbon Dioxide Coefficients[5]
[b)] Diesel Emissions[6]
[c)] Gasoline Emissions[7]
[d)] NO_x coefficient[8]
[e)] Natural gas and coal oxygen emission[9]
[f)] Diesel Emission[10]

The majority of captured CO_2 needs to be sequestrated by geological storage which involves injection of supercritical CO_2 into rock formation at more than 800 m below the surface[12]; a small fraction of CO_2 could be recycled for various applications. Both CO_2 sequestration and utilization require use of high purity CO_2, e.g. > 99% purity.

Amine-based sorbents/solvents have been considered highly promising for CO_2 capture because of their high rate and selectivity as well as their capability for regeneration for thermal swing capturing CO_2. Figure 1(a) shows the adsorption of CO_2 is conducted typically at a low temperature, below 60°C, and the regeneration of sorbent with the desorption of CO_2 at a high temperature, above 100°C. Note that the temperature of flue gas leaving the baghouse of a coalfired power plant is around 60°C. These temperature differences require an input of energy to create the perfect conditions for absorption to occur.

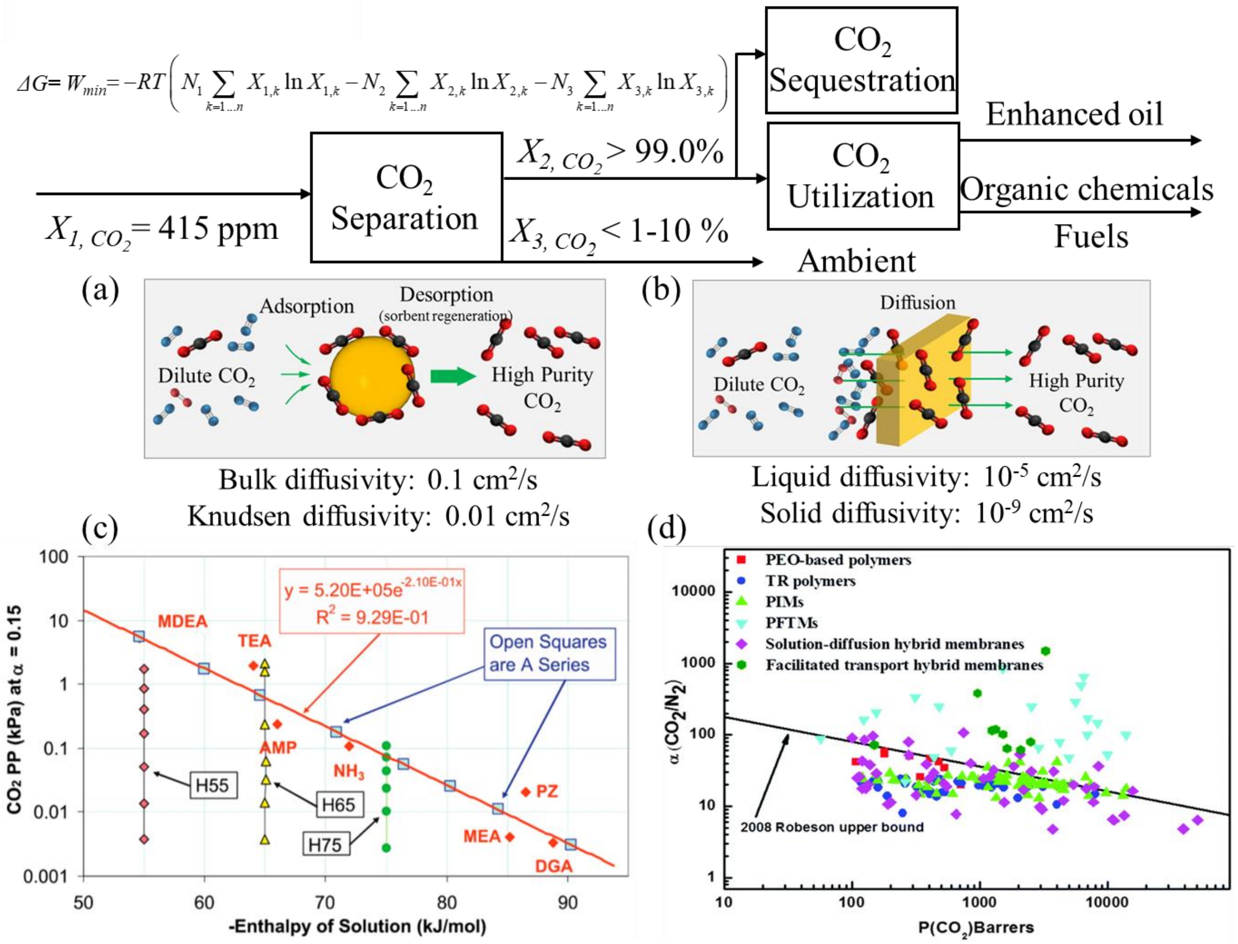
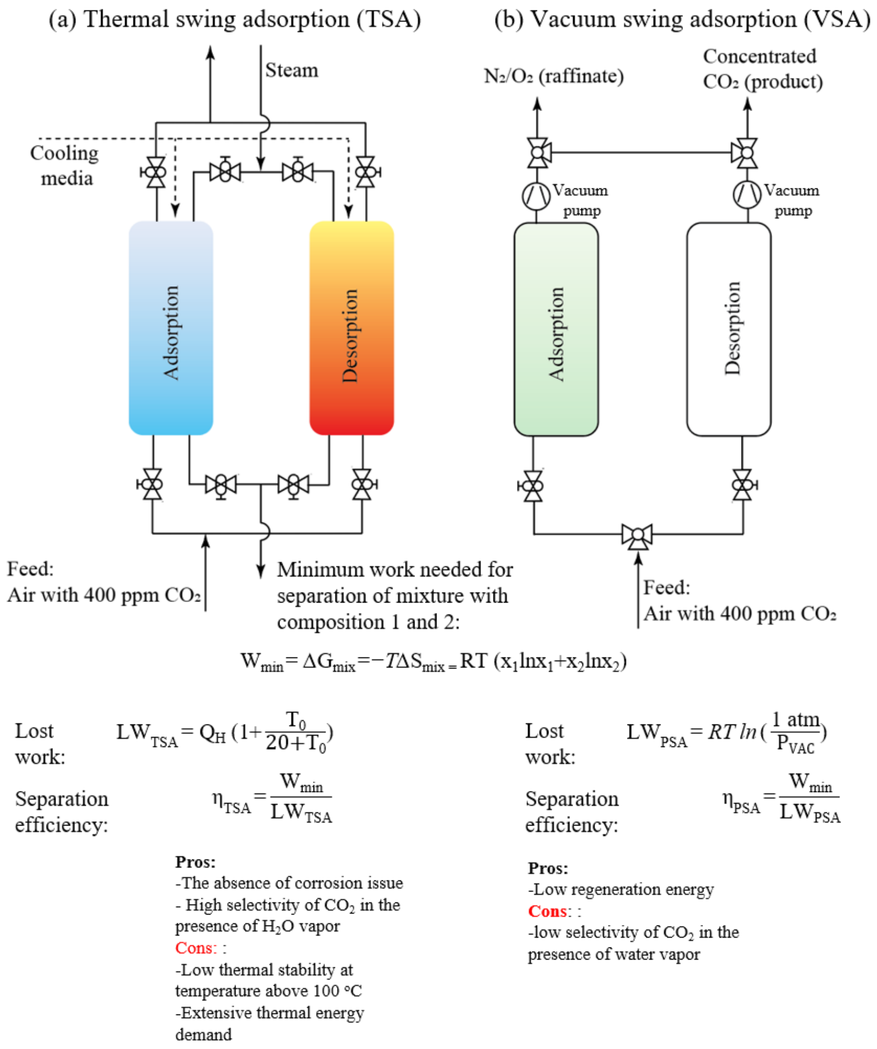


Figure 1. The scheme of CO_2 capture by sorbent/membrane and their utilization/sequestration (c) Reprinted with permission.[13] Copyright 2017, American Chemical Society. (d)Reprinted with permission.[14] Copyright 2016, Royal Chemical Society.

Utilizing VSA aims to lower this input of energy by either completely removing the need for temperature swings or by greatly reducing the energy input needed to raise/lower the temperature. Removing the need for utility steam will also lower the cost of industrial production and increase the safety of the process, as shown in **Figure 2**.



$$W_{min} = \Delta G_{mix} = -T\Delta S_{mix} = RT\,(x_1 \ln x_1 + x_2 \ln x_2)$$

Lost work: $LW_{TSA} = Q_H\,(1+\frac{T_0}{20+T_0})$

Separation efficiency: $\eta_{TSA} = \frac{W_{min}}{LW_{TSA}}$

Pros:
-The absence of corrosion issue
- High selectivity of CO_2 in the presence of H_2O vapor
Cons: :
-Low thermal stability at temperature above 100 °C
-Extensive thermal energy demand

Lost work: $LW_{PSA} = RT\,ln\,(\frac{1\ atm}{P_{VAC}})$

Separation efficiency: $\eta_{PSA} = \frac{W_{min}}{LW_{PSA}}$

Pros:
-Low regeneration energy
Cons: :
-low selectivity of CO_2 in the presence of water vapor

Figure 2. Temperature Swing Adsorption (TSA) versus Pressure/Vacuum Swing Adsorption (VSA) CO_2 Capture Processes.

At small scales, membrane separation which is operated isothermally can be thermodynamically efficient at a low volumetric flow rate of process streams. The diffusion of CO_2 molecules in the membrane is a rate-limiting step in the overall membrane separation process, shown in **Figure**

1(b). Overcoming the low rate of diffusion has shown to be difficult[15]. The use of a large pressure and partial pressure difference is needed to provide the driving force for pushing CO_2 from a dilute to a concentrated stream. Furthermore, most membranes exhibit an inverse relationship between selectivity and permeability, shown in Figure 1(d). Membrane process is suitable for small scale operation but will be inefficient when large scaling-up occurs[16].

As we try to model large scale CO_2 separation via adsorption using amine and organic solvents, it is important to understand each step of the process to ensure the highest purity possible. The adsorption process for CO_2 capture, illustrated in **Figure 1(a)**, involves two key steps: (i) capturing CO_2 with solvent (i.e., absorption of CO_2 into the solvent) and with sorbent (i.e., adsorption of CO_2 on the sorbent) (ii) solvent/sorbent regeneration (i.e., desorption of absorbed CO_2 from solvent/desorption of adsorbed CO_2 from sorbent). Two key functions of amines, (i) selective binding to CO_2 and (ii) the ability of amine sites for regeneration, are largely preserved as the amine functional group moves from an environment surrounded by aqueous solution to flue gas/ambient air. It has been found that primary amines are most suited for the adsorption/desorption cycles that the sorbent must withstand. Secondary and tertiary amines were found to have intermolecular forces that impeded the cyclic nature of the desired process.[4]

The chemistry of CO_2-amine interaction has been widely studied for its use in industrial applications. Figure 3 illustrates the CO_2-amine reaction where the amine-functional group (R-NH_2), possesses unpaired electrons, serving as a Lewis base for selectively and reversibly binding CO_2 – a Lewis acid. Nucleophilic attack of the unpaired electron on the amine to electrophilic carbon in CO_2 produces a Zwitterion, which then further react with neighboring amine groups to form ammonium carbamate and/or carbamic acid. Many spectroscopic studies have provided evidence to support the formation of ammonium carbamate and carbamic acid for

CO_2 adsorption on amine sorbents[17, 18, 19]. Carbamate has shown to be more useful in the process creating a weakly absorbed interaction with CO_2.[20] Using this prior knowledge, we aimed to create a durable polymer-amine sorbent that naturally forms ammonium carbamate when exposed to CO_2 in the presence of water.

Experimental Methods

Solution Preparation

Solutions were prepared in 20 mL vials. Various molar ratio mixtures were created utilizing the polymer solvents Polyethylene Glycol Diacrylate (PEGDA), Polypropylene Glycol Diacrylate (PPGDA), Polypropylene Glycol Diglycidyl Ether (PPGDE) with average molecular weights of 700 g/mol, 800 g/mol, and 380 g/mol respectively. These solvents were mixed with Pentaethylenehexamine (PEHA) or Polyethyleneimine (PEI), the vehicles for adsorption, with average molecular weights of 232.37 g/mol and 2000 g/mol. Next, depending on the specific experiment performed, the samples were mixed with additional solutes, such as Potassium Chloride (KCl), to be later desorbed out to create a porous structure. After the addition of the solutes, A photo initiator was added at 2%wt of the solvent to aid in the reaction. Once combined in the vial, a vortex mixer was used to facilitate mixing. The samples were then transferred to small aluminum trays and exposed to a Ultraviolet (UV) light source for approximately 20 minutes. Once polymerized, the solutions began to be tested or would be soaked in another solvent such as, water, ethanol, or isopropyl alcohol.

As testing was completed, a focus to create a short chain (Amine-Polymer-Amine) oligomer became paramount. To accomplish this goal, the reactants were exposed to UV light during solution preparation and while being mixed, and then allowed to sit under UV light for an additional 20 minutes.

Qualitative testing

Obtaining qualitative data was an important factor during the lifetime of the created samples. “Stickiness” was analyzed for all samples by monitoring how well the sample would adhere to a blade, tong, finger, or aluminum tray. The relative stickiness gave insight into how much amine was present in the solution. Changes in color were documented to show how various variables including: heating, cooling, timescale, adsorption, and exposure to new solvents would affect the sample. The solutions prepared were desired to have a soft but strong malleable rubbery texture. Brittle or glass-like samples would be unable to handle the cyclic nature of VSA. A certain "rigidity threshold" needed to be obtained so that the "hydrogel-like" substances could withstand transportation and manipulation throughout testing. A liquid sample with low viscosity performed poorly compared to a highly viscous gel. Wrinkling of the outer surface of the sample was desirable, as shown in **Figure 3**, indicating sufficient cross-linking between the polymer and amine. Smooth gels would not provide sufficient surface area for adsorption to take place. Along with sufficient wrinkling, ample porosity was needed provide a surface for weak absorption of CO2. To aid in the creation of pores, substrates such as KCl and F-127[21] were dissolved out of the solution once polymerized.

Figure 3. Pictured are 2 PPGDA-PEHA (1:2) mixtures, one with KCl added(right) and one without(left). Wrinkling of the structures provides insight that ample crosslinking did occur.

Swelling Ratio

A swelling ratio test was performed to help measure the crosslinking density of the polymer mixtures. The samples with higher amounts of amine and higher stickiness have a lower molecular weight and should also have a lower crosslinking density. The equilibrium swelling ratio (Q*) of all samples was measured by weighing fully swollen hydrogels equilibrated in their aqueous medium (m_s) followed by recording their dry mass (m_d).

$$Q^* = m_s / m_d \qquad (1)$$

The gels were soaked in water or IPA and compared to one another. Various compositions of polymer:amine molar ratios were tested: 1:0, 2:1, 1:2, 1:3.

Contact Angle

Water contact angle testing was performed to determine the relative hydrophobicity/hydrophilicity of various samples. A small portion of the polymer-amine mixture, approximately 1.5 cm in diameter was placed on a glass slide. A 5 ml glass pipet was used to place a single drop of water onto the sample. This action was recorded using the video camera feature on the iPhone 12. The angle was determined using the computer software PicPick. The application allows the user to take a still photo of a video to utilize the protractor feature. The baseline axis was placed on the top surface of the sample and the angle line was placed on the outer curve of the water droplet, as shown in **Figure 4**. A smaller angle indicates higher hydrophilicity.

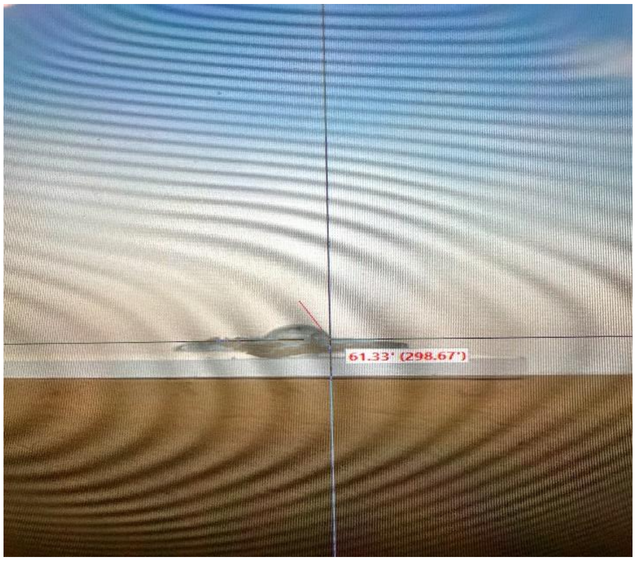


Figure 4. PicPick software example of contact angle testing of a 1:0 polymer-amine sample

Adsorption Testing

The ideal polymer will have sufficient pores for the uptake of solvent to take place. Water adsorption testing was performed to determine which combination of PPGDA and PEHA had the optimal pore size. A small portion of the polymer-amine mixture, approximately 1.5 cm in diameter was placed on a glass slide. The samples were weighed for their initial dry weight. A 5 ml glass pipet was used to place drops of water continuously onto the sample. Water droplets were added until the sample could no longer adsorb any more water and it began to spill onto the glass slide. The wetted sample was moved to a new dry glass slide and reweighed.

Subsequent adsorption testing took place later in the research. New samples of PPGDA were mixed with Pluronic-123 then mixed with either IPA, ethanol, or water. Once the samples polymerized and solidified, a razor blade was used to cut into the side of the samples. This was done to create easier access to the porous structure. The dry sample was weighed on a gram scale. A pipet was used to dispense water into the porous side. Water was added until the sample could no longer adsorb any more, and the water began to spill over. The wetted sample was reweighed and the weight % change was analyzed.

FTIR Spectroscopy Testing

Fourier transform infrared spectroscopy (FTIR) is the most commonly used spectroscopy in polymer science due to its ability to provide quick readings and preserve the sample. A sample's covalent bonds will absorb radiation of specific wavelengths depending on the atoms in the bond. Specific bonds absorb different frequencies and therefore the % transmittance pattern is different. A test run utilizing a 1:2 PPGDA-PEHA sample was placed in a DRIFT (diffusive reflectance infrared Fourier transform) cell enclosed by a dome containing two ZnSe windows to allow transmission of the IR beam. The IR spectra of the sorbents and adsorbed CO2 species before and after oxidative degradation were collected in a Nicolet-6700 FT-IR bench. The chamber was purged with Argon gas for 5 minutes to ensure no other gases could react with the sample. Temperature programmed desorption was conducted for 10 mins to desorb any water or other compound from the sample. The sample was then allowed to cool to room temperature utilizing Argon gas. Then, CO_2 was introduced to the chamber for 10 minutes, allowing for absorption to occur. Finally, the CO_2 was allowed to desorb from the sample for 10 minutes through temperature swing while Argon gas flowed through the chamber. Once the sample cooled to room temperature, the IR spectrum was able to be taken and analyzed. When reading the % transmittance vs wavelength (cm^{-1}) a peak between 3000-3500 indicates a nitrogen-hydrogen bond showing that the amine has removed hydrogen from water and thus allowing for the CO_2 to break up and the carbon to weakly bond with other hydrogen groups on the sample.

CO_2 Bubbling

CO_2 was bubbled through the leading candidate for use in VSA, several mixtures of PPGDE-PEI, to determine the ability to absorb CO_2 under ambient conditions. The solutions were created following the same procedure as previously described, exposing them to UV light to promote polymerization. Molar ratio solutions of 2:1, 1:1, 1:2 were created. The solutions were then separated between their solid and liquid portions. This was done to determine how the physical environment and phase affects CO_2 absorption. A small portion (~2 g) of the separated portions were then mixed with equal weight water and allowed to mix using a vortex mixture. The samples were then bubbled with CO_2 at a rate of 40 mg/min for 10 minutes to ensure full saturation. A glass pipet was placed inside the vial to allow for air to release, as shown in **Figure 5.**

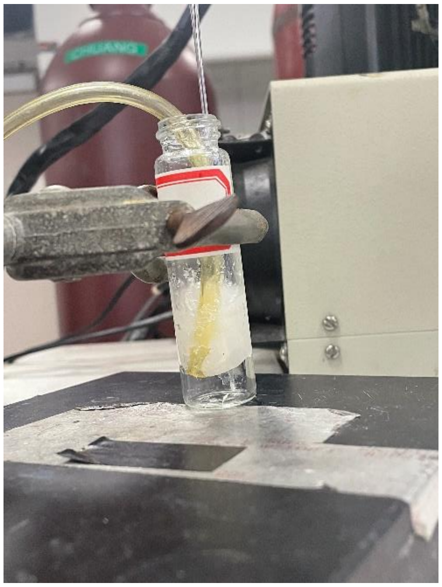


Figure 5. Depicts the CO_2 bubbling test, the tube is flowing CO_2 at 40 mg/min. The glass pipet allows for air to flow.

The size and the rate at which the CO_2 bubbles escaped through the top of the sample was monitored. The physical changes such as, color change and texture, of the sample were monitored to determine the reusability of the sample.

Raman Testing

Raman spectroscopy is similar to FTIR and can help define the structure of chemical samples. Raman testing provides a full spectrum of the specific vibrations of atoms on a molecule. Raman is less sensitive to water than FTIR and therefore may help determine the best sample to use for CO_2 adsorption. Samples were loaded into one of nine individual wells. Utilizing OMNIC software the image was focused on one of the samples. The laser was set to 0.35 W for solid samples and 0.1 W for liquid samples. The focus of the laser was adjusted until the peak-to-peak ratio was as close to 1.0 as could be obtained. A resolution setting of 4 and the number of scans taken was set to 100 to ensure the highest clarity of results. An IR spectrum with clearly defined peaks was desired. An example of a good scan vs. a noisy scan is shown in **Figure 6**. If a sample was too “noisy” meaning the laser was unable to focus well on the sample, the test was rerun until clear scans were obtained, if possible.

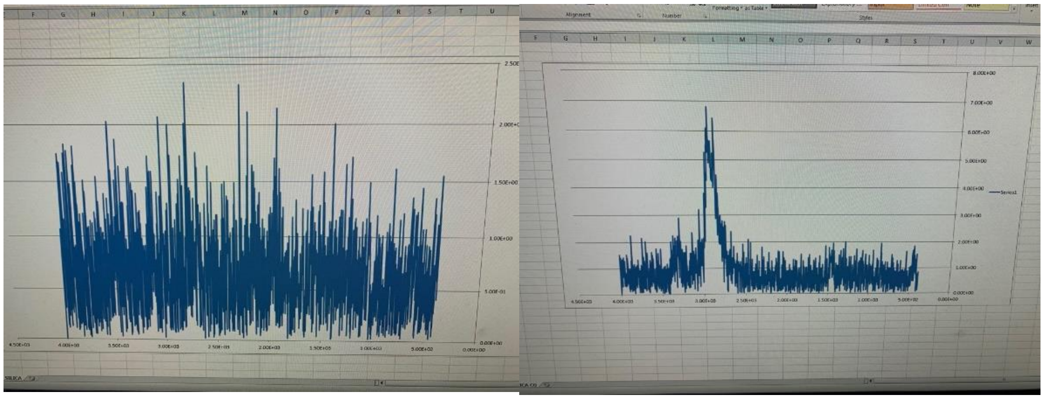


Figure 6. Depicts a poor/noisy scan on the left and a good/clear scan on the right

Data and Results

Qualitative Analysis

Qualitative testing was conducted throughout the project. Each sample created would be evaluated relative to the various other mixtures created. A sufficient amount of stickiness was required to indicate a significant amount of amine was present. Too much amine would cause the mixture to not fully polymerize, and a solid structure could not be obtained, such as in the 1:3 ratios of PPGDA-PEHA. Too much amine will inhibit efficient crosslinking. Wrinkling of the mixtures was desirable for the crosslinking of polymer with amine present. Some of the best wrinkling came from 1:2 Mixture with KCl present. Opaque samples indicated pores within the microstructure of the sample. Porosity allowed for easier adsorption of CO_2. The solutions dominant in polymer over amine were typically clear and showed that there was not enough amine or inserted substrate to bond with the polymer over itself. Photos of these solutions can be found in **Appendix A.** The decision to switch the focus of testing from PPGDA-PEHA to PPGDE-PEI mixtures was made largely in part due to qualitative analysis. PPGDE is able to disperse the amine across its surface allowing for a more hydrophobic environment for the amine, thus making it easier to adsorb CO_2. This change was made to help determine whether dispersion or hydrophobicity is more important in the creation of the sorbent. PEI is a large compound compared to PEHA and is less soluble. It is easier to desorb CO2 from the larger of the two. The physical characteristics of PEI create a thinner layer minimizing the hydrogen bonding interactions seen on the surface of the mixtures. This makes it more likely for CO2 to adsorb and desorb from the sorbent.

Swelling Ratio

Swelling ratio tests were completed PPGDA-PEHA samples containing F-127 and KCl at various compositions. The samples were soaked in IPA and water. The results of the tests can be found in **Table 2**.

Table 2. Swelling ratio results

		Water			IPA		
PPGDA-PEHA Ratio	substrate	soaked weight (g)	dry weight (g)	Q*	soaked weight (g)	dry weight (g)	Q*
1:3	KCl	0.177	0.105	1.677	0.219	0.139	1.583
1:3	F-127	samples unable to be obtained, not fully polymerized					
1:2	KCl	0.218	0.116	1.873	0.207	0.101	2.047
1:2	Pure	samples unable to be obtained, not fully polymerized					
1:2	F-127	0.244	0.173	1.411	0.216	0.100	2.152
2:1	KCl	0.102	0.063	1.609	0.067	0.049	1.351
2:1	Pure	0.056	0.045	1.249	0.080	0.058	1.393
2:1	F-127	0.205	0.177	1.156	0.149	0.109	1.362
1:0	KCl	0.112	0.079	1.414	0.121	0.092	1.320
1:0	Pure	0.132	0.099	1.333	0.136	0.092	1.486
1:0	F-127	0.205	0.177	1.156	0.027	0.015	1.740

(Note: for each condition, one sample was prepared and tested)

Based off the results from this test, the solutions soaked in IPA produced higher swelling ratios. The amine dominant samples produced higher swelling ratios indicating more crosslinking with the polymer. Higher crosslinking allows for the amine to spread out along the surface and is thus able to weakly absorb CO_2.

Contact Angle & Absorption Testing

Contact angle testing was performed for completed PPGDA-PEHA samples containing F-127 and KCl at various compositions. The 1:2 mixture containing F-127 was found to be the most hydrophobic with a large angle of 76°. The most hydrophilic sample was found to be the 1:2 mixture containing KCl with an acute angle of 19°. No general trends were able to be found between the various samples. This may be due to the various surface roughness's of the samples.

Due to the nature of how the samples were collected, one sample may have had a higher concentration of substrate in the tested sample. Testing more samples of the same concentration would help provide more accurate results and a trend may develop. The results from these tests can be found in **Table 3**. Contact angle testing with IPA instead of water was performed but failed to produce any usable results. No bubble would form on top of the sample and the IPA would immediately disperse throughout the sample.

Table 3. Results from H_2O contact angle and Adsorption (Uptake) testing

H20 contact angle testing			H20 Uptake Testing				
PPGDA PEHA Ratio	substrate	Angle (degree)	Initial mass (g)	Final mass (g)	Mass of H20 (g)	volume of H20 (cm^3)	Uptake of sample (cm^3/g)
1:3	KCl	47	0.092	0.115	0.023	0.023	0.251
1:3	F-127	33	0.079	0.095	0.016	0.016	0.206
1:2	KCl	19	0.064	0.184	0.120	0.120	1.885
1:2	Pure	55	0.052	0.093	0.041	0.041	0.792
1:2	F-127	76	0.055	0.087	0.032	0.032	0.573
2:1	KCl	0	0.038	0.087	0.049	0.049	1.276
2:1	Pure	63	0.059	0.109	0.049	0.049	0.833
2:1	F-127	27	0.048	0.107	0.059	0.059	1.246
1:0	KCl	62	0.074	0.276	0.202	0.202	2.738
1:0	Pure	70	0.076	0.219	0.143	0.143	1.898
1:0	F-127	35	0.052	0.186	0.135	0.135	2.612
1:1	F-127	48	0.032	0.110	0.078	0.078	2.438
1:1	KCl	54	0.059	0.135	0.076	0.076	1.280
1:1	Pure	53	0.026	0.054	0.027	0.027	1.038

Adsorption testing took place with the same parent solutions from contact angle testing. Of the samples with both polymer and amine present, 1:1 with F-127 and 1:2 with KCl produced the highest uptakes of 2.4 cm^3/g and 1.9 cm^3/g respectively. Results of all samples tested can be found in **Table 3**. This result, along with the qualitative aspects of the 1:2 KCl sample, leads to the conclusion that it may be the most viable option out of these samples for further research.

Raman & IR Testing

Raman testing was used for obtaining IR spectra. Raman testing was less susceptible to interference from water and was more beneficial to the intended goal of the project. Raman testing was conducted for the PPGDE-PEI mixtures. Raman tests were completed for the samples that underwent CO_2 bubbling and their parent samples that were not exposed to CO_2. The differences in these spectra were analyzed. This helped determine whether or not CO_2 was adsorbed by the species by seeing the different bonds formed. The full IR spectra of all tested samples can be found in Appendix B. Overall it was clear that some CO2 was absorbed, and bonds were changed but no clear best mixture was able to be determine. Repetitive testing of the samples must be conducted to ensure accurate spectra of the various compositions.

Discussion/Analysis

Through the examination of the tested combinations of polymers and amines along with the concurrent work of the Chuang research group, it is believed that the vacuum-assisted thermal swing operation of adsorption will be most favorably constructed with a mixture of PPGDE-PEI. The porosity of the utilized polymers will provide a beneficial workspace for the tuning of the CO_2 binding energy of amine sites. The design and fabrication of the porous structure for amine sorbent will be important in increasing the energy efficiency and reducing the cost of large-scale CO_2 adsorption and desorption. Once the most favorable amine is determined, it will facilitate the development of sorbent on a large-scale CO_2 capture process.

In agreement with Didas[4] prior work, it is believed that primary amine sources will efficiently weakly adsorb CO_2 when sufficiently spread out along the polymer surface. The amine must be suspended far enough away from other amine sites so that when CO_2 is adsorbed intermolecular forces such as, hydrogen bonding does not disrupt the eventual desorption of CO_2 later in the process. Adding substrates such as KCl and F-127 to the polymer allows the creation of porous polymer matrices to increase the adsorption area hence, increasing the adsorption capacity of the sorbents and aid in the isolation of amine sites. Dr. Chuang found similar results when creating TEPA/PEG sorbents with low amine densities[20].

Through the testing during this project, PPGDE-PEI mixtures were found to be more favorable over PPGDA-PEHA mixtures. Porous structures were easier to create, and the mixtures polymerized more easily. PEI was able to be isolated and believed to create the desired primary amine sites. Further testing will need to be conducted to determine the optimal composition of this mixture.

To improve the accuracy of these studies, further repetitive testing must be completed. The bubbling of CO2 and subsequent Raman testing must create reproducible results across many different samples. Due to the time constraints of this project, each test was only proven anecdotally to ensure the forward progress of the project. Ideally, each test would have been repeated till there were no major discrepancies in the data and proper trends were established. The relative age of the samples may have provided some inaccuracies. The mixed samples were tested over several months and this may have decreased the efficacy of CO_2 adsorption. In future work the lifespan of samples should be drastically reduced to ensure that the proper reactions are able to take place. Increased Raman testing at multiple stages of research is recommended to better analyze the effects of various tests performed on the samples.

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Appendices

Appendix A- Photos of mixed solutions

Figure 7 Solutions OF PPGDA-PEHA at different ratios combined with various substrates

Figure 8 Solutions of PPGDA mixed with different solvents to create a porous structure

Appendix B- Raman Testing

Procedure

- Mixtures were created and allowed to solidify under UV light and allowed to sit under daylight for an extended period of time
- Mixtures were then separated between solid and liquid portions
- CO2 was then bubbled through samples for ~20min
- Samples then sat for an extended period of time then Raman studies were collected

Detailed compositions

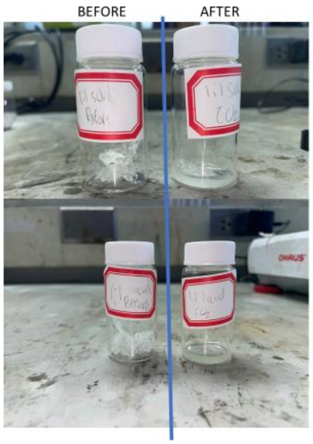
- PPGDE: MW ~380
- PEI: MW ~2000
- Mixures of 1:2, 1:1, 2:1 Polymer -Amine solutions were made
- Solutions were allowed to polymerize under UV light
- Solutions were separated between solidified hydrogel and still liquid portions
- Solutions were then mixed with equal weight water
- Samples then bubbled with CO2

2:1 (Polymer-amine) samples

- Solid: 2.716 g Polymer mix + 3.5 g H2O
- Liquid: 1.175 g polymer mix + 1.3 g H2O

1:1 (Polymer-amine) samples

- Solid: 2.12 g Polymer mix + 2.18 g H2O
- Liquid: 1.393 g polymer mix + 1.58 g H2O

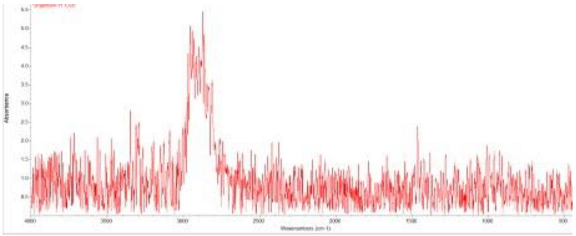


Issues in testing

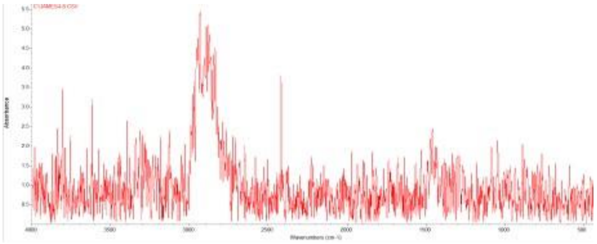
- Experimental set up getting peak-to-peak parameter is hard to get to 1.00
  - Focusing equipment is difficult
- 1:1 liquid portion samples were too liquified to get a good reading
- 1:1 solid portion had a very poor scan

2:1 mixture using solidified samples

No CO2 absorbed

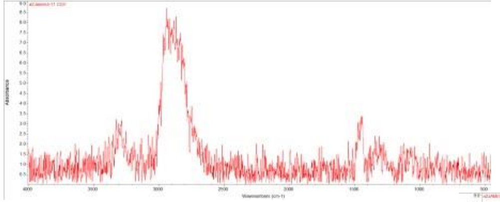


CO2 absorbed

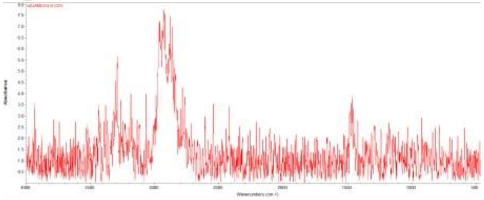


2:1 Mixture using liquidized samples

No CO2 absorbed

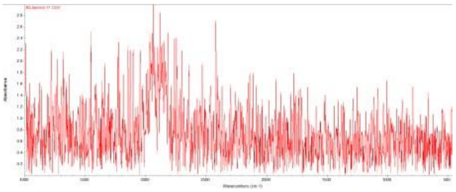


CO2 absorbed



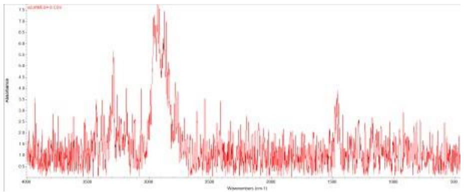
1:1 mixture using solidified samples

No CO2 Absorbed



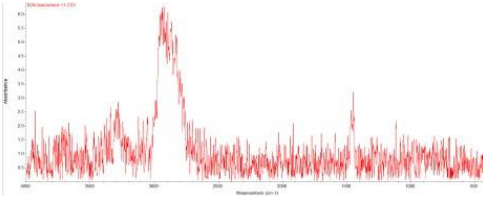
Poor Scan very noisy

CO2 Absorbed

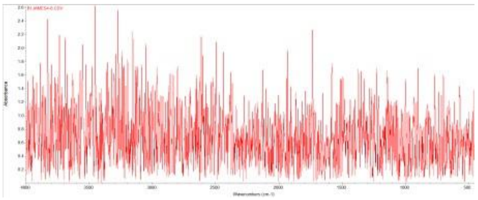


1:1 mixture using liquidized samples

No CO2 Absorbed



CO2 Absorbed



Poor scan very noisy, sample was liquid