2023

EFFECTS OF METAL ORGANIC FRAMEWORKS IN POLYETHER BLOCK AMIDE ELASTOMER

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EFFECTS OF METAL ORGANIC FRAMEWORKS IN POLYETHER BLOCK AMIDE ELASTOMER

By

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Mechanical Engineering at
The University of Texas at Arlington
May 2023

Arlington, Texas

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TEXAS
ARLINGTON

Acknowledgements

May 16, 2023

I would like to thank the University of Texas at Arlington and the Department of Mechanical and Aerospace Engineering for admitting me as a Graduate Student and allowing me to pursue my master's in mechanical engineering.

I would like to thank Dr. Michael Bozlar for taking me under his guidance and allowing me to do my thesis at the Bozlar Nanoscience Lab (BNL). I have been able to explore and learn a lot during my time with him. I will always hold in high regard the counsel and recommendations he has provided me for improving the quality of my work.

I would also like to thank Dr. Nancy Michael and Dr. Robin Macaluso for the time set aside from their busy schedules to be on my Thesis Defense Committee to examine and provide valuable feedback on my work.

I would also like to extend my gratitude to Dr. Yaowu Hao and Mr. Ryan Hart for allowing me to use their facilities for my thesis research. Also, I would like to thank Mr. Brian Shonkwiler of the Advanced Materials and Structures Lab for his time and support at the testing facility.

I would also like to thank my lab mates Ms. Sathvika Gondi, Mr. Ashish Anilal, Mr. Vitaliano Dattilo and Mr. Doğukan Yazici for their assistance and help extended during my experiments.

Finally, I would like to thank my parents Mr. Joe Binoy, Mrs. Minu Binoy, my siblings Ms. Ann Alex, and Mr. Joepaul Alex for trusting me and supporting me through my journey towards graduating with a master's degree from this prestigious university.

Abstract

Metal organic frameworks (MOFs) are highly porous materials that find extensive applications in gas absorption and separation in recent years. These hybrid materials can be designed with specific pore sizes and voids to selectively filter gases. PEBAX (MV 1074) is a commercially available polyether block amide copolymer generally used in gas separation applications. In this study, we characterize two different MOFs by means of a dispersion study and create a medium for them to be evenly dispersed into the aforementioned copolymer matrix. Polymer composite fibers are extruded using a twin-screw extruder and a winding unit at pre-determined parameters for winding speed and torque. These composite fibers are then tested for their tensile strength and gas absorptivity and compared to the neat fibers to evaluate the effects these MOFs have in the copolymer matrix.

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Chapter 1: Introduction

With the dependence on fossil fuels for the majority of the power generation in the world, removal of excess carbon dioxide (CO_2) and other greenhouse gases has become a necessity today to help tackle the consequences of climate change. With the high rates of global emissions, CO_2 capture is critical since it is the greenhouse gas responsible for warming of the earth's atmosphere and also has been linked to other environmental issues like rising sea levels, extreme changes in the weather and ecosystems. Intergovernmental Panel on Climate Change (IPCC) has emphasized the need for CO_2 capture for achieving the global climate goals [1]. In a 2020 report, The International Energy Agency (IEA) states Carbon Capture and Storage (CCS) is a key technology to achieve the Paris Agreement's goal of keeping the global average temperature well below 2°C above pre-industrial levels [2]. In order to help reduce the carbon footprint, new cost-effective technologies have been studied to improve the CCS systems. One of the promising technologies is the membrane-based CCS system [3] which uses special materials for selectively absorbing and filtering CO_2 from the atmosphere.

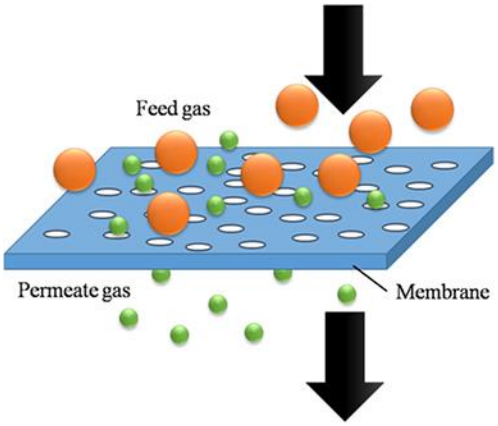


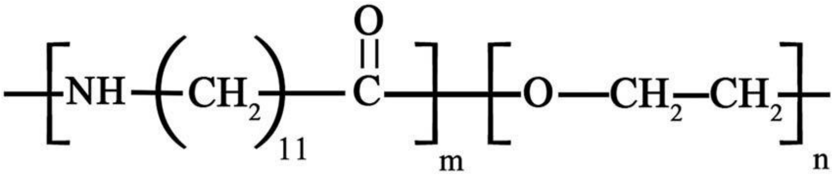
Fig 1: Schematic representation of membrane-based gas separation [4].

The main advantage of the membrane-based CCS is that it consumes less energy and has lower environmental impact compared to the traditional CCS. Membrane-based CCS can be applied in smaller scales due to its high purity (>90%) and relatively lower physical footprint. The materials used for the membrane-based CCS applications should possess high selectivity and high permeance with good durability to withstand harsh industrial conditions.

The membrane-based CCS systems are relatively new and there are new composite materials currently studied for this purpose. In this study we incorporate the highly selective properties of Metal-Organic Frameworks (MOFs) [24] and the good permeance of polyether block amide [26] to fabricate a composite material by the process of extrusion retaining their desirable properties. These composite materials are then tested for their mechanical properties and gas absorption capabilities to evaluate the feasibility of using this material in the membrane-based CCS system.

1.1 Polyether Block Amide

Polyether block amide is a thermoplastic elastomer which recently gained attention for its performance and properties. Known under its tradename PEBAX® [7] which is obtained from Arkema, it has variety of applications in sports equipment, medical products, electrical and electronic casings, and coatings, for breathable films and membranes, etc. These elastomers are a type of block copolymer composed of rigid polyamide blocks and soft polyether blocks. These blocks can be manipulated in different ratios to create a range of flexibility on either end of the spectrum without the need for any plasticizers. PEBAX is available in different grades according to its major application. For this experiment in our laboratory, we considered the PEBAX MV 1074 SA 01 series, which has high breathability and selective permeability. This hydrophilic grade of PEBAX, which does not allow liquid molecules to pass through them, can be extruded into thin films to be used as a breathable membrane while remaining waterproof. This also exhibits good permeability to gases like CO_2 and water vapor, making them a desirable choice to be used as membranes for carbon dioxide (CO_2) capture technologies [10].



$$-\left[NH-\left(CH_2\right)_{11}-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_m\left[O-CH_2-CH_2\right]_n-$$

Fig 2: Chemical structure of PEBAX® MV 1074[1].

The main characteristics of the PEBAX MV 1074 series of elastomers were made available to us from the data sheet provided to us by Arkema. This polymer has a melting point ranging from 158 - 172℃ [6]. The polymer was available to us as solid granules with a natural color as seen in the image below.

Fig 3: PEBAX® MV 1074 is available to us in the form of natural-colored granules.

1.2 Metal Organic Frameworks

Metal Organic Frameworks, also known as MOFs, are an extensive class of highly porous crystalline materials with a variety of applications ranging from drug delivery systems to clean energy applications [18]. As the name suggests, MOFs have a hybrid structure with organic linkers and metal ions or clusters. MOFs have attracted a lot of attention during recent years due to their versatility and tunability according to the applications in gas storage, separation, catalysis, sensing, drug delivery and more [13][15]. The MOFs are typically known for their sponge-like network with an extremely large surface area of up to 7000 m^2/g. Their unique pore size and shape can be tailored to fit specific molecules making them a very viable alternative for selective filtration and absorption of gases.

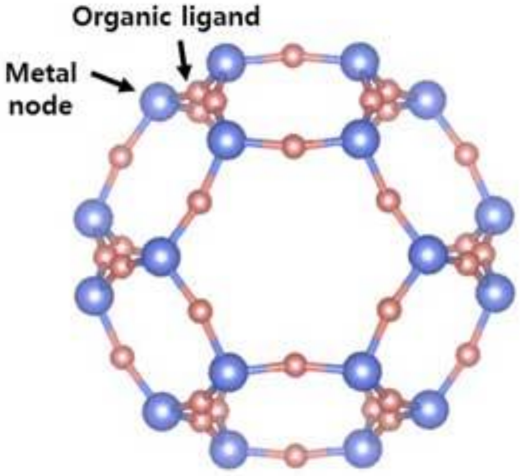
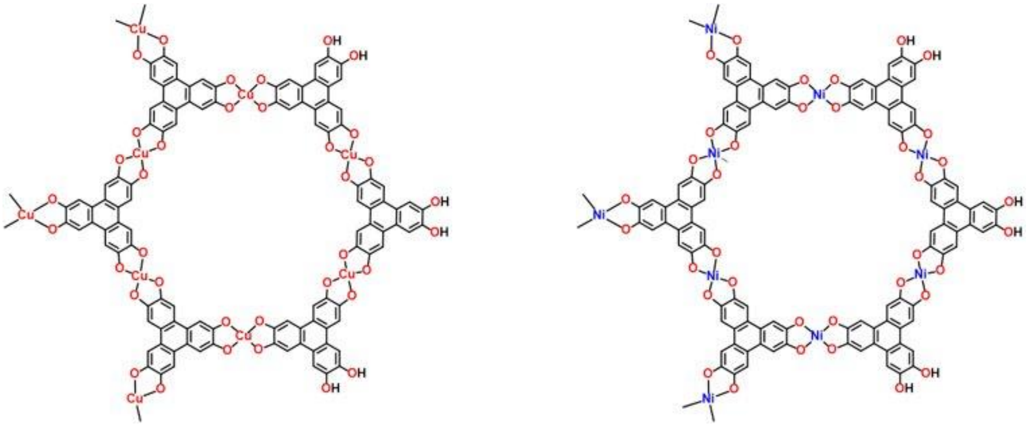


Fig 4: A schematic representation of a metal-organic framework (MOF) [14].

At the beginning the MOFs were synthesized by Solvothermal process where the metal precursors and the organic ligands are allowed to be dissolved in a suitable solvent followed by leaving it in a closed environment and then removing the solvent and any uncoordinated ligands. The solvents used, the temperature and time for crystallization generally varies for each type of

MOF. More recently, new methods of synthesis like electrochemical, microwave-assisted, mechanochemical synthesis, microfluidic synthesis, etc. have been reported [16].

For this study, we considered two different MOFs, Cu_3HHTP_2 and Ni_3HHTP_2 (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), provided to us by our collaborators [23]. Both MOFs are some of the most highly conductive 2D metal-organic frameworks reported to date [21][22].



(a) *(b)*

Fig 5: Chemical structure of (a)Cu_3HHTP_2 and (b)Ni_3HHTP_2.

Both the PEBAX and the MOFs have been studied separately in CO_2 membrane applications [24][25][26]. They have shown promising results in the literature reviewed on the separation of CO_2 from the atmosphere. In most of the research, the membranes are made using chemical processes which can be complicated when compared to something like melt mixing process using an extruder. The main objective in my study here is to synthesis filaments of PEBAX polymer with MOF particles incorporated in them without altering the chemical composition of either of the materials used and understand how this alters the properties like yield strength and the CO_2 absorptivity of the filaments in comparison to the neat PEBAX filaments.

Chapter 2: Dispersion study of Metal-Organic Framework

Metal-organic frameworks have a lot of potential in the field of polymer composites. To implement the applications of the MOFs in various polymers, we must study their dispersion characteristics in various solvents. There was not much research available on the dispersion study of the Ni and Cu MOFs we considered. These MOFs were available to us in the form of a black crystalline powder. But for my study, melt blending method was preferred for the preparation of the polymer-MOF composite. To ensure an even mixing of the MOFs into the polymer, we had to form a well dispersed medium with these MOFs suspended in it. This dispersion study helps to find the best solvent available for the preparation of the dispersion medium and incorporate the MOFs into the polymer without affecting their chemical composition.

We considered 7 different commonly available solvents for this study. The solvents considered were Deionized water (DI), Acetone, Ethanol, Isopropanol (IP), Triethylene glycol, N-Methyl-2-pyrrolidone (NMP) and Tetrahydrofuran (THF). We conducted the dispersion study of the synthesized Cu and Ni MOFs and made use of UV-Vis spectroscopy [29] to characterize their long-term suspensions. The MOFs showed some similarities in the structure to graphene, hence we decided to conduct the dispersion study by the method adapted from a similar dispersion study conducted on graphene [32].

We weighed 5mg of each MOF and dispersed them in 10 mL of the different solvents mentioned before to attain a concentration of 0.5 mg/mL. Each of the dispersions were sonicated using a bath sonicator (Branson 5800) available in our lab for 10 minutes per sample. The sonicated samples were then allowed to sit for more than 3 weeks without any external disturbances. The samples were observed every day for any changes and the observations were noted.

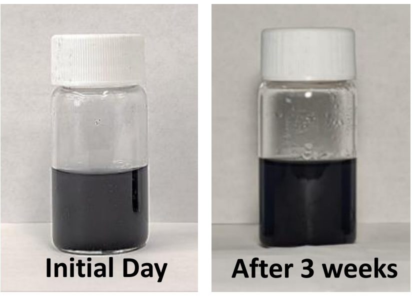


Fig 6(a): Cu MOF in Acetone

Fig 6(b): Cu MOF in Deionized water

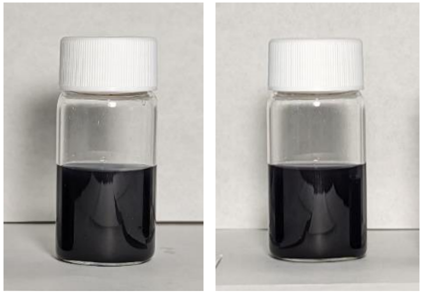


Fig 6(c): Cu MOF in Ethanol

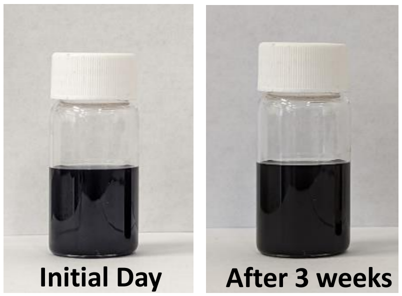


Fig 6(d): Cu MOF in Triethylene Glycol

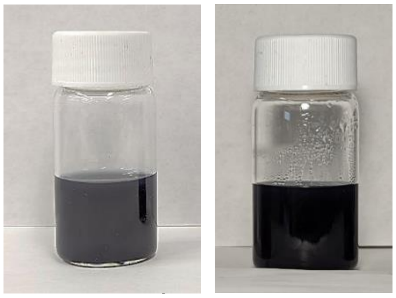


Fig 6(e): Cu MOF in Isopropanol

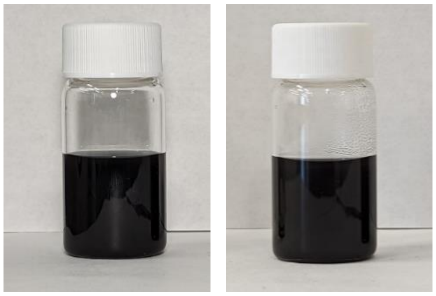


Fig 6(f): Cu MOF in N-Methyl-2-pyrrolidone

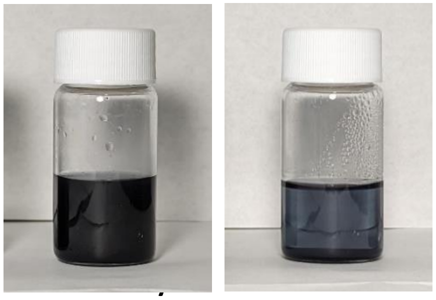


Fig 6(g): Cu MOF in Tetrahydrofuran

Figures 6(a) - 6(g) show the different samples of Cu$_3$HHTP$_2$ MOFs dispersed in different solvents that we have considered for this study. The images compare each sample on the initial day when the MOFs were dispersed in the solvent and the sample after 3 weeks.

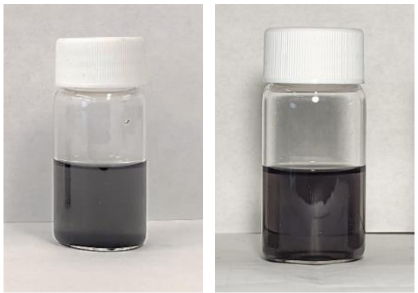


Fig 7(a): Ni MOF in Acetone

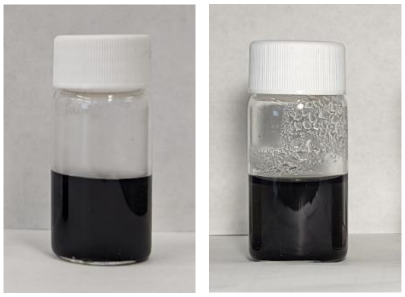


Fig 7(b): Ni MOF in Deionized water

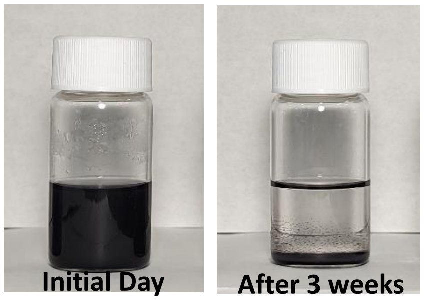


Fig 7(c): Ni MOF in Ethanol

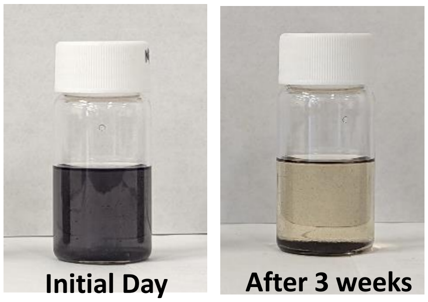


Fig 7(d): Ni MOF in Triethylene Glycol

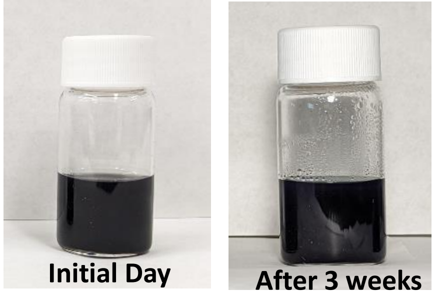


Fig 7(e): Ni MOF in Isopropanol

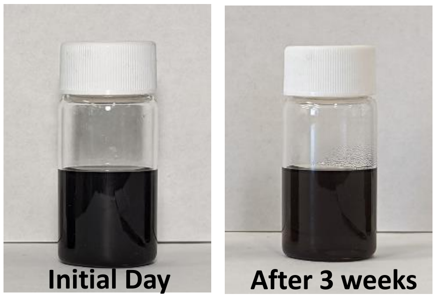


Fig 7(f): Ni MOF in N-Methyl-2-pyrrolidone

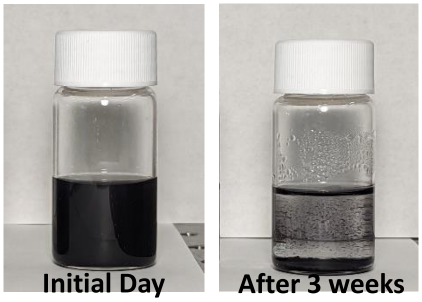


Fig 7(g): Ni MOF in Tetrahydrofuran

Similarly figures 7(a) – 7(g) compare the observation for the samples on the initial day and after 3 weeks from the dispersion for the Ni_3HHTP_2 MOFs in the solvents.

It was visually observed that the Cu_3HHTP_2 MOF particles showed more stable long-term dispersions in most of the organic solvents except for tetrahydrofuran which showed partial stability. But in the case of the Ni_3HHTP_2 MOFs, they showed mixed results. The Ni_3HHTP_2 MOFs were unstable in ethanol, triethylene glycol and tetrahydrofuran. This made them unfavorable for dispersion in the polymer matrix when compared to the Cu_3HHTP_2 particles. Further UV-Vis data was also collected for all the samples to study the dispersion characteristics of these suspensions.

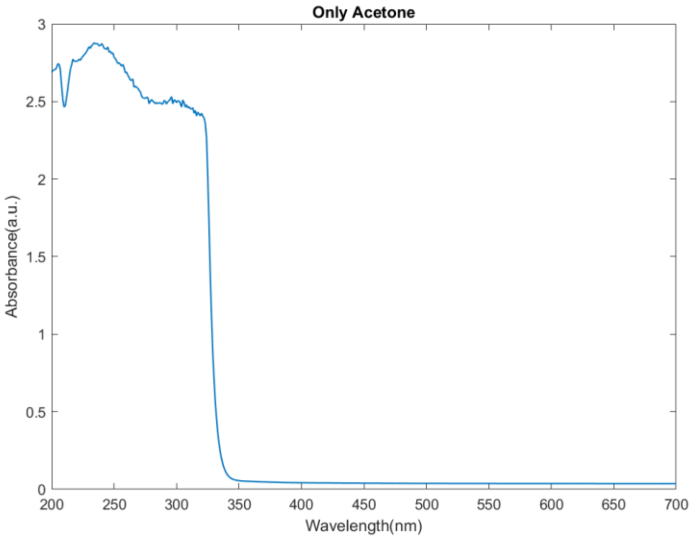


Fig 8(a)

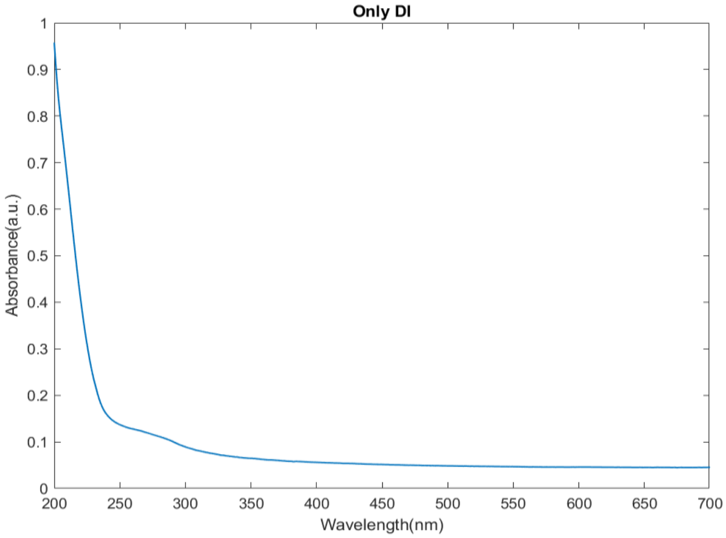


Fig 8(b)

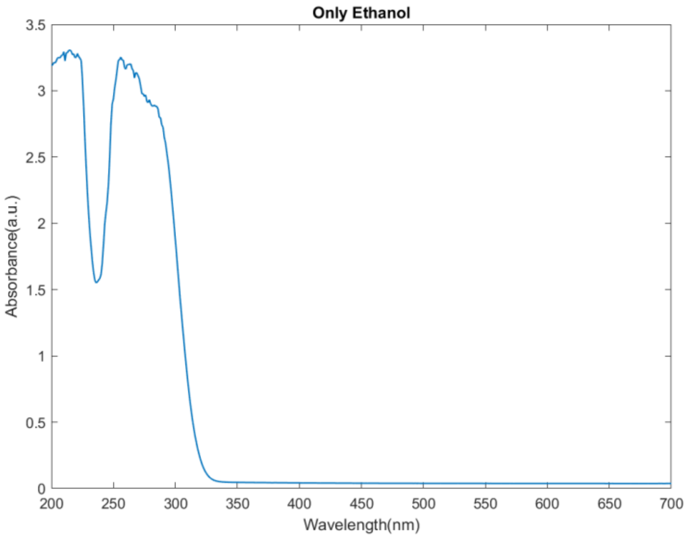


Fig 8(c)

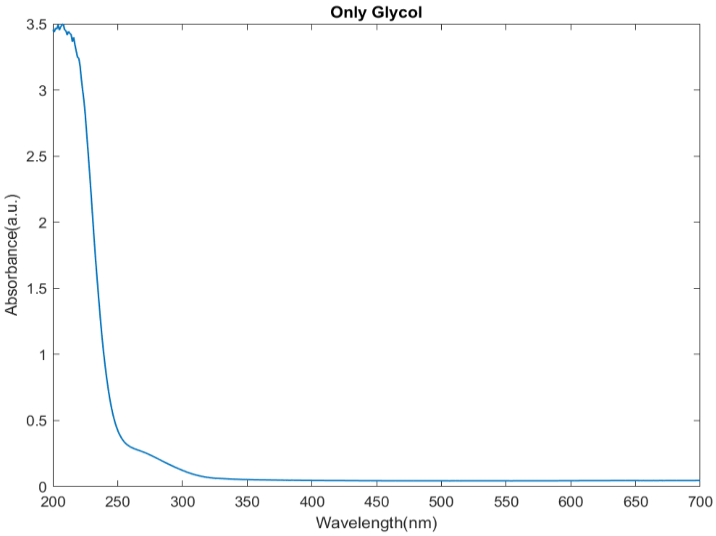


Fig 8(d)

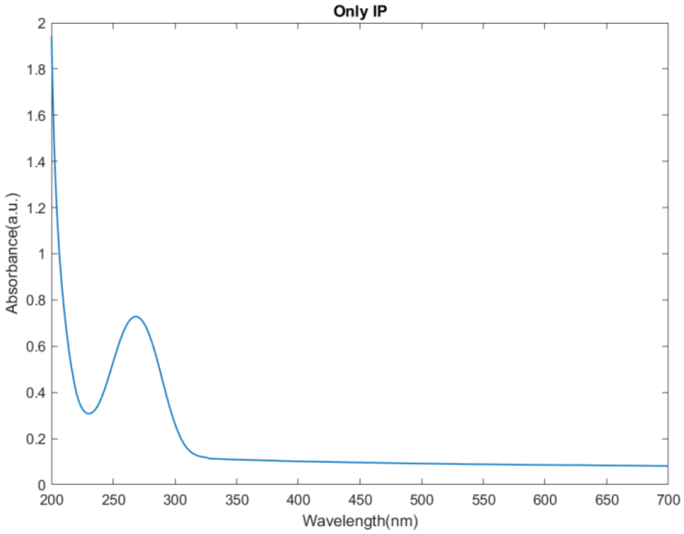


Fig 8(e)

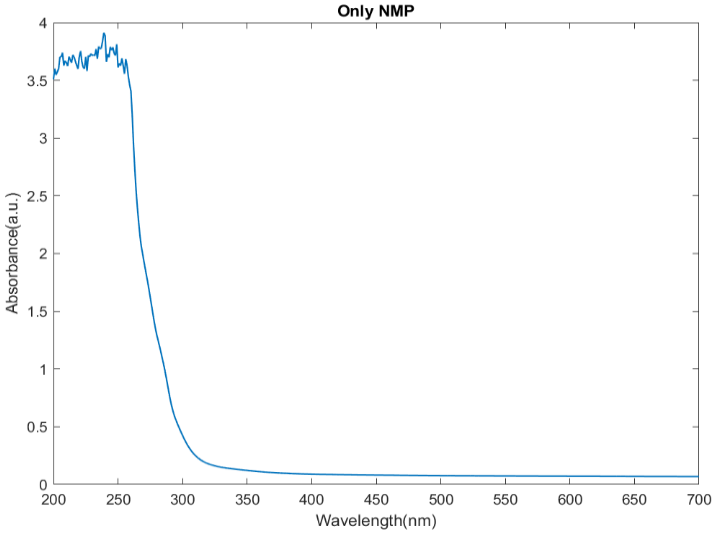


Fig 8(f)

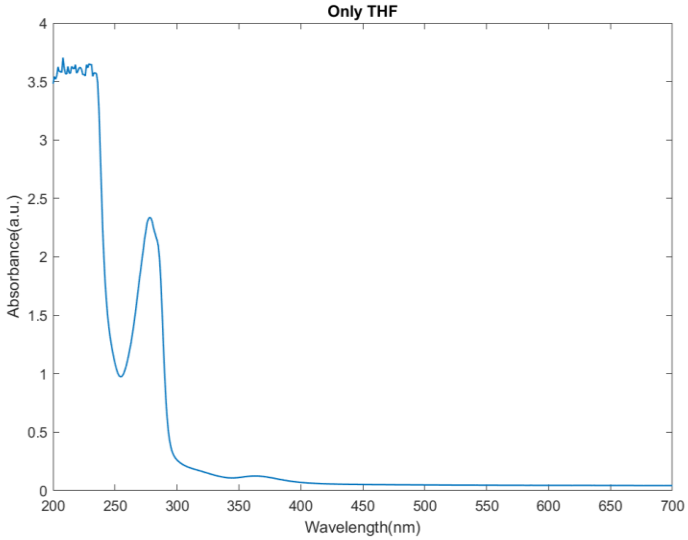


Fig 8(g)

Figures 8(a) - 8(g) show the UV-Vis spectra of the solvents used in the dispersion study. This helps us to identify the peaks caused by the MOF particles from the spectra of the dispersions.

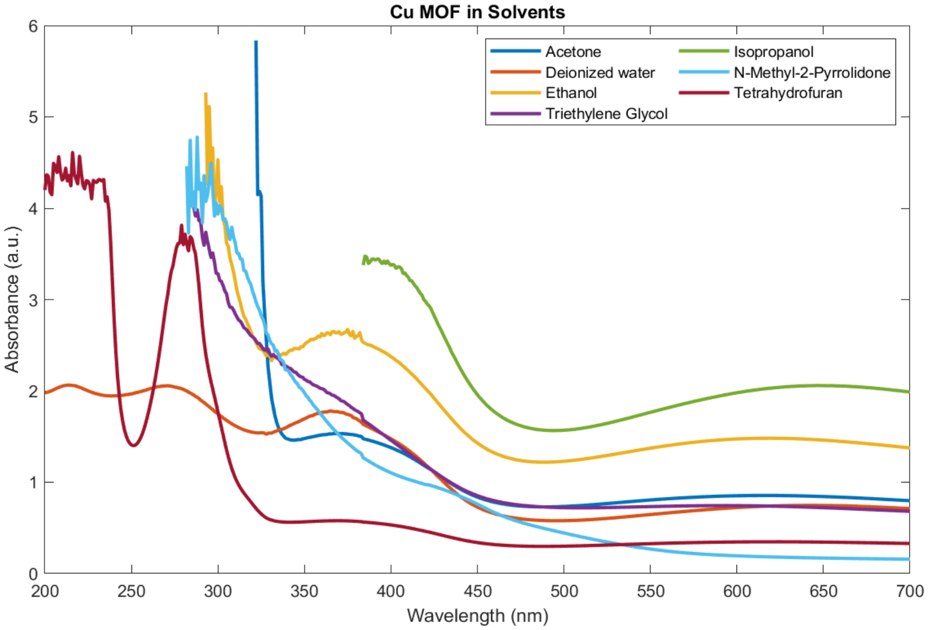


Fig 9: The UV-Vis absorbance spectra of Cu MOF in different solvents

Comparing the UV-Vis spectrum of the solvents and the Cu MOF in the solvents, we see that the isopropanol shows the highest absorbance intensity followed by ethanol when compared to the rest and hence shows the best dispersing ability. The high peaks of absorbance are due to the presence of suspended MOFs in the solvents. From both the visual observations and the UV-Vis absorption spectroscopy, isopropanol and ethanol can be used as a good medium for dispersion of the Cu MOFs for further practical applications.

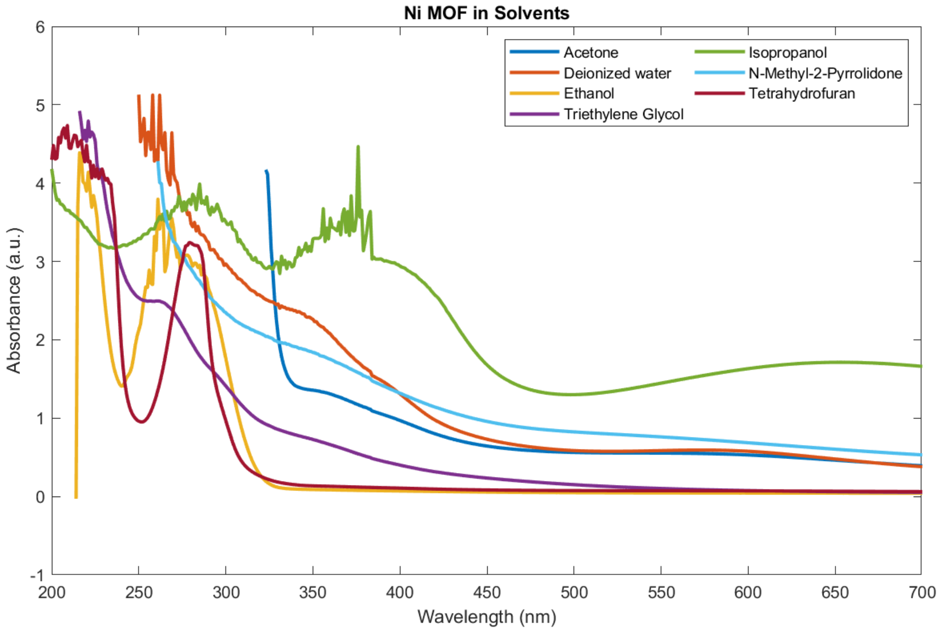


Fig 10: The UV-Vis absorbance spectra of Ni MOF in different solvents

In the case of the Ni MOFs, the results were not the same when compared to the Cu MOFs for the same concentrations. Even in the visual observations, Ni MOFs did not form stable suspensions in most of the solvents. Therefore, for this study we focused only on the application of the Cu MOFs which showed promising results.

Chapter 3: Synthesis of composite filaments

The polyether block amide filaments are extruded in the laboratory using a twin-screw extruder and a winding unit. The polyether block amides available to us were procured from Arkema, commercially known as PEBAX, is available to us in the form of natural-colored solid granules. These pellets are fed into the extrusion chamber using a hopper. The extrusion chamber is maintained at the melting point of the polymer and thoroughly mixed before being extruded in the form of a continuous filament. The filaments are wound using the winding unit at a uniform winding rate to maintain a control over the diameter.

3.1 Extruder

The extruder we have in our laboratory is the Xplore MC5 [37] micro compounder. The micro compounder has a base volume capacity of 5 ml. It has a vertical twin screw setup with a maximum of 6 Nm torque/screw and a maximum operating temperature of 450°C. There are separate heating zones along the barrel of the extruder which helps to provide good control over the processing temperature of the melt in the barrel. The twin screws facilitate for a much more homogeneous mixing which also brings down the processing time. The extruder is provided with a swappable die with two different nozzles having diameter of 0.25 mm and 2 mm. For this study, we used a bigger 2 mm diameter nozzle for thicker filament extrusions. The MC 5 is also equipped with 2 different cooling systems, an air-cooling system, and a water-cooling channel for cooling down the chamber when necessary. The figure shows the extruder we used for our study.

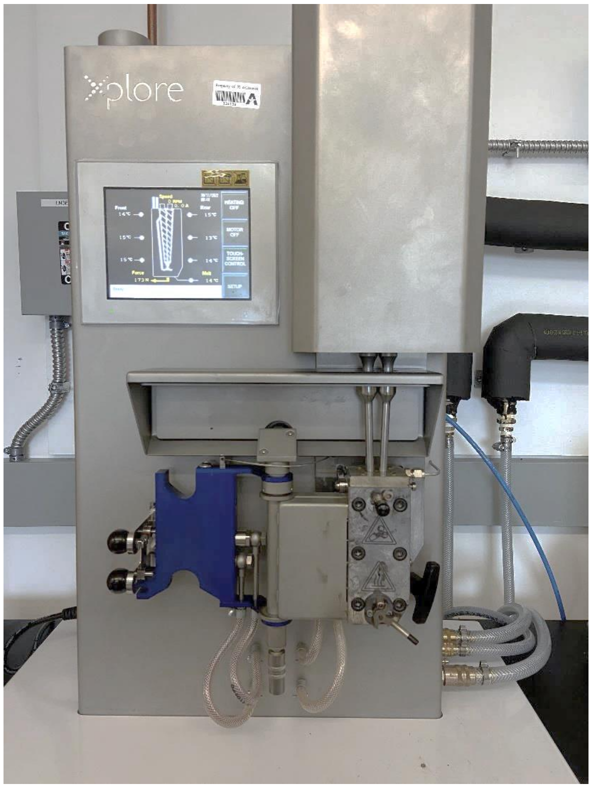


Fig 11: Xplore MC-5 micro compounder

3.2 Fiber winding unit

For the collection of the extruded filaments from the extruder, we make use of the Xplore Fiber Spin Line. It is used to stretch and elongate the extrusion to the specified diameter by controlling the speed of the winding. This unit consists of mainly two parts, a godet roll, which controls the winding speed and a torque-controlled take-up roll for an even uptake. The speed of the godet roll directly affects the diameter of the fiber that is collected at the end. There is an air-cooling system added to the godet roll to make sure the fibers are cooled maintaining their even diameter after leaving the godet.

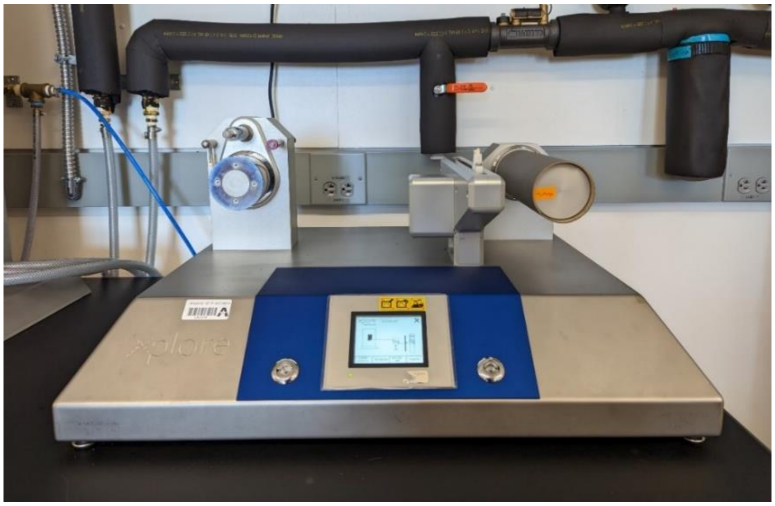


Fig 12: Xplore fiber spin unit

3.3 Filament extrusions

Filament extrusions were carried out for both the neat PEBAX filaments and for the Cu MOF dispersed composite filaments. The parameters for conducting the extrusion on PEBAX were previously studied in our lab [36]. The results from this previous study were referred and the following parameters were chosen for the extrusion of filaments.

Extrusion Parameters	**Value**
Operating temperature	170℃
Operating RPM	60
Force generated	1000 N
RPM during extrusion	25
Winding speed	8 m/min
Winding Torque	30

Table 1: Extrusion parameters selected.

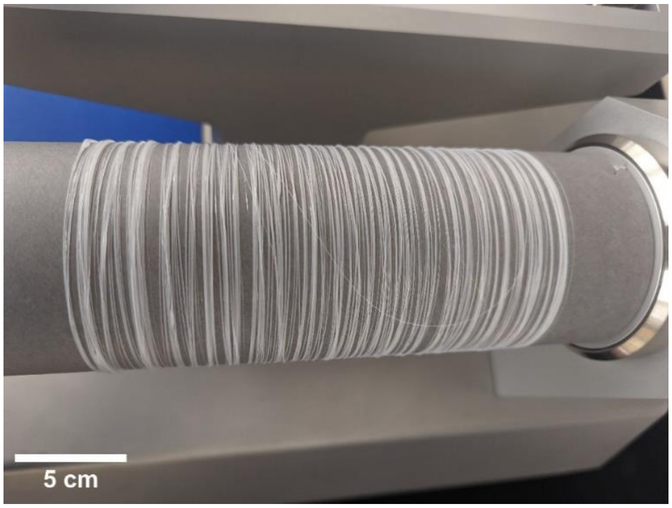


Fig 13: The image above shows the winding unit with neat fibers.

For the extrusion of metal organic framework composite filaments, a Cu MOF dispersed gel was prepared by conducting another study on the different methods of preparation of gel using the solvent selected from the dispersion study. Initially the PEBAX granules are fed into the barrel using the hopper and allowed to be evenly melted and mixed. Then we fed the MOF dispersed gel into the barrel through the inlet and allowed it to mix well inside the barrel before starting the extrusion. The extruded filaments are then spun onto the winding unit at a constant rate to make sure thickness is kept constant. The filaments with varying thickness at the beginning and towards the end of the extrusion are discarded to keep the study as accurate as possible. The filaments for this study are extruded with a thickness of 1 mm using the larger nozzle and a slower winding speed of 8 m/min.

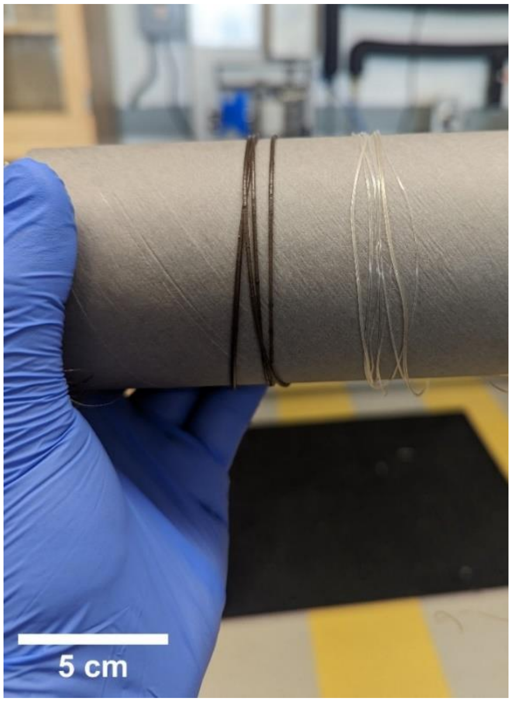


Fig 14: The image above shows both the neat PEBAX filaments (right) and the Cu MOF dispersed PEBAX composite filaments (left).

Chapter 4: Testing of Composite Filaments

The extruded filaments were tested and characterized according to their mechanical and CO_2 absorption properties. The tensile tests were conducted on both the neat and MOF dispersed composite filaments using the Shimadzu's AGS-X Table-Top Precision Universal Tester [40] at the Advanced Materials and Structures Laboratory at UTA. The gas absorption tests were also conducted on both the neat and composite filaments according to the experimental setup prepared by the members of Bozlar Nanoscience Lab.

4.1 Tensile tests on filaments

In this test, we hope to understand how the incorporation of the MOF particles in the polymer will alter the stress-strain curve of the material. Standard tensile tests were carried out on the table-top precision universal tester according to the ASTM Standard for measuring the tensile strength of fibers [38]. For PEBAX 1074 SA 01, the expected value for the tensile stress at 50% strain is 10 MPa [8][9]. The tensile tests were conducted at a test speed of 1 inch/min (25.4 mm/min) for the two specimens we extruded. Both the neat and the composite filaments with thickness 1 mm and length 9 inches (228.6 mm) were tested on the tensile testing machine using a special fiber grip designed at the AMSL facility as shown in the figure.

Mechanical Properties	Values
Stress at 50% Strain	10 MPa
Stress at Break TPE	30 MPa
Strain at Break TPE	>300%

Table 2: Mechanical properties of PEBAX MV 1074 SA 01 from the data sheet [7].

Fig 15: The fiber testing setup designed by the Advanced Materials and Structures Laboratory at UTA.

The neat PEBAX filaments were first tested on the tensile testing machine. The values obtained from the tensile test were then compared to the literature and data sheet available for the PEBAX 1074 SA 01. The obtained value of tensile stress at 50% strain was 9.97 MPa which agreed with the expected value from the data sheet. Then, the same test was repeated on the composite filaments with the Cu MOF dispersed in PEBAX. These fibers were able to give tensile stress reading at 50% strain as 11.79 MPa which was a considerable improvement over the neat fibers.

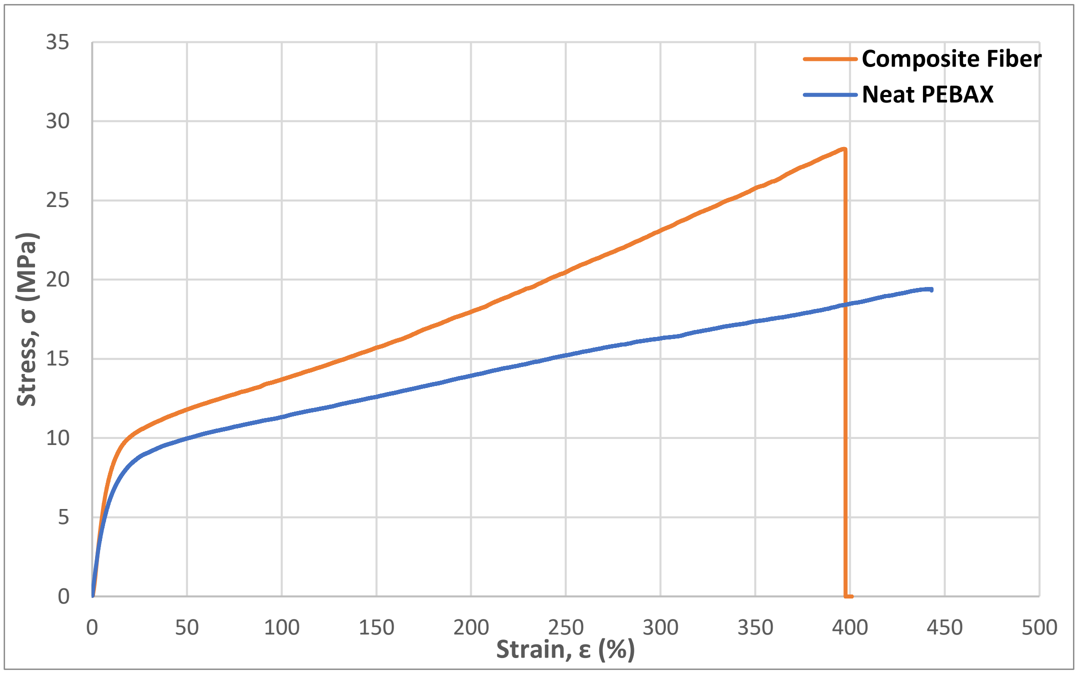


Fig 16: Shows the stress-strain graphs plotted for the Neat PEBAX fibers and for the Cu MOF dispersed composite fibers.

The neat PEBAX has an expected elongation >500%. This was beyond the capability of the testing machine we had since the crosshead movement was limited by the total z axis displacement. In the case of the composite filament, the elongation at failure was capped at 400%. From the values plotted, we observed that the MOFs dispersed in the polymer were able to improve the yield strength of the material by 18.25% over the neat fibers. We also observed that even though the Cu MOFs were able to improve the yield strength, it decreases the stretchability of the composite compared to the neat PEBAX. This can be due to the stronger interactions between the MOFs and the polymer. From these results it can be speculated that the yield strength of the material can be further improved by incorporating higher concentrations of MOFs [41]. Increasing the concentrations of MOFs can also further decrease the stretchability of these materials which is not advisable for the application in 3D printing of membranes. Hence, further tests must be conducted with different concentrations of the MOFs in the polymer to find the optimal concentration of the MOFs that gives the maximum yield strength without compromising the stretchability.

4.2 Carbon dioxide absorption tests

One of our major objectives for incorporating the MOFs into the polymer is to study how it improves the overall CO_2 absorptivity. PEBAX is known for its affinity to CO_2 and therefore is a good material for making selective permeable membranes for separation of CO_2. The MOF with its porous crystalline structure is utilized in gas filtration and storage applications. In this test, our objective is to study how the incorporation of MOFs in the PEBAX polymer matrix will affect CO_2 absorptivity when compared to the neat polymers. To test the filaments for the CO_2 absorptivity, we considered a controlled stationary system where CO_2 sensors can monitor the concentration of CO_2 over a period [42]. We used a closed incubator setup which has been calibrated for any leaks or errors. For the CO_2 sensor, we used a TELAIRE T6713 series sensor.

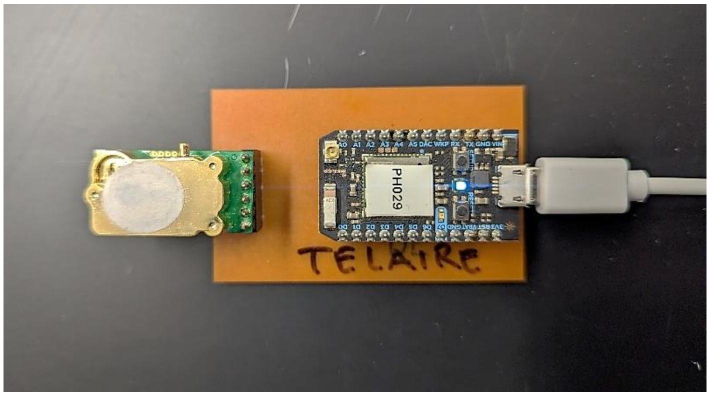


Fig 17: A TELAIRE T6713 series CO_2 sensor module connected to the Particle 'Photon' microprocessor.

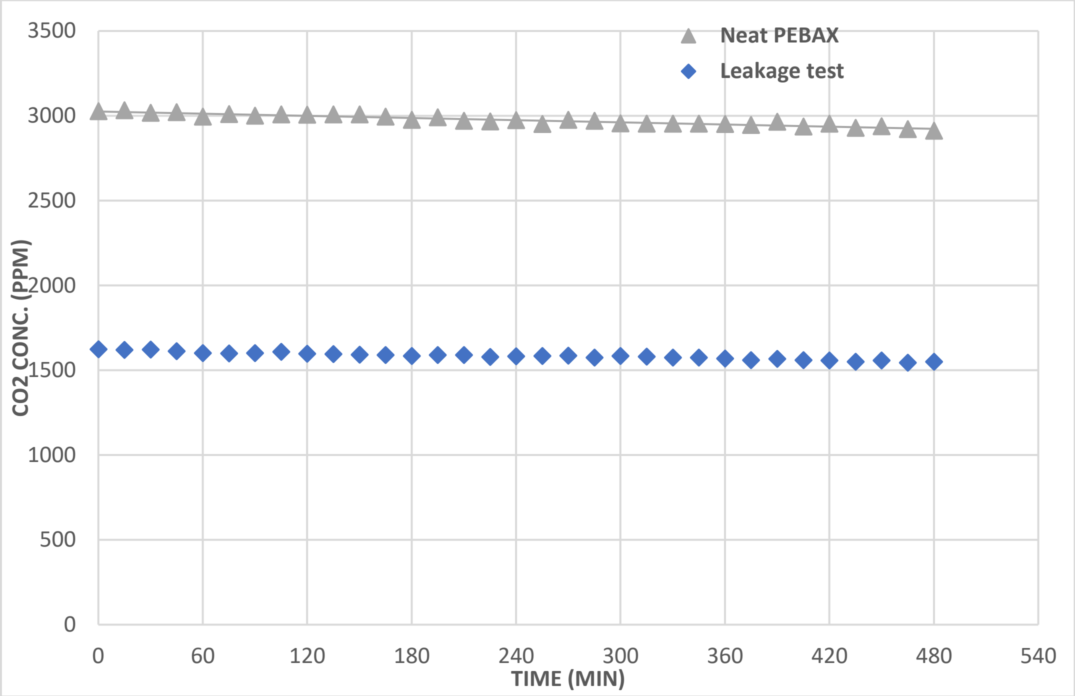


Fig 18: Graph showing the concentration of CO_2 for the empty chamber (blue) compared to the variations with just neat PEBAX (grey).

Initially, the incubator is tested for any leaks by monitoring the concentration levels of CO2 in the chamber when no filaments are placed inside it. The graph plotted from the observations shows that over the 8-hour time considered for this experiment, we do not notice any major leaks that causes a concern. Then we conduct the test by placing freshly extruded filaments inside this stationary closed system for 8 hours per sample. For this study, we are considering two specimens, a 2.4g specimen of neat PEBAX followed by a 1.6g specimen of MOF dispersed PEBAX filaments. The CO_2 concentrations are initially measured every 1 minute until the readings are stabilized and within the margin of error of the sensor which is around ± 30 ppm for the range of 400-5000 ppm [43]. The readings are then recorded every five minutes after that for the next 8 hours. Once both the filaments were tested, the values of the concentration were plotted and compared to each other.

Material	**Weight of material**	**Initial CO_2 conc. (ppm)**	**Final CO2 conc. (ppm)**	**Total CO_2 absorbed per unit weight**
PEBAX	2.4 g	3026	2912	0.0475 ppm/mg
PEBAX with Cu MOFs	1.6 g	2928	2795	0.0831 ppm/mg

Table 3: CO_2 absorption per unit mass of the filaments tested.

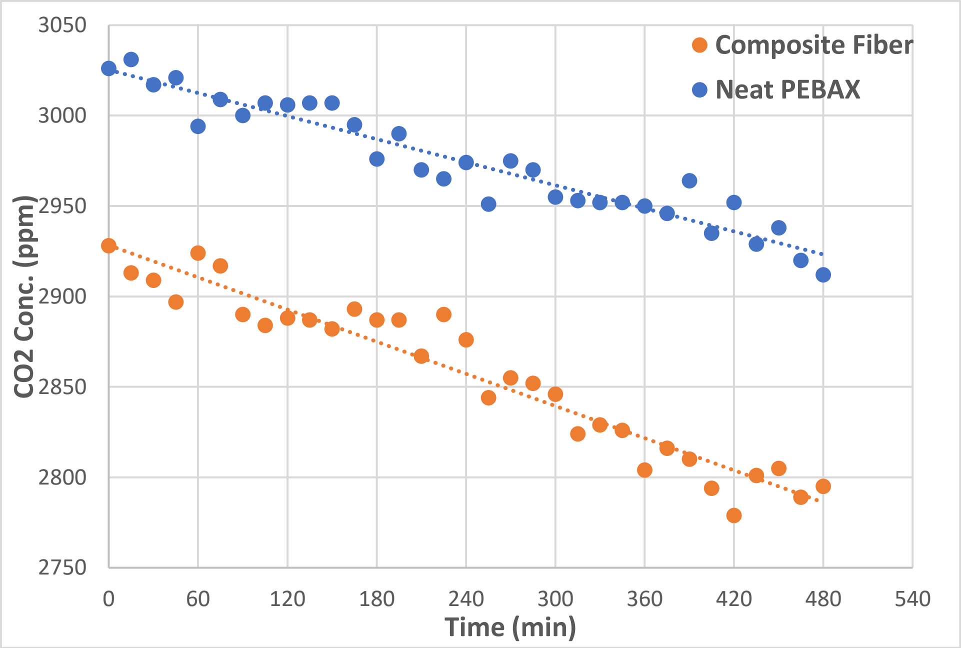


Fig 19: The graph shows the variation in the concentrations of CO_2 in ppm over a period of 8 hours with the fibers tested.

From this limited testing, the PEBAX filaments with the Cu MOF in them were able to absorb more CO_2 during the 8 hours we left them in the stationary test system. This test can be further investigated by varying the test conditions for relating it closing to an indoor ambident environment where the material can be applied for practical uses.

Conclusion and Future Work

The dispersion study of the two MOFs using the UV-Vis spectroscopy method helped in choosing a good medium of dispersion for these particles. The dispersion study of the Cu_3HHTP_2 and Ni_3HHTP_2 metal-organic framework is a relatively unexplored area and have better scope for further studies and tests to gain more in-depth understanding of the unique behavior each of the two isostructural frameworks of the same family exhibits in the solvents.

The PEBAX filaments were extruded with the Cu_3HHTP_2 MOF particles dispersed in them using the twin-screw extruder. The initial tests on the two different samples in the study show that the incorporation of MOFs in the polymer improved the yield strength of the filaments but comprises on the stretchability. The mechanical properties of these composite fibers can be further studied by conducting more testing with different concentrations of MOF particles dispersed in the polymer matrix.

The MOF dispersed PEBAX filaments also showed improvement in CO_2 gas absorption capabilities. The composite filament was able to capture 1.75 times more CO_2 than the neat filaments absorbed per unit weight of the material. This makes these composites a viable alternative material in CO_2 separation applications.

These composite fibers must be further studied for their thermal and electrical properties to better understand the material and utilize it in the additive manufacturing process to print MOF dispersed PEBAX membranes for the CO_2 capture applications that are currently being explored at our lab.

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