FUNCTIONAL PROPERTIES AND STABILITY OF PLLA-METAL ORGANIC FRAMEWORK BASED MIXED MATRIX MEMBRANES

By

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A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Packaging-Doctor of Philosophy

2013

ABSTRACT

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Poly(lactic acid) (PLA) is a commercially available bio-based, biodegradable and compostable polymer with many new applications in the packaging industry. However, PLA has certain limitations such as poor barrier, low impact resistance, poor tear resistance and low toughness, which hinder its functionality as a packaging material. The purpose of this study was to explore and understand new avenues to improve the mechanical properties and functionality of the PLA for various industrial applications including packaging. PLA-metal organic framework (MOFs) mixed matrix membranes (MMMs) were fabricated with these objectives in mind. MOFs are a new class of crystalline coordinate polymers with applications in gas storage, catalysis and gas separation, and they can be used to produce PLA composites to improve its mechanical properties and functionality.

Copper benzene tricarboxylate $Cu_3(BTC)_2$ MOF was successfully synthesized by microwave synthesis and characterized using X ray diffraction (XRD), scanning electron microscopy (SEM) and surface area studies. During the fabrication of MMMs, it is important to maintain the integrity of MOF crystals to achieve the desired properties and functionality. Activated $Cu_3(BTC)_2$ MOF crystals were incorporated into PLA by melt extrusion process using twin screw micro-compounder without any damage to the $Cu_3(BTC)_2$ MOF crystal structure, which helped in preserving the functional properties of MOF in the polymer matrix. The effect of residual water in the MOF structures was evaluated. It was found that residual water could be detrimental to the morphology of the crystals during extrusion processing and can compromise the final properties of MMM.

The presence of MOF particles in the polymer improves the toughness of the PLA matrix. We observed that under the uniaxial tensile stress the triaxial stress generated at the interface of PLA MOF crystals led to cavitation induced by debonding. Cavitation mechanism generated local plastic deformation followed by strain softening leading to the improved toughness. Parallel plate rheological studies were performed to understand the interaction of MOF particle with the PLA and the effect of these particles on the processing of MMM. Rheological and differential scanning calorimetric studies provided evidence of strong PLLA-MOF interactions.

CO₂ permeability of PLLA-20% wt. Cu₃(BTC)₂ MOF mixed matrix membranes increased by around 38% as compared to neat PLLA. The perm-selectivity ($\alpha_{CO2/O2}$) of PLLA-20% MOF increased from 7.6 to 10.3, respectively. The permeability coefficient for trans-2-hexenal increased by 60% with the addition of 20% MOF. Permeability coefficients of various gases and organic molecules are strongly influenced by the kind of interactions between the microporous materials, matrix and permeants. This study will help in the advancement of our understanding of mixed matrix membranes prepared from bio-based polymeric matrix for various industrial and commercial applications including food and pharmaceutical packaging. To Grace, and Sumiti

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Rafael Auras for his unabated motivation, support and enthusiasm. I have been truly blessed that he allowed me pursue research work under his guidance. During this dissertation work he provided a lot of freedom to conduct research which helped me to develop as a young researcher.

I would also like to thank Dr. Mohamad G. Abiad for his guidance as a friend and mentor. His sheer presence brings a lot of positive energy. To solve a problem, he brings lot of new ideas to the table along with different approach. It has been a pleasure to work with him. Some of the research work in this dissertation would not have been possible without his guidance.

Dr. Maria Rubino has been very helpful and instrumental to help me understand some of the basic fundamentals concepts. I have worked as a TA for her for Instrumental analysis course (PKG 817). She helped me a lot in absorbing the concepts during my graduate studies.

I would like to express my sincere thanks to Dr. Susan Selke for her guidance, support and motivation. She has been kind and caring as a teacher and as a mentor. I also enjoyed working with her on a project funded by the packaging industry during the first year of my doctorate studies.

I would like to thank Dr. Ramani Narayan for providing the guidance and allowing me to use his processing lab facilities. He has been inspirational. I am thankful to Dr. K. Jayaraman for providing me access to his rheological laboratory to complete a part of my studies. I would also like to thank Dr. Rahul Bhardwaj, Edward Drown, Ren

v

Weije and Shawn Shi for their useful discussions and comments during the course of this work.

I would also like to express my gratitude to faculty and staff of the School of Packaging, MSU. I am grateful to Dr. Joseph Hotchkiss, Dr. Bruce Harte, Dr. Diana Twede, Dr. Gary Burgess, Dr. Robert Clarke, Dr. Laura Bix and Dr. Laurent Matuana and Dennis Young for their wonderful teaching and support. I am thankful to Kelby Thayer, Sherrie Lenneman, Cimbery Weir, Ronald Iwaszkiewicz and Sean Harwood for providing help and support during my graduate studies.

I am thankful to my friends and colleagues from Dr. Auras research group: Dong Ho Kang, Hayati Samsudin, Sukeewan, Turk for their inputs and suggestions during various presentations in the group.

I would also like to acknowledge financial support from my parents, Bimbo bakery project and graduate assistantship funding from the School of Packaging, MSU. Without their financial support this work would not have been possible.

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KEY TO SYMBOLS OR ABBREVIATIONS

| Symbols | Key |
|------------------------------------|---|
| Tg | Glass Transition Temperature |
| T _m | Melt Temperature |
| ТМ | Trade Mark |
| К | Degrees Kelvin |
| PLLA-A-MOF | PLLA-5% activated MOF |
| PLLA-S-MOF | PLLA-5% saturated MOF |
| MOF | Metal Organic Framework |
| MMMs | Mixed matrix membranes |
| Cu ₃ (BTC) ₂ | Copper benzene 1,3,5 tricarboxylate metal organic framework |
| η* | Complex viscosity |

Chapter 1. Introduction

Chapter 1. Introduction

1.1 Introduction

Conventional petroleum derived polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) are widely utilized in packaging and other industrial applications [1]. However, their non-renewable origin, solid waste management issues, depleted landfill space and carbon footprints have spurred the development of bio-based, biodegradable and compostable polymers. Biobased polymers can be directly extracted from biomass, synthesized from bio-derived monomers or can be produced by microorganism [2]. Polymers synthesized from bio derived monomers have achieved great commercial momentum in the last decade. Polylactic acid (PLA), one such polymer in this category, is synthesized from lactic acid, which can be produced from corn, sugar beets, rice starch and cellulosic waste [3-7]. In the United States, PLA is produced from corn. It is one of the leading biopolymers with commercial applications in the packaging industry and is marketed under the trademark IngeoTM by NatureWorks LLC, a subsidiary of Cargill Incorporated. NatureWorks has an annual capacity of 300 million pounds [8]. PLA has high mechanical strength and modulus. The poor thermal stability, high permeability, poor tear strength, low heat deflection temperature (HDT), low melt strength and poor functionality of PLA hinders its large scale application in the packaging industry [9-11].

Separation of gases using polymeric membranes has increased with significant advancement in membrane technology [12-13]. Polymer based membranes are cheap, durable, easy to handle and have low operating cost [13, 14]. However, low selectivity, poor stability at elevated temperature and solubility in organic compounds limits applications of polymeric membranes [13, 15-16]. Porous inorganic, organic and hybrid materials such as zeolites, carbon molecular sieves and metal organic framework (MOF) have higher selectivity than polymeric membranes, but they are expensive, difficult to process and have poor mechanical strength [16-19]. In order to extract the benefits of both porous and polymeric membranes the focus has shifted towards the development of mixed matrix membranes (MMMs), which are composed of porous materials dispersed in a polymeric matrix. Figure 1 represents a schematic of MMM.



Figure 1.1: Schematic representation of mixed matrix membranes. For interpretation of the references to color in this and all other figures the reader is referred to the electronic version of this dissertation

Although MMMs prepared from inorganic materials like zeolites have been widely researched in the last few decades, the poor compatibility between an inorganic filler and an organic polymeric matrix can lead to sub-micron size holes in the MMMs. MOFs are a new class of organic-inorganic hybrid porous crystalline materials which consist of metal ions coordinated with organic molecules into multidimensional structure. They are popular for properties such a gas separation, gas storage and catalysis. The most attractive property of MOFs is their ultrahigh surface areas, which is greater than porous carbons or zeolites and may exceed at times 5900 m².g⁻¹ [20]. The utilization of MOFs with polymeric materials can allow the creation of new functional MMMs. MOF particles with organic linkers can offer better compatibility than zeolites [21-23].

Various researchers have reported the preparation of MMMs from MOF [14, 24-25]. The presence of MOFs in the polymers can aid and enhance the perm-selectivity of the membranes by influencing the sorption and diffusion factors [24]. Polymers such as polydimethyl siloxane (PDMS) and polysulfone (PSf) have been extensively studied for the membrane applications. These polymers have high carbon footprints. Therefore, utilization of a more carbon neutral polymeric matrix such as PLA can help in mitigating some environmental concerns. PLA matrix also offers high permselectivity for gases such as CO_2/CH_4 [2, 26]. Therefore, this can be exploited for applications such as getting high purity methane from natural gas streams, which contain CO_2 impurities, or it can be utilized to obtain high calorific value methane fuel from a biogas plant.

Thus, the synthesis of novel PLA Cu_3BTC_2 -MOF-MMMs can be used to improve functionality of PLA for various applications such as packaging, petrochemical, energy, etc. [27]. The synthesis of $Cu_3(BTC)_2$ -MOF and production of PLA- $Cu_3(BTC)_2$ -MOF-MMMs are the main focus of this dissertation.

1.2 Goals and objectives

The main objectives of this dissertation are:

- To synthesize Cu₃(BTC)₂ MOF using a microwave assisted rapid synthesis technique and to characterize it using X-ray diffraction, BET surface area analysis and scanning electron microscopy.
- To evaluate the effect of residual water on the stability of the MOF crystals during melt extrusion processing. The integrity of these crystals can significantly affect the final properties of the membranes.
- 3. To understand the toughness mechanism and PLA-MOF interactions using electron microscopy and rheological properties of the PLA-MOF MMMs.
- 4. To determine the mass transfer properties of the developed PLA-MOF composites.

1.3 Document outline

This dissertation is divided into seven chapters. A brief summary of the following chapters is as follows:

Chapter 2 provides a summary of the literature review of PLA, MOF, the difference between physical adsorption and chemical adsorption, adsorption mechanism followed by MOF, polymeric membranes and MMMs.

Chapter 3 describes the various synthesis methodologies that can be utilized for the synthesis of MOF. Benefits of microwave assisted synthesis of MOFs over other synthesis procedures as well as characterization of copper benzene 1,3,5 tricarboxylate metal organic frameworks (MOFs) using XRD, SEM and BET surface area analysis techniques.

Chapter 4 focuses on PLA–MOF based MMMs and evaluation of the morphology and stability of the MOF particles during fabrication of the MMMs. This chapter elaborates the effect of the residual water on the deterioration of the Cu₃BTC₂ MOF crystal structure.

Chapter 5 describes the effect of the MOF particles based on the thermal, mechanical, rheological and electron microscopy studies. This chapter describes the toughness mechanism, which helps in understanding the improved toughness of the PLA-MOF composites as compared to the neat PLA matrix. Rheological and thermal studies helped in understanding the interfacial interactions between PLA and MOF.

Chapter 6 presents the mass transfer properties of PLLA and the effect of the presence of metal organic framework on the mass transfer properties of mixed matrix membranes for CO₂, O₂, H₂O and trans-2-hexenal.

Chapter 7 is conclusions and recommendation for future work.

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Chapter 2. Literature Review

Chapter 2. Literature Review

2.1 Structure, synthesis and properties of PLA

Polylactic acid can be synthesized from lactic acid by polycondensation reaction, azeotropic dehydration condensation polymerization and/or by ring opening polymerization using lactide molecules [1]. Lactic acid, which is produced by the fermentation of dextrose, exists in two enantiomeric forms, D-lactic acid and L-lactic acid. Figure 1 shows the chemical structure of D and L-lactic acid.



Figure 2.1: Chemical structure of a. L-lactic acid b. D-lactic acid

Mass production of PLA is pursued using ring opening polymerization (ROP) of lactide dimer to achieve high molecular weight PLA. Lactide dimer exists in three enantiomeric forms called D lactide, L lactide and meso lactide, represented in Figure 2.2 [2]. The stereochemical configuration of the lactide molecule affects the crystal structure, degree of crystallinity, melting point, mechanical and barrier properties of the final PLA [3-6]. High molecular weight PLA, a semicrystalline polymer when the L-lactide amount is more than 92%wt., can crystallize in three-crystal form known as α , β , γ forms [6]. The processing parameters and drawing conditions strongly affect the extent of crystallinity and type of crystal formation in the final product [8]. The α crystal form is the most common form present in PLA.



Figure 2.2: Chemical structure of a. L-lactic acid b. D-lactic acid c. meso-lactide

PLA has found application in the biomedical, packaging and textile industries. However, some limitations such as poor gas barrier properties, poor impact strength and toughness, poor tear resistance, low heat deflection temperature and poor functionality hinder applications in the packaging industry [9-11]. The crazing phenomenon is primarily responsible for the brittle failure of PLA [12]. Various methodologies can be employed to improve the toughness of PLA, such as plasticization, copolymerization, melt blending, reactive extrusion and addition of fillers [13-18]. Fillers are primary added to the polymeric matrix to improve the stiffness. However, favorable interfacial interactions, distance between the particles suspended in the matrix or the right concentration of the filler can contribute to improved toughness. Toughening of polymer composites can be explained by various mechanisms such as shear yielding, cavitation, crazing, etc.

2.2 Toughnening of polymer composites

2.2.1 Cavitation

When uniaxial stress is applied on polymers filled with toughening agents or modified inorganic particles, the uniaxial stress can generate triaxial stress at the interface of the polymer and the filler, which is relieved by formation of microvoids, leading to improved toughness. This mechanism is known as the cavitation mechanism. The cavitation mechanism can progress in two fashions: (a). Interfacial debonding leading to the formation of micro size cavities [19] and (b). cavitation within the fillers such as rubber particles [20].

2.2.2 Crazing

Glassy polymers such as polystyrene and PLA undergo brittle deformation by craze formation due to the localized nature of the crazes. These Crazes are defined as microvoids separated with fibrils of 5-20 nm diameter [21]. In some cases, these crazes act as a source of energy dissipation leading to a plastic deformation. These fibrils break under stress, leading to the absorption of energy.

2.2.3 Shear yielding

Shear yielding is known as a localized plastic deformation phenomenon. During the crazing and cavitation mechanism, a change in the volume of the matrix is observed, however, there is no volume change in the case of shear yielding. Increased entanglement or cross-linking density supports shear yielding over crazing as it hinders the creation of the voids.

2.3 Adsorption

Adsorption is a surface phenomenon. It is a process where molecules condense at the surface. The adsorption of various molecules on the surface is dependent on factors such as the partial vapor pressure of the adsorbate, interaction between the adsorbate and the adsorbent, temperature, etc. Adsorption is an exothermic process and adsorption isotherms are utilized to accurately determine the performance characteristics of porous materials. The state of the adsorbate (atomic or molecular) can be determined by spectroscopic analysis. An adsorption isotherm can be generated by using gravimetric, constant volume and dynamic adsorption methods. The adsorbate can form a monolayer or multilayer over the adsorbent. There are various models such as the Langmuir and Brunauer-Emmett-Teller (BET) model which describe monolayer and multilayer adsorption.

2.3.1 Difference between physisorption and chemisorption

Based on the strength of the bond between the adsorbate molecule and adsorbant, adsorption can be divided into two classes: (a). chemical adsorption (chemisorption) and (b). physical adsorption (physisorption). Chemisorption occurs due to ionic, covalent or metallic bonds/coordinates. It may or may not be reversible. Chemisorption may or may not be dissociative in nature. Non-dissociative adsorption is also referred to as molecular adsorption. The enthalpy of adsorption is generally greater than 40 kJ/mol. On the other hand, physisorption is a reversible and non-dissociative process. Physisorption primarily occurs due to van der Waals interactions between the adsorbate and adsorbent, such as dipole-dipole, dipole quadrupole, and quadrupole-quadrupole interactions. The enthalpy of adsorption is generally less than 40 kJ/mol.

2.3.2 Methods to study adsorption isotherms

Physical adsorption or physisorption can be studied by static methods or dynamic methods. Static methods are preferred over the dynamic method because they are simple and provide more accuracy [22].

1. Volumetric technique: Sample preparation is performed using degassing where the adsorbed molecules are removed from the surface or pores of the sample at a higher temperature. The samples are typically analyzed by gases such as N_2 or Ar at their liquefaction temperature, for example 77K for N_2 . The sample is exposed to incremental (or decremental) doses of pressure to obtain an adsorption (or desorption) isotherm. The probability of gas molecules attaching to the surface increases with an increase in the relative pressure. The adsorbed volume of gas as a function of relative pressure is recorded by the instrument. This technique is popular for measuring specific surface area, pore volume and pore size. For measuring the BET surface area, a relative pressure between 0.05 and 0.3 is utilized. The disadvantages of this technique are cost and complexity, as it involves the use of vacuum pumps.

2. Gravimetric technique

This technique utilizes a precision microbalance to obtain weight gain/loss as a function of change in the pressure at a fixed temperature. For example, the VTI instrument measures the weight gain. The gravimetric technique is utilized to determine the isosteric heat of sorption and molecular interactions between the sorbate and sorbent [23]. It is also used to study the morphological stability of pharmaceutical products at elevated humidity conditions.

Porous materials are carefully engineered to perform specific functions. Their physical characteristics such as specific surface area and pore size influence the quality and utility of the material. Adsorption isotherms are utilized to accurately determine the performance characteristics of the porous materials by using gases such as N_2 , Ar. Sample preparation is performed using degassing where the adsorbed molecules are removed from the surface or pores of the sample at higher temperature. The samples are typically analyzed at the liquefaction temperature of the gas for example 77K for N_2 . A gas molecule is attracted to the surface by intrinsic surface energy of the sample. The physisorption of the molecules tend to increase with the increasing partial pressure over the sample. The shape of the pore, pore size and pore size distribution strongly affects the adsorption behavior of the porous materials. Therefore, the texture of a porous material can be analyzed using the shape of the isotherm.

The majority of the isotherms can be classified into six types; type I to type VI; as per the IUPAC classification depicted in the figure 2.5 [24].



Figure 2.3 IUPAC classifications of sorption isotherms

Type I isotherm also known as the Langmuir isotherm does not generally exhibits hysteresis. This type of isotherm is associated with microporous materials (pores<2 nm). A plateau is observed at a low relative pressure because the pores are so small that they are filled at low pressure. Once the pores are filled the remaining adsorption occurs on the exterior of the porous material. The Type II isotherm is generally observed in non-porous or macroporous materials. The knee observed in the isotherm indicates the formation of a monolayer. At higher relative pressures, multilayer adsorption is observed in such type of isotherms. Type III isotherms are also related to macroporous materials; however, there is no knee formation in these types of curves. These isotherms indicate weak adsorbate and adsorbant interactions. Type IV isotherms are typically observed in

mesoporous materials (2 to 50 nm). A hysteresis effect is commonly observed in such the porous materials as the shape and size of the pores causes the adsorption or desorption portions of the isotherm to have different path. In the type V isotherm there is no plateau indicating the completion of a monolayer. This effect is due to poor interaction between adsorbate and adsorbent, for example adsorption of water on carbon. The hydrophobic carbon does not absorb on the carbon and the observed adsorption can be attributed to the condensation of water rather than the adsorption. Type VI isotherms shows step-by-step formation of multilayers on a nonporous material.

2.4 Metal organic frameworks

Porous materials can be categorized into three categories based on the ingredients: inorganic porous material, hybrid organic-inorganic solid (coordination polymers) and carbon based high surface area materials. Some examples of high surface area porous materials are zeolites, silica gel, metal organic frameworks, carbon nanotubes, fullerene, activated carbon, and carbon fiber composite molecular sieves. Charcoal and activated carbon have surface area of 500-1000 m²/g. Silica gel has a surface area of around 800 m²/g. Zeolites have surface area ranging from 500 to 800 m²/g. Metal organic frameworks (MOFs), a relatively new class of porous materials, have been discovered in late 1990's. MOFs are popular for various properties such as catalysis, gas separation, sorption and high internal surface area, etc. [25-26]. They are coordinate polymers formed by the co-ordinate bond between the organic linkers and metal ion. These coordinate bonds are weak in comparison to the Si/Al–O bonds present in the zeolite structure. Therefore, these coordination polymers have poor thermal stability compared to zeolites. However, they have sufficient strength for many applications. Some MOFs have surface areas in excess of 5900 m²/g [26]. High selective interaction of MOF with various gases and molecules opens various avenues for deploying these materials in various applied disciplines such as the petrochemical, energy, environmental and packaging industries [27]. These materials are easy to design and can also be tailored to required applications. MOF based membranes can be used to selectively purge molecules considered undesirable in the package over a period of time, which can affect the quality of the product, aroma or otherwise influence the customer perception.

The adsorption mechanism of various molecules is governed by factors such as electrostatic interactions, dipole moment, magnetic dipole moment, ionization potential, vapor pressure of adsorbent, pore size in the MOF, etc. Permanent magnetic dipole moment in atoms, molecules or ions originate from the orbital motion of the electrons and from the spin of the electrons. Adsorption of various molecules by MOF can occur through various ways:

- a. Adsorption of the molecules by unsaturated metal sites present in the MOF.
- b. Interaction between the ligand and the molecules.
- c. Interaction between the polar groups attached to the metal and the molecules.

Better chemical specificity for the guest molecule can be achieved by engineering customized metal sites and organic linkers. The metal or metal oxide sites present in the MOF get saturated very quickly. Molecules can bind to metal/metal oxide more strongly as compared to ligands. This can be ascribed to electrostatic and orbital donation interactions between the transition metal and the adsorbed molecule. The structure of the d electron shell plays a significant role in interactions. A strong magnetic effect is observed when d and f electrons are involved. Such interactions can lead to dissociate chemisorption of the molecules on the metal [28]. However, chemisorption is also dependent on the strength of the bond of the molecule to be dissociated. Van der Waal forces dominate the interactions between the ligand and the adsorbed molecule [29]. The heat of adsorption defines the bond strength between the metal and sorbates. Initial heats of adsorption in metals follow this trend [30]:

Torrisi et al [31, 32] studied the van der Waal interactions between CO₂ and the aromatic structures present in the ligands using ab initio PW 91/DNP Approximation (GGA) density functional theory (DFT). Two classes of functional group were selected for substitution on the benzene rings: (i) electrophilic halogen groups (ii) nucleophilic methyl groups. It was observed that the halogen substitution of the benzene rings destabilizes the π -quadrupole interactions. This was ascribed to the charge withdrawal effect of hydrogen-substituted groups. Methyl and polymethyl substitution on the benzene ring increased the CO₂ affinity.



Fig 2.4 a. Benzene



Fig 2.4 b. Hexaflourobenzene

Rowsell et al [33] studied H₂ adsorption by Zn₄O (BDC)₃, Zn₄O (NDC)₃, Zn₄O

(HPDC)₃, Zn₄O (TMBDC)₃ and Zn₄O (BTB)₃ MOF up to pressure of 750 Torr. They observed that the interaction of the guest molecules varies with the chemical structure of the ligand. It was observed that the uptake of H₂ increases with the number of organic rings per unit formula. Initial hydrogen uptakes revealed that Zn₄O (NDC)₃ and Zn₄O (HPDC)₃ have more affinity for the H₂ molecules than to the other MOF structures utilized in the study.

The ubiquitous presence of aromatic linkers in the various varieties of MOF can be related to the thermal stability of the benzene ring. The presence of the delocalized π electrons in the benzene ring in the MOF structure also helps in the secondary forces between the ligand structure and the sorbent [31, 32]. The interaction between these aromatic ligands or secondary building units attached to the metal ions also defines the geometry and pore size in these porous molecules [34, 35]. The stacking interactions of these aromatic molecules are also affected by the substitute groups attached to the aromatic ring. Electron donating groups help in ramping up the electron density of the delocalized π electrons of the aromatic group whereas electron withdrawing groups like NO₂ can reduce the electron density of the delocalized π electrons. All these groups in turn will effect on the geometry of the MOF.


Figure 2.5: Some carboxylate based ligands

The good stability, and good water and CO_2 sorption properties of $Cu_3(BTC)_2$ MOF inclined us to further explore its synthesis and characterization. It is also commercially manufactured by BASF under the trade name BasoliteTM C 300. By embedding $Cu_3(BTC)_2$ MOF we can enhance the permeability and permselectivity of polymeric membranes.

2.5 Mixed Matrix Membranes

Gas separation using polymeric membranes is popular because of their adequate mechanical strength, inherent transport properties, ease of processing and upscaling. Conventional non-porous polymeric membranes follow a solution-diffusion model for the gas separation [36]. The slow rate of diffusion through polymers reduces their commercial attractiveness. Molecular interactions between the permeants and polymer play important roles in determining the perm-selectivity. Solubility of polymers to organic compounds and their segmental mobility limits the gas selectivity. The use of polymeric membranes at elevated temperature can reduce the life of polymeric membranes.

Polyimide, polydimethylsiloxane (PDMS), polysulfone (PSf) and polyethylene oxide (PEO) are some of the widely used polymeric membranes. Polyimide is commercially available under the trade name MatrimidTM. It has high thermal stability, good chemical resistance and high mechanical strength [37]. PEO is popular for its high CO₂ selectivity due to strong interactions between CO₂ and the polar ether oxygens present in PEO [38]. However, crystallization due to aging can reduce the permeability of

such membranes. The crystallization process can be reduced through copolymerization, controlling the molecular weight or by branching the main chain [38, 39]. PSF is popular for membrane applications for water purification, ultra filtration, reverse osmosis and gas separation [39]. It is a glassy polymer ($T_g \sim 186^{\circ}$ C) with good mechanical strength, excellent chemical stability and ease of processing [39, 40].

Low cost and easy processibility of the polymers and high selectivity of porous membranes motivates the fabrication of polymer-porous material composite membranes also known as MMMs [41]. These MMMs can provide attractive properties for gas separation. Appropriate selection of the porous material and polymeric matrix is necessary for producing efficient MMMs. The choice of polymeric matrix and porous material should be synchronized to achieve the desired selectivity and mass transfer properties [42]. The polymer should be compatible with porous material and the polymer-porous material interface should be free of voids [42-45].

Traditionally, MMMs have been fabricated by dispersing zeolite particles in polymeric membranes. Different types of Zeolites have been widely researched with a variety of polymeric materials [42-50] to obtain increased permeability and superior selectivity as compared to polymeric membranes alone. Most of the studies indicated the surface modification need to achieve the good compatibility. Mahajan *et al* [46] studied MMMs prepared from zeolite 4A and Matrimid[®]. They reported voids at the interface of zeolite 4A and Matrimid[®] polymer which reduced the perm-selectivity of the MMMs. Modification of the zeolite 4A with silane linkers before fabrication of MMMs can help in eliminating the voids at the interface of the seives and polymer matrix [47].

However, Yuzay *et al* [48] fabricated PLA - zeolite type 4A composites using melt extrusion processing. The authors observed void free interface of PLA and zeolite type 4A in the microscopic images, indicating good interfacial interactions between PLA and zeolite type 4A.

In recent years MOFs have attracted great attention for fabrication of MMMs because of their high surface area, ease of synthesis and availability of thousands of different structures [49-57]. In addition MOFs are composed of metal ions connected together by organic linkers, the presence of these organic linkers helps to improve the interfacial interactions [52, 58-59]. Elongavon *et al* [59] studied PLLA and Cu₃(BTC)₂ MOF using contact angle studies using geometric and harmonic means and obtained low interfacial tension and high work of adhesion, indicating good compatibility between the MOF and the PLLA. Adams *et al* [49] prepared MMMs from poly(vinyl acetate) (PVAc) and 15% copper-terephthalic acid based (CuTPA) MOF by polymer solution processing. SEM images of the MMM cross section showed well dispersed CuTPA MOF particles. The synthesized MMMs had increased permeability for He, O₂, N₂ and CH₄ gases as compared to neat polymer. The authors also reported improved selectivity for various combinations of gases such as CO_2/CH_4 and O_2/N_2 .

Car *et al* [50] studied copper benzene 1,3,5-tricarboxylate (Cu₃(BTC)₂) MOF and Mn(HCOO)₂ (manganese (II) formate) MOFs with rubbery dimethylsiloxane (PDMS) and glassy polysulfone (PSf). The authors reported slight improvement of CO_2/N_2 selectivity for PDMS-10% Cu₃(BTC)₂. Increased H₂, N₂, O₂, CH₄ and CO₂ permeability

was observed for PSf-5% $Cu_3(BTC)_2$ MOF and PSf-10% $Cu_3(BTC)_2$ MOF. In other research [51] on Matrimid[®] with 10, 20 and 30% MOF-5 w/w, strong polymer-MOF interactions were observed by SEM microscopy. Plastic deformation was observed in the Matrimid-MOF-5 composites due to the formation of cavities. The permeability of various gases increased up to 120%, however there was no improvement in the selectivity of the membranes.

Bae *et al* [52] fabricated MMMs containing zeolitic imidazolate framework-90 (ZIF-90) porous crystals. Good adhesion was observed between ZIF-90 and the polyimide polymer matrix. The authors reported increased CO_2 permeability without any loss of CO_2/CH_4 selectivity.

Various computational analyses have been published to estimate and validate the performance of MMMs [54-56]. Keskin *et al* [54] theoretically studied Cu(hfipbb)(H₂hfipbb)_{0.5} particles in a Matrimid[®] film and their calculation predicted that MMMs provided high selectivity for CO₂/CH₄ separations but mediocre selectivity for H₂/CO₂. They also concluded that MMMs prepared from a particular polymer and porous microporous crystalline material may act as a good membrane for a particular gas combination but it may not work for other gas combination.

Apart from the separation of gases, such composite systems can be used to selectively purge or scavenge gases from the headspace of the food or pharmaceutical package. These porous materials can also be encapsulated in canisters and caps, opening windows for various packaging applications. REFERENCES

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Chapter 3. Synthesis and characterization of $Cu_3(BTC)_2 MOF$

Chapter 3. Synthesis and characterization of Cu₃(BTC)₂ MOF

3.1 Introduction

Coordination polymers or supramolecules first came into attention in the 1960s. However, the interest in porous coordination polymers and MOFs was invigorated in the late 1990s [1]. The synthesis of MOFs has attracted increasingly attention in the last two decades [2]. Thousands of MOF structures can be synthesized by varying the metal and organic components, two primary building blocks required for the synthesis of MOF. The synthesis of MOF can be pursued using various routes as summarized below:

- 1. Solovothermal or hydrothermal synthesis
 - a. Synthesis using autoclave
 - b. Microwave assisted synthesis
 - c. Ultrasonic synthesis
- 2. Slow diffusion process
- 3. Synthesis under ambient pressure using refluxing
- 4. Mechano-chemical synthesis
- 5. Electrochemical synthesis

As the name suggests, the solvothermal or hydrothermal technique uses heat with a solvent or aqueous solution for the synthesis of crystals. In this technique, the synthesis has traditionally been carried out in an autoclave. The conventional heating process is inconsistent; there is variation in the temperature across the solution. It may take days to a week to synthesize MOF crystals using an autoclave, and it is not viable for commercial production of MOF. Solvothermal and hydrothermal reactions can be carried out by microwave assisted rapid synthesis or sonochemical synthesis. Uniform morphology, small distribution of crystal size, even nucleation and fast reaction rate are some of the popular benefits of microwave synthesis as compared to autoclave [3-5]. Sonochemical synthesis, also known as ultrasonic synthesis, is another energy efficient synthesis technique, which decreases the reaction time significantly.

Ni *et al* [4] reported that microwaves create uniform seeding conditions which generates the narrow size distribution. The fast reaction rate also leads to shorter reaction time and higher energy efficiency for microwave synthesis. Solvothermal synthesis by autoclave generates crystals, that can be analyzed using single crystal X ray diffraction analysis [5] whereas microwaves synthesis cannot generate single crystals, which are big enough for single crystal X-ray analysis [4] and high temperature and pressure are still required for the synthesis of these crystals.

Li *et al* [6] utilized sonochemical synthesis technique for the synthesis of $Cu_3(BTC)_2$ MOF at atmospheric pressure and room temperature for 1 hour. Sonochemical synthesis induces homogeneous nucleation and rapid crystal synthesis. It is environmental friendly, efficient, easy and cheap process [6,7].

Li *et al* [8] fabricated $[Zn(BDC)(H_2O)]n$ (BDC = 1,4 benzenedicarboxylate) MOF using synthesis times of 10, 20, 30, 60 and 90 minutes. Nanocrystals were obtained at 10 to 60 minutes. However, at 90 minutes of reaction time ultrasound radiations damaged the crystals. Hartmann *et al* [9] synthesized $Cu_3(BTC)_2$ MOF by solvothermal synthesis, electrochemical synthesis, and synthesis under ambient pressure. The authors reported surface areas between 1153 to 1624 m²/g. The selection of the synthesis process affected the surface area and specific pore volume. The highest surface area was achieved at ambient temperature by a rigorous stirring and refluxing process followed by solvothermal process using an autoclave. The electrochemical synthesis provided the lowest surface area. The authors compared ethanol and 50% ethanol plus 50% water as solvents for solvothermal synthesis. Ethanol as a solvent yielded higher pore volume and higher specific surface area as compared to ethanol-water solution. For example, autoclave synthesis in ethanol yielded a surface area of 1510 m²/g whereas autoclave synthesis in ethanol water solution provided 1253 m²/g.

Pichon *et al* [10] utilized a mechanochemical synthesis technique for the synthesis of $Cu(INA)_2$ MOF (INA = isonicotinic acid). The authors ground copper acetate with isonicotinic acid using a ball mill at a 25 Hz oscillation rate for 10 minutes without any heat or solvent to synthesize the MOF. The grinding process generated acetic acid as a byproduct. The authors suggested that the grinding process was required to uniformly mix the reactants, and the reaction can be initiated after 1 minute of grinding, and it can be completed in 6 hours unaided. However, continuation of grinding accelerated the rate of reaction.

Biemmi *et al* [11] studied the influence of reaction temperature and time on the synthesis of HKUST-1 [Cu₃(BTC)₂] MOF and MOF-5. They synthesized Cu₃(BTC)₂ at 348, 393, 423 and 453 K. The formation of Cu₂O (2θ = 36.43) in a significant amount

was observed at 423 and 453 K in the XRD patterns. The authors obtained a max yield of 80% at a synthesis time of 320 h. The choice of salt also affected the purity of the MOF.

Krawiec *et al* [12] synthesized $Cu_{3(}BTC)_2$ by pressure free synthesis using 50 mmol copper (II) acetate monohydrate and 50 mmol trimesic acid (TMA) in dimethyl formamide. The mixture was refluxed and stirred for 12 h. After cooling and filtering the solution, the powder was heated in 150 mL DMF for 1 h at 423 K to remove the residual TMA and washed with water for 1 h at 403 K. The product was activated at 433 K for 48 hr and analyzed for BET surface area. The $Cu_3(BTC)_2$ powder had a single point BET surface area of 1239 m²g⁻¹ with pore volume of 0.62 cm³g⁻¹, as measured by N₂ physical adsorption isotherm.

 $Cu_3(BTC)_2$ has also been synthesized by electrochemical synthesis route [13]. The authors utilized copper as anode and cathode in the electrochemical cell with TMA dissolved in methanol as the electrolyte. The electrochemical process was carried out at 12-19 V for 150 min using 1.3 A current level and generated Cu_3BTC_2 MOF with a surface area of 1650 m²g⁻¹. The crystal structure of various biomolecules is influenced by the Pai-Pai interactions between the aromatic molecules. The benzene ring has quadrupole moment of -29.0×10^{-40} cm². Hunter *et al* [14,15] described quadrupole-quadrupole interactions benzene ring for stack. Similar forces might be responsible for the creation of the rigid framework with micropore structure in the MOF. Synthesis at elevated temperature and pressure increases the adhesion between the particles.



Figure 3.1: Dicopper (II) tetracarboxylate building block or repeating unit for HKUST-1

 $Cu_3(BTC)_2$ is a good water and carbon dioxide adsorbent. The chemical structure of the buiding block of $Cu_3(BTC)_2$ is represented in Figure 3.1. To take advantage of faster reaction rates, we decided to use a microwave assisted solovothermal synthesis technique for the synthesis of $Cu_3(BTC)_2$ MOF also known as HKUST-1.

3.2 Methodology

3.2.1 Microwave Synthesis

An Ethos EZ microwave digester system from Milestone Inc., CT was utilized for increasing the rate of chemical reaction. The Microwave digester was equipped with an SK-10 segmented rotor. The rotor has a closed PTFE vessel, and it is designed to withstand 100 bar pressure and 300°C. The PTFE vessel has an inbuilt thermo well to insert thermocouple, which controls the temperature of reaction. Figure 3.2 shows the picture of Ethos Ez Microwave digester.



Figure 3.2: Ethos Microwave, adapted from http://www.speciation.net/

Hydrothermal synthesis of the MOF utilized in this study was conducted according to the following steps:

Synthesis of MOF

Twenty-four mL of water was mixed with 24 mL of ethanol. After that, 0.84 g of benzene 1,3,5 tricarboxylic acid and 1.75 g of copper nitrate trihydrate were added into the reaction vessel. The solution was allowed to react in the closed

vessel in the Ethos microwave for 4 h at 110°C under autogeneous conditions and cooled. The blue powder recovered by filtering the solution was washed once with water followed by one wash with ethanol. After evaporating the residual alcohol from the powder, the powder was heated overnight at 120°C using vacuum oven.

The presence of ethyl alcohol in the reaction reduces the hydrophobic repulsions between water and benzene 1,3,5 tricarboxylic acid since smaller carboxylic acids are soluble in water. Nitrate ions exist as counter anions in the copper (II) nitrate trihydrate. Copper (II) nitrate trihydrate can form hexa aqua metal ions with water. These hexa aqua metal ions are stable in the acid solution, but they tend to be less stable in alkaline solutions.





Figure 3.3: Images of activated (left) and partially saturated Cu₃(BTC)₂

Figure 3.3 shows the activated MOF $Cu_3(BTC)_2$ which is dark violet and partially saturated MOF – $Cu_3(BTC)_2(H_2O)_3xH_2O$. After complete saturation the MOF acquires a turquoise color. The water molecules axially coordinated to the two exchangeable copper sites can be removed by heat activation under vacuum, yielding a lewis acid site with catalytic properties. The effect of the adsorbed water on the X-ray diffraction pattern is discussed in chapter 4 in more detail.

3.3 Characterization of Cu₃(BTC)₂ MOF

3.3.1 Surface Area and Porosity Measurement

A micromeritics accelerated surface area and porosity system (ASAPTM) 2020 was used to determine surface area and porosity of the micro porous material. Degassing was carried out at 200^oC for 48 h. The MOF was allowed to cool for half an hour and then mounted on the analysis port. BET surface area analysis was performed using N₂ gas at 77 K using pressure ratios between 0 and 0.3. The ASAP[®] 2020 software was utilized to calculate the BET (Brunauer, Emmer and Teller) surface area. Generally, relative pressures between 0.05 and 0.3 are utilized for BET surface area calculation using a static volumetric technique [16]. From the isotherm data BET surface area can be calculated using equation 1.

$$\frac{P}{v(P_o-P)} = \frac{1}{cv_m} + \frac{c-1}{cv_m} \frac{P}{P_o}$$
⁽¹⁾

Where,

P_o = Saturation Vapor Pressure

P = adsorption pressure

v = quantity of the gas adsorbed

C = constant, which constant c can be mathematically expressed as:

$$c = \exp(\frac{E_1 - E_L}{RT})$$

R= Gas constant = 8.314 J/K/mol

 E_1 is the heat of adsorption for the first layer.

 E_L = Heat of adsorption for the subsequent layers.

T = Absolute temperature

The volume of the monolayer calculated from the equation 1 is then utilized to estimate the BET surface area using equation 2.

$$S_{BET} = \frac{v_m N s}{V}$$
⁽²⁾

S = area occupied by a small gaseous molecule = 0.16 nm^2 for N₂.

N = Avogadro number = 6.023×10^{23}

 $V_m = Volume of the monolayer$

V = Molar volume of the adsorbate gas



Figure 3.4: Micromeritics ASAPTM 2020 adapted from www.micromeritics.com

3.3.2 Scanning electron microscope (SEM)

The MOF crystals were sputter coated with gold using an Emscope SC500 (Emscope Laboratories Ltd, Ashford, UK) sputter coater. The SEM analysis was carried out using a Joel JSM 6400 SEM. The microscope was equipped with a LaB_6 filament. Images were acquired with a 3 nm resolution. The images were collected at 12keV accelerating voltage and 39 mm working distance.

3.3.3 X-Ray Powder Diffraction

X-ray diffraction studies on the MOF crystals were performed using a Bruker D8 advance X-ray diffractometer (Bruker AXS G mgH, Karlsruhe, Germany) at 40kV, 40mA using Cu K α radiation ($\lambda = 1.5418$ Å). A 1.2 mm primary beam slit and 2.0 mm detector slit were used. The X-ray scans were carried out using 0.02 degrees per second. Data was collected in triplicate.

3.4 Results and discussions

Figure 3.5 shows the N₂ isotherm of the Cu₃BTC₂ MOF. The isotherm is a Type 1 isotherm (IUPAC classification) also known as a Langmuir isotherm. Such isotherms are associated with microporous materials (pores<2 nm) like MOFs and activated carbon [17]. A Plateau was observed at low relative pressure because the pores are so small that they get filled at low pressure. Once the pores are filled the remaining adsorption occurs on the exterior of the porous material. We obtained an average BET surface area of 1236 ± 103 m² g⁻¹.

The SEM images of the Cu_3BTC_2 MOF crystal acquired using the JEOL 6600 are presented in figure 3.6. The crystal size ranges from 5-30 µm with average crystal size ~15 µm.



Figure 3.5: N₂ isotherm of Cu₃(BTC)₂ MOF



Figure 3.6: SEM images of Cu₃(BTC)₂ MOF acquired at 12kV and 39 mm working distance

The powder X-ray diffraction pattern (PXRD) of the Cu₃(BTC)₂ MOF is represented in Fig. 3.7. The crystals are in agreement with already published PXRD patterns of Cu₃(BTC)₂ MOF [18, 19]. Hartmann *et al* [19] reported that peak at $2\theta = 36.43$ and $2\theta = 35.5$ and 38.7 relate to Cu₂O and CuO, respectively. These impurities are generated at reaction temperature above 110°C. Our samples were free of Cu₂O and CuO impurities.



Figure 3.7: X ray diffraction pattern of Cu₃(BTC)₂ MOF

The Cu₃(BTC)₂ MOF was successfully synthesized using microwave assisted synthesis process. However, for the simplicity, ease and reproducibility we used BasoliteTM C 300, supplied by sigma Aldrich, for the fabrication of membranes discussed in detail in chapter 4, 5 and 6.

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Chapter 4. Deterioration of metal organic framework crystal structure during fabrication of poly(L-lactic) acid mixed matrix membranes*

*version of the article Kathuria A, Abiad MG and Auras R. Polymer International 2013; 62: 1144-1151.

Chapter 4. Deterioration of metal organic framework crystal structure during fabrication of poly(L-lactic) acid mixed matrix membranes

Poly(L-lactic acid) (PLLA) and metal organic framework (MOF) mixed matrix membranes (MMM) were prepared by melt extrusion of PLLA with 5% w/w of either activated or water saturated Cu₃(BTC)₂ (Cu₃(C₉H₃O₆)₂(H₂O)₃·*xH*₂O or HKUST-1). The morphology and the stability of injection-molded samples were evaluated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The presence of activated and saturated MOF crystals increased the cold crystallization onset temperature as compared to neat PLLA. It can be attributed to the MOF crystals incorporated in the PLLA matrix, which decreased the mobility of PLLA and thus impeded the crystallization process. According to the XRD results, the activated MOF crystals were successfully incorporated into the PLA matrix without altering the crystal structure of the MOF. Moreover, the findings from the permeability and tensile tests as well as SEM imaging indicated good interfacial interactions between PLLA and activated MOF. However, during melt extrusion of PLLA with saturated MOF, water molecules from the saturated MOF altered the MOF crystal structure and contributed to the degradation of the PLLA polymer by reducing its molecular weight (M_w) by around 21%.

4.1. Introduction

During the last couple of decades, growing environmental concerns along with limited petroleum resources and technological improvements provided impetus to the development of new bio-based, biodegradable and compostable polymers such as poly(lactic acid) (PLA). Due to technological advancements, PLA has become one of the most remarkable commercial polymers in this category particularly for medical and packaging applications [1, 2].

PLA is generally synthesized by ring opening polymerization of lactide monomers which are linked together in one of the three isomeric forms – (D,D) lactide, (L,L) lactide and (D,L) lactide. The final properties of the PLA such as thermal, mechanical, and barrier properties are significantly impacted by the isomeric composition of the resin. Although PLA has many appealing properties such as transparency, low processing temperature, and compostability, it is brittle and has low heat deflection temperature (HDT) which limits the scope of its application. Consequently, researchers attempted to use different methodologies including plasticization, chemical modification, composite fabrication as well as blending to reduce PLA's inherent brittle nature and improve its HDT, gas and water vapor barrier properties among others [3-6].

Metal organic frameworks (MOFs) is a class of crystalline materials with high porosity, which are composed of metal ions (Cu⁺, Cu²⁺, Ag⁺, Zn²⁺, Co²⁺, K⁺, etc.) linked together by organic bridging ligands forming multi-dimensional structures [7]. They exhibit high thermal and mechanical stability [8]. Perhaps the most attractve property of MOFs is their ultrahigh surface areas, which is greater than porous carbons or zeolites and may exceed at times 5900 m².g⁻¹ [9], large pore sizes and high micro-pore

volume. The porosity and large surface area of these materials along with their varied chemical compositions render them candidates for high capacity adsorption of various gases and molecules [10]. The structure of MOFs allows guest molecules to diffuse into the bulk structure while the size, shape and affinity of these pores provide selectivity among the guests, which can be incorporated into them. There is a plethora of literature investigating various applications of MOFs in the fields of catalysis [11], gas purification and separation [12], hydrogen storage [13] and as an option for efficient controlled drug delivery [14].

One of the commercially available MOFs is $Cu_3(BTC)_2 [Cu_3(C_9H_3O_6)_2(H_2O)_3]$, also known as HKUST-1. $Cu_3(BTC)_2$ is characterized by a face centered cubic (FCC) cell as the repeating unit [15]. The Cu^{2+} dimer coordinated with four oxygen atoms of benzene tricarboxylate makes a paddle wheel which constitutes the building block of HKUST-1 whose structure is represented in Figure 4.1 [15]. The water molecules axially coordinated to the two exchangeable copper sites can be removed by heat activation under vacuum yielding a Lewis acid site with catalytic properties [16].



Figure 4.1: Chemical structure of building block of Cu₃(BTC)₂ MOF

Interest in improving the functionality of polymer based membranes have led researchers to develop new mixed matrix membranes (MMM) by integrating inorganic particles such as zeolites, MOFs, carbon, and carbon nanotubes, among other sieving materials, within the organic matrices [18-23]. The thermal and mechanical stabilities are key factors in the development of such systems. For this reason, the aim of the present study was to understand the effect of the adsorbed water present in Cu₃BTC₂ MOF on the morphology and stability of poly(L-lactic acid)–Cu₃BTC₂ based MMMs prepared by melt extrusion followed by injection molding.

4.2. Methodology

4.2.1 Materials

Poly(L-lactic acid) (PLLA) resin grade 4043 D, 98% L-lactide, with weight average molecular weight (M_w) , number average molecular weight (M_n) and polydispersity index (M_w/M_n) of 111 Kda, 84 Kda and 1.3 respectively, was procured

from NatureWorks LLC (Minnetonka, MN, USA). Trimesic acid (TMA) - Benzene 1,3,5 tricarboxylic acid- (95 wt.% pure) and BasoliteTM C300 Metal Organic Framework $[Cu_3(BTC)_2]$ were purchased from Sigma Aldrich (St Louis, MO, USA). BET surface area of $Cu_3(BTC)_2$ MOF as reported by the manufacturer ranges between 1500 and 2100 m².g⁻¹, and was previously measured as 1566 m².g⁻¹ [24]. The particle size of $Cu_3(BTC)_2$ averages to 15 µm measured using a JEOL JSM 6400 SEM (Japan Electron Optics Laboratories Ltd., Tokyo, Japan) with an accelerating voltage of 12 kV and 39 mm working distance (Figure 4.2). The detailed methodology of SEM is provided below.



Figure 4.2: SEM image of BasoliteTM C300 acquired at 12 kV and 39 mm working distance
4.2.2 Sample preparation

Prior to processing and extrusion, the PLLA resin was dried at 80°C for 4 h while activated BasoliteTM C 300 MOF [Cu₃(BTC)₂) - to be referred to as *'activated MOF'* here after - was activated for 24 h at 200° C using vacuum oven. On the other hand, saturated BasoliteTM C 300 MOF – to be referred to as *'saturated MOF'* here after – was obtained by conditioning at 23°C and 50% RH for 4 days to equilibrate and reach water storage capacity. This time was predetermined to be sufficient for the MOF to saturate and stabilize [25].

MMMs (PLLA + 5% wt. MOF) were extruded using a vertical co-rotating twinscrew micro-compounder (DSM Research, Geleen, The Netherlands) followed by injection molding. The extruder was equipped with a 150 mm screw and L/D ratio of 18. The volume of the barrel was approximately 15 cm³. The extruded compositions were transferred into a transferring cylinder and injected to the mini-injection molder (DSM Research, Geleen, The Netherlands). The temperature profile for the extrusion process from the top to bottom zone was set at 190 °C with an extrusion cycle time of 5 min. The pressure for injection molding was ~1 MPa (140 psi) while the transfer cylinder and mold temperatures were set at 195 and 65 °C; respectively. Dogbone tensile bars and XRD discs of PLLA, PLLA-5% activated MOF and PLLA-5% saturated MOF composites were prepared and stored in a desiccator over desiccant (Drierite[®]) at room temperature (~23 °C). The PLLA-5% activated MOF and PLLA-5% saturated MOF will be represented as (PLLA-A-MOF) and (PLLA-S-MOF), respectively. MOF 5 wt.% was previously determined as enough MOF to produce a meagninful change in the MMMs final thermal, mechanical and barrier properties [24, 25].

4.2.3 Characterization

4.2.3.1 Thermogravimetric analysis (TGA)

The thermal stability of $Cu_3(BTC)_2$ MOF, PLLA and PLLA-MOF composites was examined using a TGA model 2950 from TA-Instruments (New Castle, DE, USA). TGA was also used to determine the initial water content in the Cu_3BTC_2 MOF. Approximately 5 mg of sample were heated from 23 to $700^{\circ}C$ at a rate of $10^{\circ}C.min^{-1}$. The TGA data was analyzed using the Universal Analysis software version 2000 (TA Instruments, New Castle, DE, USA). Samples were run in triplicate.

4.2.3.2 X-Ray diffraction (XRD)

X-ray diffraction data was collected for the injection molded XRD discs of PLLA, PLLA-A-MOF, and PLLA-S-MOF stored at 23° C in a desiccator over desiccant (Drierite[®]) as well as for activated and saturated Cu₃BTC₂ MOF powder using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmgH, Karlsruhe, Germany) at 40kV, 40mA (1,600W) using Cu K α radiation ($\lambda = 1.5418$ Å), a 1.2 mm primary beam slit and 2.0 mm detector slit. The X-ray scans were carried out using 0.02 degrees per second. Data was collected in triplicate.

4.2.3.3 Differential scanning calorimetry (DSC)

DSC analysis was performed using a DSC Q100 from TA instruments. The samples were equilibrated to 0° C followed by heat/cool/heat cycles from 0 to 180° C at a rate of 10° C.min⁻¹. The melting temperature (T_m) and associated heat enthalpy (Δ H_m) were computed from the first heating cycle. On the other hand, the glass transition (T_g) temperature and cold crystallization onset (T_{co}), cold crystallization peak (T_{cc}) and enthalpy of cold crystallization (Δ H_c) were calculated from the second heat cycle to eliminate any thermal history caused by processing or storage. DSC data were obtained in triplicates and were analyzed using the Universal Analysis software version 2000.

The percent crystallinity of the samples was determined using equation (1):

$$X_{c}(\%) = \frac{\Delta H_{m} - \Delta H_{c}}{\Delta H_{m}^{c}(1-x)} \times 100$$
⁽¹⁾

where ΔH_m is enthalpy of fusion; ΔH_c is the enthalpy of cold crystallization; ΔH_m^c is enthalpy of fusion of pure crystalline PLA; $\Delta H_m^c = 93.1$ J/g [26]; and x is the mass fraction of the MOF in the MMM.

4.2.3.4 Tensile test

Tensile properties were evaluated according to ASTM D638-10 using a Universal Tensile Machine model UTS SFM 20 from United Calibration Corporation, (Huntington Beach, CA, USA). The machine was equipped with a laser extensometer. Injection molded dogbone samples with a gauge length of 25.4 mm were stored at room temperature in a dessicator over desiccant (Drierite[®]) for 40 h prior to testing. The samples were then tested at room temperature (~23°C) using a 453 kg load cell at 0.023 kg of preload. PLLA and PLLA-MOF composites were tested at the crosshead speed of 50.8 mm.min⁻¹ (2 in/min), whereas PLLA and PLLA-Trimesic acid (TMA) composites were tested at the crosshead speed of 2.54 mm.min⁻¹ (0.1 in/min) (later elaborated in section 3.4). At least five replicates were tested for each type of sample.

4.2.3.5 Weight average molecular weight

In order to examine the effect of processing conditions and water content of the Cu₃(BTC)₂ MOF on the molecular weight of the PLLA matrix, M_w , and M_n of the PLLA resin, extruded PLLA resin and PLLA-A-MOF and PLLA-S-MOF were determined using a GPC (Waters Inc., Milford, MA, USA). A flow rate of 1 mL.min⁻¹ and runtime of 45 min at 35°C were used. The instrument was calibrated with polystyrene standard materials with a molecular weight ranging from 2.9 x 10³ to 3.64 x 10⁶ Da using a third order polynomial equation. The Mark-Houwink corrected constant K = 0.000174 (mL·g⁻¹) and a = 0.736 for dilute PLLA solution in tetrahydrofuran (THF) were used [27]. The instrument was equipped with a Waters 1515 isocratic pump, Waters 717 autosampler, a series of Waters Styragel Columns (HR4, HR3 and HR2) and Waters 2414 refractive index detector. Approximately 20 mg of specimen were dissolved in 10 mL of HPLC grade Tetrahydrofuran (THF) with 99.99 % purity (Pharmco-Aaper, Brookfield, CT,

USA) in order to determine the M_w , M_n , and the polydispersity index (*PI*). The solution was then filtered with a 0.45 µm filter.

4.2.3.6 Scanning electron microscopy (SEM)

A JEOL JSM 6400 scanning electron microscope equipped with a Lanthanum Hexaboride (LaB₆) electron gun was utilized to study the surface topography of the PLLA, BasoliteTM C 300, PLLA-A-MOF and PLLA-S-MOF. The samples were sputter-coated with 10nm gold using an Emscope SC 500 (Emscope Laboratories Ltd., Ashford, UK). SEM photomicrographs were acquired at accelerating voltage of 12 kV.

4.2.3.7 CO₂ and O₂ permeability coefficients

The films used for the permeability studies were prepared using a PHI 30 ton compression molding machine (City of Industry, CA, USA) with 12" x 12" plate size. The injection molded samples prepared using the twin screw DSM micro-compounding instrument were compressed at 170° C and ~1.0 MPa for 5 min. The CO₂ and O₂ permeation rates were measured using a PermatranTM C 4/41 and an OxtranTM 2/21 (MOCON Inc, Minneapolis, MN, USA); respectively, at 23°C, 0% RH, and 100% permeant gas between aluminum masks with areas of 3.14 and 5 cm². The permeability coefficients of CO₂ and O₂ were calculated using equation (2):

Permeability = Gas Transmission Rate
$$\times \frac{1}{\Delta P} \times t$$
 (2)

where ΔP is the difference in permeant partial pressure across the films expressed in Pa, and *t* is the film thickness.

4.2.3.8 Data analysis

Statistical analyses were performed using SAS 9.0 Software (SAS Institute Inc., Cary, NC, USA). Tukey's HSD (Honestly Significant Differences) tests were used to determine significance at the 95% confidence ($\alpha = 0.05$).

4.3. Results and discussion

4.3.1 Thermo-gravimetric analysis

The TGA thermographs for activated MOF, saturated MOF, PLLA, PLLA-A-MOF and PLLA-S-MOF are shown in Figure 4.3. The saturated MOF which was stored at 23°C and 50% RH for 4 days adsorbed around 36% w/w moisture while the activated MOF exhibited 5% w/w moisture, mostly attributed to water adsorbed during sample handling. Comparably, Schlichte *et al* [28] obtained similar results for HKUST-1 dried in a vacuum oven at 100 °C, rehydrated in air, and rehydrated in moist argon stream and they reported 2, 27 and 36.4% w/w moisture; respectively.

Figure 4.3 also shows that the organic component of the framework, benzene tricarboxylate, starts degrading at around 325°C. The thermal degradation onset of the polymer matrix (PLLA) and the MMM (PLLA-A-MOF and PLLA-S-MOF) starts at around 322° C. Difference can be observed in the final decomposition temperature (T_d) for PLLA, PLLA-S-MOF and PLLA-A-MOF – reported as 385, 410 and 500°C; respectively. The final plateau for the PLLA-A-MOF and PLLA-S-MOF samples can be mainly attributed to the copper present in the MOF.



Figure 4.3: TGA thermograms of PLLA, PLLA-A-MOF, PLLA-S-MOF, saturated and activated MOF before extrusion

Huang et al [29] studied the thermal stability of Cu_3BTC_2 MOF using ReaxFF reactive molecular dynamics (RMD). They reported good thermal stability of the MOF structure for temperatures up to 300°C while observing structural collapse at temperatures above 327°C. The simulation from 327 to 427°C indicated that MOF retained the molecular formula but sacrificed the microporous nature of the material as further heating released CO₂ and CO.

4.3.2 X-Ray Diffraction (XRD)

XRD diffraction patterns of activated MOF and saturated MOF are represented in Figures 4.4a and 4.4b; respectively, matching previously reported XRD patterns [28, 30, 31]. The percentage intensity of various planes is denoted in Table 4.1. The data presented in this study confirms the observations previously reported by Schlichte et al [28] regarding the intensity ratios I_{200}/I_{220} and I_{331}/I_{420} which are significantly higher in activated MOF than saturated MOF as observed. The crystal retained all the planes of FCC crystal structure, the changes in the intensity ratio of plane (200), (400), and (441) planes are due to the adsorption of water by the Cu₃BTC₂ MOF crystal [28]. Figures 4.5a, 4.5b and 4.5c represent the diffractograms of PLLA-A-MOF, PLLA-S-MOF, and PLLA XRD discs; respectively. The crystalline peak (Figure 4.5c) observed for PLLA composites at $2\theta = 16.4^{\circ}$ corresponds to α -PLLA crystals with a broader background hump, suggesting a primarily amorphous nature of the polymer [32, 33, 34]. The high amorphous content of the injection molded PLLA, PLLA-A-MOF, and PLLA-S-MOF composites can be ascribed to the slow crystallization kinetics of the PLLA [35]. This observation was further endorsed by the DSC analysis discussed in the next section. The X-ray diffractogram of injection molded PLLA-A-MOF discs is represented in Figure 4.5a. PLLA-A-MOF have similar peaks with minor changes in the intensity ratios calculated from the area under the curve at the same planes as observed in the $Cu_3(BTC)_2$ MOF as shown in Table 4.2. The extensive change in the intensity ratio of plane (200) in the case of activated MOF and PLLA-A-MOF may be related to the possible hydration of MOF during sample handling after MMMs fabrication.



Figure 4.4: XRD patterns of (a) activated MOF and (b) saturated MOF



Figure 4.5: XRD patterns of (a) PLLA-A-MOF disc, (b) PLLA-S-MOF disc, and (c) injection molded PLLA disc

| Plane | 2.0 | d spacing (\mathring{A}) | Intensity Ratio* | | |
|-------|------|------------------------------|------------------|---------------|--|
| Tiane | 20 | u spacing (N) | Activated MOF | Saturated MOF | |
| (111) | 5.7 | 15.5 | 1.1 | 0.9 | |
| (200) | 6.6 | 13.5 | 97.8 | 35.2 | |
| (220) | 9.5 | 9.3 | 52.8 | 46.0 | |
| (222) | 11.6 | 7.6 | 100 | 100 | |
| (400) | 13.5 | 6.6 | 12 | 32.4 | |
| (331) | 14.6 | 6.1 | 9.5 | 5.5 | |
| (420) | 15.0 | 5.9 | 1.2 | 5.8 | |
| (422) | 16.4 | 5.4 | 4.3 | 7.1 | |
| (333) | 17.4 | 5.1 | 12.4 | 13.8 | |
| (440) | 19.0 | 4.7 | 10.3 | 20.8 | |

 Table 4.1 XRD intensities of activated and saturated MOF

*Background subtracted intensity

| Plane 2.0 d -spacing | | d-spacing | PLLA-A-1 | PLLA-A-MOF | | PLLA-S-MOF | |
|------------------------|------|-----------|----------------------|------------------|----------------------|------------------|--|
| Flatte | (Å) | | Area under the curve | Intensity Ratio* | Area under the curve | Intensity Ratio* | |
| (111) | 5.7 | 15.5 | 195 | 19.8 | - | - | |
| (200) | 6.6 | 13.5 | 661 | 59.9 | - | - | |
| (220) | 9.4 | 9.4 | 348 | 47.0 | 68 | 51.5 | |
| (222) | 11.5 | 7.7 | 1172 | 100 | 132 | 100 | |
| (400) | 13.4 | 6.6 | 136 | 14.5 | 25 | 47 | |
| (331) | 14.6 | 6.1 | 79.5 | 5.3 | - | - | |
| (420) | 15.0 | 5.9 | - | - | - | - | |
| (422) | 16.4 | 5.4 | 53 | 4.7 | 17.95 | 14 | |
| (333) | 17.4 | 5.1 | 128 | 9.0 | - | - | |
| (440) | 19.0 | 4.7 | 167.5 | 15.8 | | | |

Table 4.2 Intensity ratio, and area under the curve of PLLA-A-MOF and PLLA-S-MOF

*Background subtracted intensity

The *d*-spacing, peak intensity and area under the peak for various planes of PLLA-S-MOF are presented in table 4.2. It can be observed that peaks (111) and (200) which were present in the saturated MOF disappeared in the PLLA-S-MOF and the peak intensity of other planes such as (220) and (222) were also drastically reduced. The absence of these peaks in the diffraction pattern indicates that saturated Cu₃(BTC)₂ MOF lost the face centered cubic (FCC) crystal structure after extrusion. The loss of FCC crystal structure of the MOF during compounding of the composites can be attributed to the exposure to both moisture and temperature during extrusion. Prestipino et al [36] utilized a combination of extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), UV-Vis and Infrared (IR) spectroscopy techniques and reported that the water sorption properties of HKUST-1 are provided by "an open framework with an intersecting 3D-channel system – composed by dimeric cupric tetracarboxylate." The tetracarboxylate and the benzene rings in the MOF (see Figure 1b) are responsible for the sorption properties. Prestipino *et al* [35] also illustrated that the adsorption properties of HKUST-1 are not only given by unspecific van der Waals interactions, but also by specific Coulomb-type electrostatic interactions. They demonstrated that upon dehydration at 453 K under vacuum the first coordination sphere of Cu²⁺ sites was significantly altered. The shortening of the Cu-Cu distance and the distortion of the Cu-O bonds produce coordinately unsaturated Cu²⁺ dimer sites overlooking the cages. Küsgens et al [37] also studied the water stability of Cu₃(BTC)₂ (HUKST-1) MOF at elevated temperatures by dipping the MOF particles into de-ionized water at 50°C for 24 h. After filtering and drying the MOF at room temperature they performed XRD studies and evaluated the surface area demonstrating the presence of irreversible changes in the MOF structure along with reduction in BET surface area from 1340 to 647 m².g⁻¹ [37]. Mustafa *et al* [38] studied the stability of the Cu₃(BTC)₂ MOF under steam conditions. They observed changes in the MOF structure starting at 70°C, with the formation of unidentified low crystalline material at 120° C. The Cu₃(BTC)₂ MOF transformed completely to an irreversible form [Cu₂OH(BTC)(H₂O)]_n.2nH₂O at 150°C. The alterations in the crystal structure during processing attributed to the presence of adsorbed water in the saturated Cu₃(BTC)₂ MOF embedded in the PLLA may have led to permanent changes in the pore size and sorption capacities of the final MMMs.

4.3.3 Differential Scanning Calorimetry (DSC)

Figures 4.6a and 4.6b represent the thermograms of the injection molded PLLA, PLLA-A-MOF and PLLA-S-MOF obtained during the first and second heating cycles; respectively. Table 4.3 summarizes the glass transition, crystallization and melting enthalpies and temperatures. The average percentage crystallinity of PLLA, PLLA-A-MOF and PLLA-S-MOF obtained from the second heating cycle were 2.0, 1.0 and 0.6%; respectively, suggesting the amorphous nature of the PLLA, PLLA-A-MOF and PLLA-S-MOF composites and complementing the observations from the XRD spectra. The mass fraction percentage crystallinity of PLLA, and PLLA-A-MOF as calculated from the XRD are 2.8 and 0.6 %; respectively. The presence of activated MOF particles slightly reduced the crystallinity of the MMMs compared to neat PLLA.

| Somula | $T_g(^{o}C)$ | Cold Crystallization | | Melting | | | |
|------------|--------------------|------------------------------|----------------------------|-------------------------|--------------------------|--------------------------|------------------------------------|
| Sample | | $T_{co}(^{o}C)$ | T_{cc} (^o C) | $\Delta H_c (J/g)$ | $T_{mo}(^{o}C)$ | $T_{m}(^{o}C)$ | $\Delta H_m (J/g)$ |
| PLLA | 60.8 ± 0.1^A | 103.8 ± 0.2^{A} | 119.1 ± 0.1^{A} | 19.6 ± 0.9^{A} | 143.3 ± 0.1^{A} | 147.9 ± 0.2^{A} | 21.9 ± 0.5^A |
| PLLA-A-MOF | 60.9 ± 0.0^{A} | 113.8 ± 0.2^{B} | 129.8 ± 0.4^B | 3.6 ± 0.1^B | 145.5 ± 0.1^B | 150.8 ± 0.1^B | $6.9\pm0.3^{\hbox{\scriptsize B}}$ |
| PLLA-S-MOF | 59.8 ± 0.4^{B} | $109.8 \pm 0.6^{\mathbf{C}}$ | $123.7 \pm 1.5^{\text{C}}$ | $25.0\pm0.9^{\hbox{C}}$ | $145.0\pm0.3^{\hbox{C}}$ | $149.2\pm0.4^{\hbox{C}}$ | $27.2 \pm 2.1^{\text{C}}$ |

 Table 4.3 Detailed DSC analysis information of PLA and its composites

Note: Values in the same column with same capital superscript letters are not statistically significantly different at α =0.05



Figure 4.6: DSC thermograms of PLLA, PLA-A-MOF and PLA-S-MOF: (a) first heating cycle; (b) second heating cycle

The addition of 5 wt.% activated and saturated MOF increased the cold crystallization onset (T_{co}) and the cold crystallization (T_{cc}) temperatures. For PLLA-A-MOF T_{co} increased from 103.8 to 113.8 °C and T_{cc} from 119.1 to 129.8 °C, whereas for PLLA-S-MOF T_{co} increased from 103.8 to 109.8 °C and T_{cc} from 119.1 to 123.7 °C. It was also observed that the enthalpy of crystallization (ΔH_c) of PLLA-A-MOF decreased from 19.6 to 3.6 J.g⁻¹, designating a decrease in PLLA mobility and thus a decline in the ability for the PLA matrix to crystallize in the presence of 5 wt.% activated MOF. No crystallization peak was observed in the cooling cycle at the cooling rate of 10°C.min⁻¹ for any of the materials (Figure 4.6b).

4.3.4 Tensile Test

The tensile strength of MMM depends on various factors such as interfacial interactions, aspect ratio, dispersion of the fillers, and thermal stability of the filler [39]. Fillers can also influence the crystallinity of the matrix, leading to change in various properties including strength, elongation, permeability, etc. PLLA is known for high tensile strength and poor flexibility [40]. Elangovan et al [25] studied the surface energy, interfacial tension and spreading coefficient of PLLA and HUKST-1 MOF using the contact angle measurement. The contact angles of PLLA and HKUST-1 measured using ethylene glycol were 57.1 and 53.3^o respectively, whereas the contact angles of PLLA and HUKST-1 obtained from methylene iodide were 37.6^o and 45.4^o. The authors utilized the geometric and harmonic means and obtained low interfacial tension and high

work adhesion indicating good compatability between the MOF and the PLLA. They also observed improved flexibility of PLLA added with more than 1 wt.% MOF.

The stress strain graph of PLLA, PLLA-A-MOF and PLLA-S-MOF is presented in Figure 4.7. The corresponding tensile strength, elongation at break, and modulus of elasticity values are presented in Table 4.4. The average tensile strength and percentage (%) elongation of injection molded neat PLA samples were 76.9 MPa and 3.6% respectively. Bhardwaj et al [6] studied the modification of PLA with hyberbranched polymers. They reported that PLA has tensile strength 76.5 MPa and 5.1 % elongation. The elongation of PLLA-A-MOF and PLLA-S-MOF were 16.9 and 9.14 %, respectively. Improvement in the elongation of PLLA-A-MOF as compared to neat PLLA can be attributed to good interfacial interaction between the activated MOF particles and PLLA matrix, as observed in the SEM images (Figure 4.8). PLLA-S-MOF has 300% improvement in elongation over neat PLLA. Elongation of PLLA-S-MOF was less than the PLLA-A-MOF. The presence of water in the MOF might have affected the interfacial interactions between MOF and PLLA. The tensile strength of PLLA-A-MOF decreased by around 23% as compared to neat PLLA. We observed 13% reduction in the tensile strength of PLLA-S-MOF as compared to neat PLLA. The exact mechanism of the improved toughness of the PLLA-A & S-MOF composites is not fully understood. Benzene based carboxylic acid and other small molecule polyhydric carboxylic acid ester based compounds have been used as plasticizers [41, 42]. Wang et al [43] investigated the co-polycondensation of lactic acid with TMA and reported a decrease in the glass transition (T_g) temperature of the copolymer. In order to further explore this behavior, PLLA samples added with 1, 2.5 and 5% wt TMA, the basic constitutional unit of MOF,

were produced to isolate the possible plasticizing effect of TMA due to any possible release of benzene 1,3,5 tricarboxylate (organic linker) to PLLA after detachment from MOF during processing. Table 4.5 shows that melt extrusion of PLLA with TMA did not substantially increase the elongation at break for PLLA samples added with 1, 2.5 and 5 wt % TMA. Therefore, the extension at break improvement can be mainly attributed to the MOF particles.



Figure 4.7: Stress-strain curves of PLLA, PLLA-A-MOF and PLLA-S-MOF

| Material | Tensile Strength (MPa) | Elongation at break (%) | Modulus of Elasticity (GPa) |
|------------|---------------------------|--------------------------|--------------------------------|
| PLLA | $76.9 \pm 1.5^{\text{A}}$ | 3.6 ± 1.5^{A} | $3.0 \pm 0.3^{\text{A}}$ |
| PLLA-A-MOF | 58.9 ± 0.8^B | 16.9 ± 3.2^{B} | 3.0 ± 0.2^{A} |
| PLLA-S-MOF | 66.7 ± 1.1^{C} | $9.1 \pm 2.5^{\text{C}}$ | 3.1 ± 0.1^{A} |

Table 4.4 Tensile properties of PLLA, PLLA-A-MOF and PLLA-S-MOF

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

Table 4.5 Tensile strength and elongation at break of PLLA, PLLA-TMA composites

| Material | Tensile Strength (MPa) | Elongation at break (%) |
|---------------|-------------------------|----------------------------|
| PLLA | $66.3\pm0.4^{\text{A}}$ | $3.8 \pm 0.6^{\text{A}}$ |
| PLLA-1 % TMA | 59.8 ± 0.5^B | 5.8 ± 1.1^B |
| PLLA-2.5% TMA | $55.9\pm0.4^{\hbox{C}}$ | 5.5 ± 0.8^B |
| PLLA-5% TMA | 52.2 ± 0.9^{D} | $6.5 \pm 1.0^{\mathrm{B}}$ |

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

4.3.5 Gel Permeation Chromatography (GPC)

The M_w , M_n , and polydispersity index (PDI= M_w/M_n) of the PLLA resin, extruded PLLA, PLLA-A-MOF and PLLA-S-MOF are shown in Table 6. The M_w of PLLA resin, extruded PLLA, PLLA-A-MOF, and PLLA-S-MOF were 110, 105, 98.6, and 83.5 kDa, respectively. The 6 % drop in M_w of PLLA-A-MOF as compared to extruded PLLA can be associated with oxidative degradation. However, this M_w reduction cannot contribute to 470% improvement in the elongation. [44]. Hydrolytic degradation might be partially responsible for degradation of PLLA-A-MOF because of the minor water adsorption by the MOF before feeding into the extruder. The M_w of PLLA-S-MOF dropped by around 21% as compared to extruded PLLA. This can be ascribed to oxidative degradation plus hydrolytic degradation due to the release of the moisture from the MOF during extrusion processing [45].

| | PLLA resin | PLLA | PLLA-A-MOF | PLLA-S-MOF |
|-----------------------------|-------------------------|--------------------|--------------------|-------------------------|
| M _{n,} Kda | $83.8\pm7.8^{\hbox{A}}$ | $76.7\pm0.4^{A,B}$ | $67.6\pm4.5^{B,C}$ | 55.6 ± 4.3^{C} |
| M _W , <i>Kda</i> | 110.8 ± 3.5^A | 105.0 ± 0.2^{A} | 98.6 ± 3.2^B | $83.5\pm2.0^{\text{C}}$ |
| PDI | 1.3 ± 0.1^{A} | 1.4 ± 0.0^{A} | $1.5\pm0.1^{A,B}$ | 1.5 ± 0.1^{B} |

Table 4.6 Molecular weight of PLLA, PLLA-A-MOF and PLLA-S-MOF

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

4.3.6. Carbon dioxide (CO₂) and Oxygen (O₂) Permeability

The selective permeability of a polymer or membrane is important for industrial applications such as membranes, gas separation, packaging etc. Table 7 shows the CO₂ and O₂ permeability coefficients of the PLLA, PLLA-A-MOF and PLLA-S-MOF. Similar CO₂ and O₂ permeability coefficients have been reported for PLA films [46]. Although there was no statistically significant difference in the CO₂ and O₂ permeability coefficient among PLLA, PLLA-A-MOF and PLLA-S-MOF, Figure 4.8 shows that the CO₂ permeability coefficients of PLLA-S-MOF have high deviation from the average values as compared to PLLA and PLLA-A-MOF. The low standard deviation in the PLLA-A-MOF indicates good interfacial adhesion in the PLLA and activated metal organic framework as supported by Fig 4.9. High standard deviation values of PLLA-S-MOF could be ascribed to the presence of voids at the interphase of PLLA and saturated MOF as observed in the SEM image (Fig 4.10 a) producing larger variations in the barrier properties of the end films. Figure 4.10 b shows a collapsed metal organic framework crystal, the crystal structure may have collapsed during the extrusion processing.



Figure 4.8: Permeability coefficients of PLLA, PLLA-A-MOF and PLLA-S-MOF

| | Permeability Coefficient x 10^{-18} (kg.m.m ⁻² .s ⁻¹ .Pa ⁻¹) | | |
|------------|--|---------------------------|--|
| | CO ₂ | O ₂ | |
| PLLA | 45.5 ± 2.72^{A} | $6.00\pm0.400^{\text{A}}$ | |
| PLLA-A-MOF | $49.9\pm4.08^{\text{A}}$ | $6.59\pm0.843^{\hbox{A}}$ | |
| PLLA-S-MOF | $65.0\pm2.11^{\text{A}}$ | $6.07 \pm 0.7.53^{A}$ | |

Table 4.7 CO_2 and O_2 permeability coefficients of PLLA, PLLA-A-MOF and PLLA-S-MOF

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$



Figure 4.9: SEM image of PLA-A-MOF fractured surface at 12 kV and 39 mm working distance.



Figure 4.10 a: SEM image of PLLA-S-MOF fractured surface acquired at 12 kV and 47 mm working distance.



Figure 4.10 b: SEM image of PLLA-S-MOF XRD disc surface acquired at 12 kV and 39 mm working distance.

4.4. Conclusions

The presence of moisture in the Cu₃BTC₂ MOF at elevated temperatures during melt compounding processes can significantly contribute to the degradation of the MOF crystal structure. In addition, the adsorbed moisture in the MOF particles may also accelerate the degradation of the PLLA matrix as observed in GPC studies. As demonstrated in the tensile studies incorporating Cu₃BTC₂ MOF improves the flexibility and tensile properties of PLLA-MOF matrices. Improvement in toughness and SEM images of PLLA-A-MOF indicated good interfacial interactions between activated MOF and PLLA. The MOF particles have a tendency to hinder the crystallization of the polymeric matrix. REFERENCES

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Chapter 5: Toughening of poly(L-lactic acid) with $Cu_3(BTC)_2$ metal organic frameworks crystals

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Poly(L-lactic acid) (PLLA) and metal organic framework (MOF) composites were prepared by melt extrusion of PLLA with 5, 10 and 20% w/w of activated Cu₃(BTC)₂ MOF. The morphology and stability of injection-molded samples were evaluated using thermogravimetric analysis, differential scanning calorimetry (DSC), gel permeation chromatography, X-ray diffraction, and scanning electron microscopy (SEM). The composites showed improved toughness during the tensile tests as compared to the neat PLLA matrix. The toughness mechanism of the composites was studied using SEM and rheological studies. SEM images indicated that cavitation induced by debonding at the interface of PLLA and MOF particles during the uniaxial stress were primarily responsible for the improved toughness of the composites. The SEM images of the composites, the solid like plateau observed in the PLLA composites during the parallel plate rheology at low frequency, and the decrease in the cold crystallization enthalpy during the DSC studies indicated good interactions between the PLLA chains and MOF in the composites. The developed composites have potential for various applications, which includes gas separation, energy and active packaging.

5.1 Introduction

High petroleum prices, corporate environmental awareness and favorable legislation have provided an increased demand for bio-based and biodegradable polymers. Poly(lactic acid), PLA, the main commercially available bio-based and compostable polyester produced by the monomeric synthesis of L-lactic acid derived from renewable resources such as corn, cassava, or sugar beets has successfully gained market acceptance for consumer goods applications [1, 2]. PLA has similar mechanical, thermal and barrier properties to poly(styrene) and poly(ethylene terephathalate). It has high perm-selectivity to gases like (CO_2/CH_4) [3, 4] so it has potential to be used for gas separation. However, the brittleness of PLA along with low heat deflection temperature and poor barrier properties hinders its wide market applications [5-7].

In general, fillers such as talc, carbon black and/or zeolites are added to a polymeric matrix to reduce the cost or to achieve desired properties like specific perm-selectivity. Mixed matrix membranes (MMMs), which traditionally consist of zeolite, carbon molecular sieves or other porous particles embedded in a polymeric matrix, are increasingly being used for improving mechanical properties, thermal properties and perm-selectivity of polymers [8-10]. Although MMMs prepared from inorganic materials like zeolites have been widely researched in the last few decades, the poor compatibility between the inorganic fillers and organic polymeric matrix can lead to sub-micron size holes in the MMMs [11-12]. Mahajan et al [11] studied MatrimidTM, a thermoplastic polyimide, with 20% zeolite 4A; they grafted the polyimide chains on the zeolite using a silane-coupling agent to improve compatibility between the zeolite 4A and MatrimidTM.

Metal organic frameworks (MOFs) are a class of porous crystalline compounds manufactured from metal ions (Cu⁺, Cu²⁺, Ag⁺, Zn²⁺, Co²⁺, K⁺, etc.) bridged together by organic ligands forming multi-dimensional structures. MOFs offer a promising alternative to zeolites and other molecular sieves in the production of MMMs since they have high surface area, selective sorption, gas separation potential and storage capacity. However, high cost and poor mechanical properties of the MOF reduces possibility of commercial applications of these compounds. Incorporating MOFs in polymers is one of various solutions to contain the cost of membranes and achieve the desired mechanical properties. The hybrid inorganic-organic composition of the MOF compounds may offer better compatibility with organic polymeric materials as compared to zeolites and other inorganic molecular sieves. Various researchers have synthesized MMMs using different MOFs and polymers to improve the permeability and selectivity of the matrix [12-15]. Ploegmakers et al [13] studied polyimide-copper benzene 1,3,5 tricarboxylate MOF MMMs for ethylene and ethane separation. They observed that 20% addition of Cu₃(BTC)₂ MOF in the polyimide increased the selectivity to ethylene/ethane of polyimide from 4.1 to 7.1. Scanning electronic microscopy images suggested good compatibility between polyimide and Cu₃(BTC)₂, and the glass transition temperature (T_{ϱ}) of the polyimide decreased from 345 to 329 ^oC with the addition of 20% Cu₃(BTC)₂. Elangovan et al [16] reported that PLLA and Cu₃(BTC)₂ MOF were compatible as determined by contact angle measurement offering improved composite characteristics like mechanical properties and selective barrier properties as compared to PLLA.

We have previously observed that strong polymer filler interactions played an important role in improving toughness of PLA-MOF composites [17]. Rheological studies can be helpful in understanding the complex microscopic interaction of polymeric chains with filler particles, which ultimately affects the macroscopic properties of the composites. Thus, the main purpose of this work was to understand the effect of the Cu₃(BTC)₂ MOF on the toughness, viscoelastic properties, morphology and stability of the PLLA composites.

5.2 Methodology

5.2.1 Materials

Poly(L-lactic acid) (PLLA) resin grade 4043 D, 98% L-lactide, with weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) of 111 kDa, 84 kDa and 1.3; respectively, was provided by NatureWorks LLC (Blair, NE, USA). BasoliteTM C300 MOF [(Cu₃(BTC)₂] with surface area ranging from 1500-2100 m².g⁻¹ and particle size ranging from 5 to 30 µm was purchased from Sigma Aldrich (St Louis, MO, USA).

5.2.2 Sample preparation

PLLA resin was dried at 80°C for 4 h and and BasoliteTM C 300 MOF [(Cu₃(BTC)₂] was activated at 200°C for 24 h using a vacuum oven at 0.1 MPa. PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF composite samples were processed using a vertical co-rotating twin-screw micro-compounder (DSM Research, Geleen, The
Netherlands) attached to an injection molder. The extruder has 150 mm screw long screws with L/D ratio of 18. The volume of the barrel is ~15 cm³. The material was processed at 190° C using 5 min cycle time at ~1 MPa (140 psi) injection pressure. The transfer cylinder and mold temperatures were set at 195 and 65°C, respectively. Dog bone tensile bars, flexural samples, and X-ray diffraction (XRD) discs of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF composites were prepared and stored in a desiccator at room temperature (~23°C) until further testing.

5.2.3 Characterization

5.2.3.1 Tensile test

Tensile properties were evaluated according to ASTM D638-10 using a Universal Tensile Machine model UTS SFM 20 from United Calibration Corporation, (Huntington Beach, CA, USA). The machine was equipped with a laser extensometer. Injection molded dogbone samples with a gauge length of 25.4 mm were stored at room temperature in a dessicator over desiccant for at least 40 h prior to testing. The samples were then tested at room temperature (~23^oC) using a 453 kg load cell at 0.023 kg of preload. PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF were tested at a crosshead speed of 50.8 mm.min⁻¹ (2 in.min⁻¹).

5.2.3.2 Rheology

Dynamic frequency sweep tests of PLLA and PLLA composites were performed using AR 2000 advanced rheometer from TA-Instruments (New Castle, DE, USA) at 175^oC

using 25 mm diameter parallel plates with a gap of 1100 μ m and frequency ranging from 0.01 to 100 rad.sec⁻¹. The strain used for the frequency sweep tests was selected as 2%, which is in the linear viscoelastic range of the material as determined by strain sweep.

5.2.3.3 X-Ray diffraction (XRD)

X-ray diffraction spectroscopy was performed on XRD discs of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF stored at 23^oC using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmgH, Karlsruhe, Germany) at 40kV, 40mA (1,600W) using Cu K α radiation ($\lambda = 1.5418$ Å). The studies were conducted using a 1.2 mm primary beam slit and 2.0 mm detector slit. The X-ray scans were carried out at speed of 0.02 degrees per second. Data was collected in triplicates.

5.2.3.4 Differential scanning calorimetry (DSC)

A DSC Q100 (TA instruments) was used to perform DSC analysis using heat/cool/heat cycles from 0 to 180° C at a rate of 10° C.min⁻¹. The melting temperature (T_m) and the associated heat enthalpy (Δ H_m) were calculated from the first heating cycle. The glass transition (T_g) temperature, cold crystallization onset (T_{co}), cold crystallization peak (T_{cc}) and enthalpy of cold crystallization (Δ H_c) were calculated from the second heating cycle to eliminate any thermal history, which may have been introduced during processing or storage. The samples were run in triplicates.

Consequently, the percent crystallinity of the samples was estimated using equation (1):

$$X_{c}(\%) = \frac{\Delta H_{m} - \Delta H_{c}}{\Delta H_{m}^{c}(1-x)} \times 100$$
⁽³⁾

where ΔH_m is enthalpy of fusion; ΔH_c is the enthalpy of cold crystallization; ΔH_m^c is enthalpy of fusion of pure crystalline PLA; $\Delta H_m^c = 93.1$ J/g [18]; and x is the mass fraction of the MOF in the MMM.

5.2.3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis of Cu₃(BTC)₂ MOF, PLLA, PLLA-5% MOF, PLA-10% MOF and PLA-20% MOF was performed using a TGA 2950 (TA-Instruments, New Castle, DE, USA) under nitrogen flow of 100 ml.min⁻¹. Samples weighing between 5 and 10 mg were heated at a rate of 10^oC.min⁻¹ from 25 to 700^oC. The data was analyzed using Universal Analysis software version 2000 (TA Instruments, New Castle, DE, USA). The TGA samples were run in triplicate.

5.2.3.6 Weight average molecular weight

To study the effect of processing conditions and MOF content on the stability of the PLLA, gel permeation chromatography (GPC) analysis was performed on the PLLA resin, extruded PLLA and PLLA-MOF composites using a GPC by Waters Inc. (Milford, MA, USA). Calibration was done using polystyrene standard materials with a molecular weight ranging from 2.9 x 10³ to 3.64 x 10⁶ Da using a third order polynomial equation. The analyses were performed at a flow rate of 1 mL.min⁻¹ and runtime of 45 min at 35°C using the Mark-Houwink corrected constant K = 0.000174 (mL·g⁻¹) and a = 0.736 for

dilute PLLA solution in tetrahydrofuran (THF)[19]. The instrument was equipped with a Waters 1515 isocratic pump, Waters 717 autosampler, a series of Waters Styragel Columns (HR4, HR3 and HR2) and Waters 2414 refractive index. Approximately 20 mg of specimen were dissolved in 10 mL of HPLC grade THF with 99.99% purity (Pharmco-Aaper, Brookfield, CT, USA). The solution was then filtered using a 0.45 µm filter.

5.2.3.7 Scanning electron microscopy (SEM)

To understand the morphology of the composites, gold coated samples sputtered using an Emscope SC 500 (Emscope Laboratories Ltd., Ashford, UK) were analyzed using a JEOL JSM 6610 LV (JEOL, Japan) scanning electron microscope (SEM) at 12kV accelerating voltage. The microscope was equipped with a tungsten filament.

5.2.3.8 Data analysis

Tukey's HSD (Honestly Significant Differences) tests were performed to determine if the means were significantly different from each other at 95% confidence interval ($\alpha = 0.05$). The analyses were conducted using SAS 9.0 Software (SAS Institute Inc., Cary, NC, USA).

5.3. Results and discussion

5.3.1 Tensile test/Toughness

Craze formation is primarily responsible for the brittle failure of PLA under tensile stress. The low entanglement density of amorphous glassy PLA favors crazing over shear yielding leading to a brittle fracture [20-22]. The toughness of the PLA can be improved by various methodologies such as the addition of impact modifying rubber particles, inorganic particles, blending, plasticization, etc. [22-26]. In heterogeneous matrix the organic/inorganic particles or other fillers serve as a stress concentrators [27-30]. Good interfacial interactions between the particles and the matrix are a prerequisite to achieve better mechanical properties. Under uniaxial stress, the triaxial stress generated at the interface of the filler particles and the organic matrix can promote debonding and cavitation. Debonding at the interface releases the triaxial stress and cavitation triggered matrix-shearing can dissipate the energy leading to the plastic deformation and improved toughness of the composite materials. A schematic representation of the cavitation process is presented in Figure 5.1.



Figure 5.1: Toughening mechanism of PLLA-MOF composites adapted from references [28, 30]. Step I: polymer MOF composite, step II: debonding at the interface of the polymer-MOF interface under tensile stress, step III: plastic deformation.

| Material | Tensile Strength (MPa) | Elongation at break (%) | Modulus of Elasticity (GPa) | Toughness (MJ/m ³) |
|--------------|---------------------------|-----------------------------|-----------------------------|--------------------------------|
| PLLA | $76.9 \pm 1.5^{\text{A}}$ | 3.6 ± 1.5^{A} | 3.0 ± 0.3^{A} | $1.70 \pm 1.06 \\ ^{A}$ |
| PLLA-5% MOF | 58.9 ± 0.8^B | $16.9 \pm 3.2^{\mathrm{B}}$ | $3.0\pm0.2^{A,B}$ | $8.49 \pm 1.45 ^{B}$ |
| PLLA-10% MOF | $52.4 \pm 1.2^{\text{C}}$ | $9.8 \pm 3.9^{\text{C}}$ | $2.8\pm0.1^{A,B}$ | $4.33 \pm 1.86 ^{\text{C}}$ |
| PLLA-20% MOF | 44.5 ± 0.1^D | $5.4 \pm 1.4^{A,C}$ | 2.6 ± 0.2^B | $1.86\pm0.51^{A,C}$ |

Table 5.1 Tensile properties of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

Stress strain graphs of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF composites can be observed in Figure 5.2. Brittle fracture was observed for the PLLA matrix without any plastic deformation. However, PLLA-MOF composites showed considerable plastic deformation especially for PLLA-5% MOF composites. Tensile force generated stress concentration at the interface of the matrix and the Cu₃(BTC)₂ MOF led to debonding initiated cavitation process at the interface of MOF particles and PLLA matrix as observed in SEM micrographs represented in Figure 5.3 b to d [29-31]. The stress generated by the tensile force at room temperature was diffused around the voids, generating local plastic deformation followed by strain softening. The decrease in the yield stress of the composites can be ascribed to the dilative stress component, which decreases the yield stress or the onset of the plastic deformation [32, 33]. The yield stress decreased with the increase in the MOF concentration from 5 to 20% due to increased dilatation with increased MOF concentration under tensile stress [33-35]. Parson et al [36] also observed increased dilatation with increase in CaCO₃ concentration from 10 to 20% in an HDPE matrix. Wu et al [37] studied toughening of polymers using rubber particles. The authors concluded that interparticle distance (matrix ligament thickness) is a crucial factor for the toughening effect due to cavitation. This effect was primarily due to yielding of the ligament. We observed decrease in the elongation of the composites with increase in the concentration from 5 to 20 %. The matrix ligaments present between the cavities are primarily responsible for the increased toughness. The increase in the concentration of the MOF particles decreased the distance between the cavities, which may have worked as a fracture initiating flaw / cluster

constraining the plastic deformation [35]. The bigger size cavities are easily visible in microscopic images of PLLA-20% MOF composition in Figure 5.3d.



Figure 5.2: Stress-strain graph of PLLA and PLLA MOF composites

Several researchers have studied surface modified or coated inorganic particles [24, 28, 31]. Meng et al [31] fabricated PLA composites with nano-titania particles and nano-titania particles coated with polycaprolactone (PCL) in various concentrations ranging up to 40 percent. The authors reported significant improvement in the toughness of the PCL coated nano-titania composites due to debonding at the interface and cavitation. Improved toughness was also attributed to the even distribution of stress around the interface of the matrix and uniformly dispersed fillers in the heterogeneous systems. The maximum strain at break of 64.7% was achieved at 26.5% wt. percent loading of coated TiO₂. On the other hand, in PLA uncoated TiO₂ composites, the TiO₂ particles agglomerated, leading to insignificant improvement in the mechanical properties. Zuiderduin et al [28] studied the effect of CaCO₃ and steric acid modified CaCO₃ particles on the toughening of polypropylene. Steric acid modified CaCO₃ particles dispersed well and provided good mechanical properties, while partial agglomeration was observed in CaCO₃ particle especially at higher concentration, which led to brittle transition. Above 40 wt % CaCO₃ particles, brittle failure was observed due to agglomeration. Glassy thermoplastics undergo plastic deformation in pure shear [38]. In the plastic deformation region, the decrease in the tensile strength with the increase in the strain could be related to the increase in the shear flow with the increase in the void size.



Figure 5.3: Tensile fractured cross section of a) PLLA, b) PLLA-5% MOF c) PLLA-10% MOF, d) PLLA-20% MOF

5.3.2 Rheological studies

The storage modulus (G'), loss modulus (G''), and tan δ (G''/G') of PLLA, PLLA-5% MOF, PLLA-10% MOF, and PLLA-20% MOF as a function of oscillatory frequency are represented in Figure 5.4 a, b and c, respectively. The storage modulus of PLLA follows typical entangled polydisperse melt. A secondary plateau or terminal shoulder was

observed in the G' of the PLLA-MOF composites at low frequency. This solid like behavior can be ascribed to the three dimensional network formation [21, 40] caused by bridging of the strong polymeric chains between the MOF particles due to strong PLLA-Cu₃BTC₂ MOF interactions [17]. These topological restraints may have contributed towards the immobilization of the polymeric chains in the PLLA-MOF composites, limiting their ability to relax at low frequency. This observation was also supported by DSC studies discussed later in this chapter. At high frequency the polymeric chains were able to overcome these restraints as represented in Figure 5.5 [40].

Tan delta (G"/G) of PLLA and PLLA composites as a function of frequency sweep is represented in Figure 5.4c. The tan δ showed a decreasing trend with increasing frequency in the case of PLLA. However, mild peaks were observed for the PLLA-MOF composites around the frequency of 0.5 rad.s⁻¹.

Figure 5.4d represents the complex viscosity (η^*) of the PLLA, PLLA-5% MOF, PLLA-10 % MOF and PLLA-20 % MOF composites. The decrease in complex viscosity of the composites as compared to PLLA may be attributed to the free volume change and the decrease in entanglement. Similar observations were made by other researchers during the fabrication of composites with modified inorganic particles [41, 42]. Luo *et al* [41] studied composites of PLA and TiO₂ functionalized with lactic acid. They observed decrease in the complex viscosity with the addition of the functionalized TiO₂. The authors attributed the decrease in the complex viscosity to the decrease in entanglement of linear polymeric chains. Lin *et al* [42] observed a 40% decrease in the complex viscosity of PLA-2.5% hyperbranched polyester amide blend as compared to PLA, further decrease in the complex viscosity was observed with increasing hyperbranched polyester amide content up to 15 percent, which was attributed to the increase in the free volume and decrease in entanglement.



Figure 5.4: (a) Storage Modulus (G') of PLLA and PLLA MOF composites as a function of oscillatory frequency



Figure 5.4: (b) Loss Modulus (G") of PLLA and PLLA MOF composites as a function of oscillatory frequency



Figure 5.4: (c) Tan delta curves of PLLA and PLLA-MOF composites



Figure 5.4: (d) Complex viscosity of PLLA and PLLA MOF composites



Figure 5.4: (e) Cole-Cole plot of PLLA and PLLA MOF composites



Figure 5.4: (f) Van Gurp Palmen plot of PLLA and PLLA MOF composites



а



Figure 5.5: Schematic representation of the configuration of polylactide MOF composites a. at rest b. low shear rates c. at high shear rates adapted from reference [40]

A Cole-Cole Plot of the PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF are represented in Figure 5.4 e. G' and G" represents the elastic and viscous parts of the complex viscoelastic fluids. At low frequencies, the viscoelastic properties are very sensitive and indicative of the underlying molecular architecture of the structure. At 175°C PLLA primarily demonstrated viscous behavior than the elastic behavior. However, with the addition of MOF particles the elastic component of the PLLA increased at low frequency with increasing MOF content due to favorable interactions between PLLA matrix and the MOF crystals.

The van Gurp-Palmen plot of PLLA, PLLA-5% MOF, PLA-10% MOF and PLLA-20% MOF composites is represented in Figure 5.4 f. The high phase angle of the composites at low frequency indicates that the composites were free of percolation. PLLA curve approaching phase angle close to 90° also indicates primarily viscous behavior. The addition of Cu₃BTC₂ MOF crystals provides minor improvement in elastic behavior, which increases with the increase in the MOF concentration from 5 to 20%.

5.3.3 X-Ray Diffraction (XRD)

Diffraction patterns of PLLA, PLLA-5% MOF, PLLA-10 % MOF and PLLA-20% MOF composites are represented in Figure 5.6. The wide PLLA hump suggests amorphous nature of injection molded PLLA samples. In case of composites we can see the crystalline peaks of metal organic framework at the top of amorphous PLLA background. During extrusion process PLLA composites retained their face centered cubic (FCC) crystal structure. In our previous study [17], we observed that the adsorption of water by MOF particles before extrusion were detrimental to the final properties of the composites.



Figure 5.6: X-ray diffraction patterns of PLLA-MOF composites

Detailed analysis of the effect of heat and moisture on the $Cu_3(BTC)_2$ MOF crystal structure during extrusion with PLLA was presented in chapter 4.

5.3.4 Differential Scanning Calorimetry (DSC)

The average crystallization onset temperatures for PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF observed in the DSC studies were 103.8, 113.8 115.1 and 115.2 $^{\circ}$ C, respectively. The shift in the onset of the cold crystallization temperature of the PLLA-MOF composites to higher temperatures with the increase in MOF content can be attributed to the good interactions between the polymeric chains and MOF crystals, which hindered the mobility of the chains. Such interactions between the polymeric chains and MOF crystals support the finding of the increase in the shear storage modulus in the rheology studies in the terminal region as observed in Figure 5.4 a. Table 5.2 represents the detailed DSC analysis of PLLA and its composites. We can also observe that the cold crystallization enthalpy decreased with the addition of the MOF. The decreased mobility of the polymeric chains can be ascribed to strong interactions between the Cu₃BTC₂ MOF crystals and PLLA. There was no significant change in the *T_g* of the composites as compared to PLLA, which indicates that the addition of the MOF crystals does not provide any flexibility to the chain.

5.3.5 Thermogravimetric analysis (TGA)

The TGA thermographs for activated MOF, PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF are represented in Figure 5.7. The activated MOF has 5% w/w moisture content, mostly adsorbed during the loading of sample into the machine. The

organic component of the framework, benzene tricarboxylate, starts degrading at around 325°C. The average onset of thermal degradation of PLLA, PLLA-5% activated MOF and PLLA-10% activated MOF and PLLA-20% MOF is at 324.5, 322.5, 320.5 and 315.8°C, respectively. The increase in the concentration of MOF decreases the onset of thermal degradation of the composites. We observed T_d for PLLA around 385°C, whereas the PLLA–MOF composites have T_d around 500°C. This could be ascribed to the conversion of the remaining benzene tricarboxylate groups present in the MOF to CO and CO2, as observed by Huang et al in their ReaxFF reactive molecular dynamics (RMD) simulation studies [45]. They observed that Cu₃(BTC)₂ MOF has good thermal stability up to 300°C, at higher temperatures the structural collapse of MOF has been simulated [45]. The difference in the final plateau for the PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF is mainly attributed to the difference in the metal content in the composites.



Figure 5.7: Themogravimetric analysis of PLLA, Cu₃(BTC)₂ MOF and PLLA- MOF composites.

| Sample | $T_{g}(^{0}C)$ | Cold Crystallization | | | Melting | | |
|--------------|-------------------------|--------------------------|----------------------------|-------------------------------|--------------------------|-----------------------|--------------------|
| | | $T_{co}(^{o}C)$ | T_{cc} (^o C) | Δ H _c (J/g) | $T_{mo}(^{o}C)$ | T_m (°C) | $\Delta H_m (J/g)$ |
| PLLA | 60.8 ± 0.1^{A} | $103.8\pm0.2^{\text{A}}$ | $119.1\pm0.1^{\text{A}}$ | 19.6 ± 0.9^{A} | $143.3\pm0.1^{\text{A}}$ | $147.9\pm0.2^{\rm A}$ | 21.9 ± 0.5^{A} |
| PLLA-5% MOF | 60.9 ± 0.0^{A} | 113.8 ± 0.2^{B} | 129.9 ± 0.4^B | 3.6 ± 0.1^B | 145.5 ± 0.1^B | 150.8 ± 0.1^{B} | 6.9 ± 0.3^B |
| PLLA-10% MOF | 62.8 ± 0.0^B | $115.1\pm1.1^{\text{B}}$ | $131.2 \pm 1.2^{\text{B}}$ | $5.6 \pm 1.4^{\text{B,C}}$ | 145.8 ± 0.8^B | 152.9 ± 1.0^{B} | 11.0 ± 0.7^{C} |
| PLLA-20% MOF | $62.2\pm0.3^{\hbox{C}}$ | 115.2 ± 0.4^B | 129.7 ± 0.1^B | 6.7 ± 0.3^D | 145.4 ± 0.5^B | $152.2\pm1.3^{\rm B}$ | 15.0 ± 2.5^D |

Table 5.2 Detailed DSC analysis information of PLA and its composites

Note: Values in the same column with same capital superscript letters are not statistically significantly different at α =0.05

| Table 5.3 Molecular weight of PLLA, PLLA-5%-MOF, PLLA-10% MOF and PLLA-20%-MOF | | | | | | |
|--|---------------------------|---------------------|----------------------------|------------------------------|--|--|
| | PLLA control | PLLA-5% MOF | PLLA-10% MOF | PLLA-20% MOF | | |
| M _{n,} kDa | $71.9 \pm 1.2^{\text{A}}$ | 72.8 ± 3.1^A | 73.4 ± 0.6^A | $71.7 \pm 3.8^{\text{A}}$ | | |
| M _W , kDa | 103.0 ± 0.7^{A} | 102.7 ± 1.2^{A} | $102.2 \pm 0.2^{\text{A}}$ | $107.1 \pm 1.7^{\mathbf{B}}$ | | |
| PDI | $1.4\pm0.0^{A,\ B}$ | $1.4\pm0.0^{A,\ B}$ | 1.4 ± 0.0^{B} | 1.5 ± 0.1^{A} | | |

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

5.3.6 Gel Permeation Chromatography (GPC)

GPC analysis was performed on PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF. Table 5.3 shows the M_w , M_n , and PDI data of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF. No statistically significant difference in the PLLA and PLLA MOF composites were found, indicating that the presence of MOF does not degrade PLA.

5.4 Conclusions

The PLLA-hybrid MOF composites were prepared by a melt extrusion process. The uniformly dispersed MOF particles in the polymer matrix increased the toughness of the PLLA matrix by a debonding initiated cavitation process. Large plastic deformation was observed for PLLA-5 wt. % of Cu₃(BTC)₂ MOF. Favorable interfacial interactions necessary between Cu₃(BTC)₂ MOF and PLLA for improved toughening were further endorsed by rheological, microscopy and thermal analysis (DSC). Strong interactions between MOF particles and PLLA restrict the mobility of the polymeric chains. The MOF crystals retained their structure during extrusion processing, as observed in the XRD studies. Gel permeation chromatography indicated that processing of PLLA with MOF did not have any significant effect on the molecular weight of the polymer in the final MMMs compositions.

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Chapter 6. Mass transfer properties of PLLA- Cu₃(BTC)₂ MOF

Chapter 6. Mass transfer properties of PLLA- Cu₃(BTC)₂ MOF

6.1 Introduction

Poly(lactic acid) (PLA) has increased its market presence due to competitive resin prices and biodegradability especially in the packaging and the textile industries. Permeability of various gases and water molecules plays an important role in the selection of packaging materials. PLA is a poor barrier material for CO₂ and water vapor as compared to traditional petroleum based polymers like poly(vinyl chloride), poly(ethylene terephthalate) and poly(propylene) [1-3]. Thermal and mechanical properties are significantly impacted by isomeric composition of the PLA. However, it has been reported that the stereo isomeric content of PLA (i.e., PLLA or PDLA) does not significantly impact its water permeability [4, 5]. Tsuji and Tsuruno reported that PLLA/PDLA blend films with only stereocomplex crystallites showed lower water permeability coefficients than PLLA or PDLA polymers [6].

Metal organic frameworks (MOFs), a class of micro-porous materials, have attracted a lot of attention due to their high sorption properties, catalysis and high surface area [7-9]. MOFs can host various molecules in their pores, depending on their interaction. The host-guest interactions between MOFs and gaseous molecules, water vapor or organic molecules have been credited to: (i) the available metal sites which interact/co-ordinate with the gases or water molecules and (ii) organic linkers which can physisorb gases due to secondary forces [10-12]. Careful selection of a MOF for a particular application is important to obtain the desired results. The ability of a particular MOF to host a particular species of gas strongly depends on the type of the functional groups attached to the organic linkers or metal species. In this research, copper benzene 1,3,5 tricarboxylate $[Cu_3(BTC)_2]$ MOF was selected due to its suitable interactions with CO_2 [13].

Optimum presence of CO_2 in the head space of a package can inhibit the growth of microorganisms. However, a high concentration of CO2 in packaged fresh produce is always expected due to their respiration process, in which fresh produce consumes oxygen and releases CO₂. A high concentration of CO₂ can encourage the fermentation process generating compounds such as acetaldehyde, ethanol, etc, which can decrease the acceptability of the product [14-15]. Therefore, it is important to maintain an optimum level of CO2 in the headspace by avoiding its accumulation. Membranes with high permeability to CO₂ can help to prolong the shelf life of the fresh produce. The water vapor transmission rate (WVTR) of a packaging material is crucial to maintain the shelf life of various food and pharmaceutical products [16-17]. The shelf life of dry products like crackers and cereal is compromised if the moisture content in the package crosses the critical moisture content level. On the other hand, in certain products like fresh produce, it is crucial to maintain a high water activity to maintain the shelf life. Oxidative changes in the food can produce biochemical changes leading to deterioration of food product such as food chips, coffee, etc. compromising the sensory quality of the product [18-19].

Trans-2-hexenal is an aroma compound present in various fruits [20-22]. The retention of trans-2-hexenal provides an impression of fresh odor of the fruits. Corbo *et al* [23] studied the shelf life of sliced apples using hexanal and trans-2-hexenal. The

inclusion of these aromatic compounds in the packaging atmosphere considerably depressed yeast growth. Joo *et al* [24] reported production of antimicrobial film using trans-2-hexenal encapsulated in cyclodextrin, and the reduction of *Alternaria solani* growth due to the release of around 0.08 μ L trans-2-hexenal/L air.

It has been demonstrated that presence of mesoporous or microporous fillers such as zeolites [25-26], carbon molecular sieves [27] and metal organic frameworks (MOFs) [28-29] can improve the gas permeability and separation properties of a polymeric matrix. MOFs have been primarily in focus for over a decade for their ease of synthesis, high surface area, gas adsorption and selectivity [30]. The hybrid organic-inorganic compositions of the MOFs make them good candidates for polymer matrix based MMMs, as such hybrid compounds can offer defect free MMMs and good thermal stability [31-33].

Cu₃(BTC)₂ MOF has been investigated for its affinity with CO₂ and H₂O [34-39]. Torrisi *et al* [34-35] reported that the aromatic organic linkers (benzene tri carboxylate) present in the Cu₃(BTC)₂ MOF can interact with CO₂ due to strong quadrupole-quadrupole interactions. They studied the van der Waals interactions between CO₂ and the aromatic structures present in the Cu₃(BTC)₂ MOF ligands. Two classes of functional group were selected for substitution on the benzene rings: (i) electrophilic halogen group such as C₆H2F₄, C₆H₅Cl, C₆H₅Br and (ii) nucleophilic methyl group such as C₆H₅CH₃, C₆H₄(CH₃)₂, etc. It was observed that the halogen substitution of the benzene rings destabilize the π -quadrupole interactions. The destabilization effect was
ascribed to the charge withdrawal effect of hydrogen substituted group. Methyl and polymethyl substitution on the benzene ring increased the CO₂ affinity.

Kusgen *et al* [36] characterized Cu₃(BTC)₂ MOF using water adsorption. They suggested that water adsorption follows two steps: (a). axial coordination of the water molecules to the polar hydrophilic copper sites, and (b). filling of non-polar hydrophobic sites due to organic linkers at higher pressure. Castillo *et al* [37], studying the interaction of various hydrocarbons, gaseous and water molecules using *Monte Carlo* molecular simulation, found that Cu₃(BTC)₂ MOF has strong affinity towards water molecules compared to other gaseous molecules in the following order $CO_2 > O_2 > N_2$. This indicates that during an application water molecules will compete with other gases for available sites. Supronowicz *et al* [38] recently calculated the adsorption energies of H₂O, CO₂, and O₂, among other gaseous molecules, using ab initio density functional theory. Adsorption enthalpies for H₂O, CO₂, O₂ calculated in this study were -53.8, -20.1 and -5.7 kJ/mol. These last three studies [36-38] indicate good van der Waals interactions of Cu₃(BTC)₂ MOF with water and CO₂ molecules.

The purpose of this study was to understand the effect of the presence of $Cu_3(BTC)_2$ MOF on the permeability and perm-selectivity of PLLA for packaging and other MMM industrial applications. The mass transfer properties of PLLA- $Cu_3(BTC)_2$ MOF based membranes to water (H₂O), carbon dioxide (CO₂), oxygen (O₂) and trans-2-

hexenal were evaluated by assessing the permeability to these compounds for PLLA-MOF mixed matrix membranes.

6.2. Methodology

6.2.1 Materials

Poly(L-lactic acid) (PLLA) grade 4043 D with 98% L-lactide content was provided by NatureWorks LLC (Minnetonka, MN, USA). PLLA resin has an average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) of 111 kDa, 84 kDa and 1.3, respectively. BasoliteTMC300 metal organic framework [Cu₃(BTC)₂] with surface area ranging from 1500-2100 m².g⁻¹ and particle size ranging from 5-30 µm was purchased from Sigma Aldrich (St Louis, MO, USA). Trans-2hexanal with at least 95% purity was supplied by SAFC, US.

6.2.2 Fabrication of membranes

PLLA resin was dried for 4 h at 80°C and BasoliteTM C 300 MOF was activated at 200° C for 24 h using vacuum oven. PLLA and PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF composite samples were processed using a vertical co-rotating twinscrew micro-compounder (DSM Research, Geleen, The Netherlands) attached with an injection molder. The extruder has 150 mm screw long screws with L/D ratio of 18. The volume of the barrel was approximately 15 cm³. The material was processed at 190°C using 5 min cycle time at ~1 MPa (140 psi) injection pressure. The transfer cylinder and mold temperatures were set at 195 and 65°C; respectively. XRD discs of PLLA, PLLA-

5% activated MOF, PLLA-10% activated MOF and PLLA-20% activated MOF composites were prepared and stored in a desiccator at room temperature (~23 °C).

The films used for the permeability studies were prepared using a PHI 30 ton compression molding machine (City of industry, CA, USA) with 12" x 12" plate size. The injection molded samples prepared using the twin screw DSM micro-compounding instrument were compressed at 170° C and ~1.0 MPa for 5 min.

6.2.3 Mass transfer properties

6.2.3.1 Carbon dioxide transmission rate (CO₂TR)

Carbon dioxide transmission rate (CO₂TR) of the PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF were measured as per ASTM F2476 05 using an Permatran[®] 4/41 (MOCON Inc., Minneapolis, MN, USA) at 23^oC and 0% RH using 100% CO₂ . N₂ was used as a carrier gas at flow rate of 50 sccm. The tests were performed using an exam time of 30 minutes. The transmission was measured using an aluminum mask with 3.14 cm^2 area. The average value of the last ten stable points in steady state was used to calculate the permeability values using equation 6.1. The data was analyzed for at least three samples.

gas permeability =
$$\frac{\text{transmission rate (kg/m2.s) x thickness)}}{\text{partial pressure (Pa)}}$$
 (6.1)

6.2.3.2 Water vapor transmission rate (WVTR)

The water vapor transmission rates of the PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF were measured according to ASTM F1249 using a Permatran[®] W3/31 (MOCON Inc., Minneapolis, MN, USA) at 23° C and 100% RH using N₂ gas as a carrier at flow rate of 100 sccm. The tests were performed using exam time of 30 minutes. The transmission was measured using aluminum masks with 3.14 cm² area permeability. The average value of last ten stable points was used to calculate the permeability values using equation 6.1. The data was analyzed for at least three samples.

6.2.3.3 Oxygen transmission rate (OTR)

The oxygen transmission rates of the PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF were measured as per ASTM D3985-05 using an Oxtran[®] 2/21 (MOCON Inc., Minneapolis, MN, USA) at 23° C and 0% RH using 100% as permeant and 98 % N₂/ 2% H₂ as carrier gas at flow rate of 20 sccm of the test gas and 10 sccm flow rate of carrier gas. The tests were performed using an exam time of 30 minutes. The transmission was measured using aluminum masks with 3.14 cm² area. The average value of the last ten stable points was used to calculate the permeability values using equation 6.1. The data was analyzed for at least three samples.

6.2.3.4 Aroma transmission rate

The aroma vapor transmission rate of trans-2-hexanal was measured using a modified ASTM E-96 cup method at 23 ± 0.1 °C, $50 \pm 2\%$ RH and partial pressure difference of 1436 Pa. The aroma vapor permeability coefficients of the PLLA and PLLA-20% MOF were calculated from the slope of the weight loss from the cup with respect to time using equation 6.2.

aroma permeability =
$$\frac{\text{slope (kg/s) x thickness (m)}}{\text{partial pressure difference (Pa) x area (m2)}}$$
 (6.2)

6.2.4 Data analysis

Tukey's HSD (Honestly Significant Differences) tests were performed to determine if the means were significantly different from each other at a 95% confidence interval ($\alpha = 0.05$). The analyses were conducted using SAS 9.0 Software (SAS Institute Inc., Cary, NC, USA).

6.3. Results and discussion

6.3.1 Carbon dioxide permeability coefficient

Carbon dioxide permeability coefficients of PLLA, PLLA-5% MOF, PLLA-10%MOF and PLLA-20% MOF are presented in Table 6.1. There were no statistically significant difference in the permeability coefficients of PLLA, PLLA-5% MOF and PLLA-10% MOF. However, with the addition of 20% $Cu_3(BTC)_2$ MOF in the PLLA matrix, we observed ~ 38% increase in the permeability coefficient as compared to neat PLLA. Favorable interaction energies between the $Cu_3(BTC)_2$ MOF and CO_2 might be responsible for the increased rate of transportation of the CO₂ through PLLA-Cu₃(BTC)₂ MOF [29, 37-38]. Basu *et al* [28] studied CO_2/CH_4 and CO_2/N_2 gas separations using polyimide- $Cu_3(BTC)_2$ MOF based MMMs. The authors reported an increase in the permeability and selectivity of membranes with increase in the filler loading due to the strong quadrupole moment of CO_2 and poor electrostatic interactions of N_2 and CH_4 molecules with the $Cu_3(BTC)_2$ MOF.

Table 6.1 CO₂ and O₂ permeability coefficients of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF

| | Permeability Coefficient x 10^{-18} (kg.m.m ⁻² .s ⁻¹ .Pa ⁻¹) | | Permselectivity |
|--------------|---|--------------------------------------|-----------------------|
| | CO ₂ | O ₂ | $\alpha_{\rm CO2/O2}$ |
| PLLA | $45.54\pm2.72^{\text{A}}$ | 6.00 ± 0.40^{A} | 7.59 |
| PLLA-5% MOF | $49.85\pm4.08^{\hbox{A}}$ | $6.59\pm0.84^{\hbox{A}}$ | 7.56 |
| PLLA-10% MOF | $42.89\pm3.13^{\text{A}}$ | $6.18\pm0.88^{\hbox{\scriptsize A}}$ | 6.94 |
| PLLA-20% MOF | 63.03 ± 1.86^B | $6.14\pm0.87^{\hbox{A}}$ | 10.26 |

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

6.3.2 Oxygen permeability coefficient

The oxygen permeability coefficient of PLLA, PLLA-5% MOF, PLLA-10%MOF and PLLA-20% MOF are presented in Table 6.1. There were no statistically significant differences in the permeability coefficients of PLLA and PLLA-Cu₃(BTC)₂ MOF based MMM, which can be ascribed to poor van der Waals interactions of O_2 with Cu₃(BTC)₂ [37].

The perm-selectivity of PLLA ($\alpha_{CO2/O2}$) improved from 7.6 to 10.3 with the addition of 20% MOF crystals. The increased perm-selectivity can be attributed to the favorable interactions between MOF crystals and CO₂ gas than O₂ gas.

6.3.3 Water vapor permeability coefficient

Water vapor permeability coefficients of PLLA, PLLA-5% MOF, PLLA-10% MOF and PLLA-20% MOF are presented in Table 6.2. The presence of MOF did not affect the permeability coefficients of PLLA. As permeability is a product of solubility and diffusivity, (equation 6.3), The relatively strong interactions (>40KJ/mol) [25, 26] of H₂O molecules with $Cu_3(BTC)_2$ MOF might have hindered the diffusivity of the water molecules resulting in unchanged permeability of the PLLA-MOF MMMs by increasing the water sorption in the PLLA-MOF membranes as indicated by Elangovan *et al* [40] and reducing the diffusion coefficient.

$$Permeability = Diffusion x Solubility$$
(6.3)

Table 6.2 Water vapor permeability coefficients of PLLA, PLLA-5% MOF, PLLA-10%MOF and PLLA-20% MOF

| | Permeability Coefficient x 10 ⁻¹⁴ (kg.m.m ⁻² .s ⁻¹ .Pa ⁻¹) | | |
|--------------|---|--|--|
| | H ₂ O | | |
| PLLA | $3.29\pm0.31^{-A,B}$ | | |
| PLLA-5% MOF | $3.72\pm0.16\stackrel{A}{}$ | | |
| PLLA-10% MOF | $3.13\pm0.09\ ^{\mathrm{B}}$ | | |
| PLLA-20% MOF | $3.28\pm0.23~^{\rm A}$ | | |

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

6.3.4 Trans-2-hexenal permeability coefficient

Trans-2-hexenal permeability coefficients of PLLA and PLLA-20% MOF are presented in Table 6.3. The permeability coefficient of the PLLA-20% MOF membranes increased by 60% as compared to the PLLA matrix. The coordination of trans-2-hexenal with the unsaturated copper atoms might have contributed to increased permeability of MMMs. To the best of author's knowledge, there is no published literature to date which discusses the interactions of trans-2-hexanal with Cu₃(BTC)₂ MOF, any other MOF or mixed matrix membranes.

| | Permeability Coefficient x 10 ⁻¹³ (kg.m.m ⁻² .s ⁻¹ .Pa ⁻¹) |
|--------------|---|
| | Tran-2-hexenal |
| PLLA | $2.92\pm0.16\overset{A}{}$ |
| PLLA-20% MOF | $4.70\pm0.24\ ^B$ |

Table 6.3 Tran-2-hexenal permeability coefficients of PLLA and PLLA-20% MOF

Note: Values in the same column with same capital superscript letters are not statistically significantly different at $\alpha = 0.05$

6.4 Conclusions

The mass transfer properties of PLLA- $Cu_3(BTC)_2$ MOF based membranes to water (H₂O), carbon dioxide (CO₂), oxygen (O₂) and tran-2-hexenal were evaluated. The CO₂ and trans-2-hexanal permeability coefficient of PLLA-20% MOF increased by around 38% and 60% respectively as compared to PLLA. However, there was no change in the O₂ and water vapor permeability coefficients of PLLA with the addition of MOF. The MMM permeability coefficient of various gases and organic molecules is strongly influenced by the kind of interactions between the microporous materials and permeants. The perm-selectivity of PLLA-20% MOF ($\alpha_{CO2/O2}$) improved from 7.6 to 10.3.

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Chapter 7 Conclusions and recommendation for future work

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7.1 Conclusions

This dissertation research work was divided into four parts: (a). synthesis and characterization of $Cu_3(BTC)_2$ metal organic framework (MOF), (b). effect of the processing parameters on the stability of $Cu_3(BTC)_2$ MOF crystals during fabrication of poly(L-lactic acid) (PLLA)- $Cu_3(BTC)_2$ MOF based mixed matrix membranes, (c). understanding the effect of MOF crystals on the toughening mechanism of PLLA , and (d). evaluation of mass transfer properties of PLLA)- $Cu_3(BTC)_2$ mixed matrix membranes.

7.1.1 Synthesis and characterization of Cu₃BTC₂ MOF

Cu₃(BTC)₂ MOF was synthesized using a microwave assisted synthesis process. The characterization of the Cu₃(BTC)₂ MOF was performed using X-ray diffraction studies, scanning electron microscopy, thermo-gravimetric analysis and BET surface area studies. A highly crystalline chemical structure was observed during X-ray diffraction, with average BET surface area of $1236 \pm 103 \text{ m}^2/\text{g}$. The MOF crystals had particle sizes ranging from 5-30 µm as observed from SEM. Thermo-gravimetric studies indicated that particles were generally stable up to 300° C.

7.1.2 Stability of Cu₃BTC₂ MOF crystals during fabrication of mixed matrix membranes.

Poly(L-lactic acid) was melt compounded with 5% of activated $Cu_3(BTC)_2$ MOF and 5% of water saturated $Cu_3(BTC)_2$ MOF. During melt compounding of $Cu_3(BTC)_2$ MOF with PLLA, the presence of moisture in the water saturated Cu_3BTC_2 MOF significantly contributed to the deterioration of the MOF crystal structure. The water released from the saturated MOF particles during extrusion contributed to the degradation of the PLLA matrix due to hydrolysis of PLLA as observed in GPC studies. The weight average molecular weight of PLLA-5% saturated MOF dropped to 83.5 kDa as compared to 110.8 kDa for PLLA resin. Cu₃BTC₂ MOF increased the toughness of PLLA-MOF. Improvement in toughness, increase in the CO₂ permeability coefficient, and SEM images of PLLA-5% saturated MOF indicated good interfacial interactions between activated MOF and PLLA. The activated MOF particles retained their structure and morphology. The presence of 5% activated MOF hindered the crystallization of PLLA due to strong interfacial interactions between PLLA and Cu₃BTC₂ MOF as observed in the SEM images.

7.1.3 Effect of MOF crystals on the toughness of PLLA

Large plastic deformation was observed for PLLA-5 wt. % of Cu₃BTC₂ MOF. The toughness of PLLA-5% activated MOF composites improved by approximately 500%. The uniformly dispersed MOF particles in the polymer matrix increased the toughness of PLLA matrix by debonding initiated cavitation process. The improvement in the toughness decreased with further increase in the MOF concentration from 5% to 20% due to decrease in the interparticle distance of MOF incorporated in the PLLA matrix. Rheological studies indicated the composites demonstrated solid like behavior due to strong interactions between PLLA and MOF, the elastic component of the PLLA matrix improved with the addition of the MOF crystals and the composites were free of percolation. Favorable interfacial interactions necessary between Cu₃(BTC)₂ MOF and PLLA for improved toughening were further endorsed by rheological, microscopy studies and thermal analysis (DSC studies). Strong interactions between MOF particles and PLLA restricted the mobility of the polymeric chains.

7.1.4 Mass transfer properties of PLLA

 CO_2 permeability of PLLA-20% wt. $Cu_3(BTC)_2$ MOF mixed matrix membranes increased from 45.54 to 63.03 kg.m.m⁻².s⁻¹.Pa⁻¹ as compared to neat PLLA. The permselectivity ($\alpha_{CO2/O2}$) of PLLA-20% MOF improved from 7.6 to 10.3, respectively. The permeability coefficient of tran-2-hexenal increased by 60% with the addition of 20% MOF. Permeability coefficients of various gases and organic molecules are strongly influenced by the kind of interactions between the microporous materials, matrix and permeants. These composites can be used for packaging application in which the CO_2 evolved over time or entrapped in the headspace can affect the quality and shelf life of the food product. The increased CO_2 permeability can be helpful for gas separation. For example, the calorific value of the methane produced in the biogas plant can be improved by removing CO_2 .

7.1.5 Overall conclusions

The brittle nature of PLLA has hindered its mass scale applications. This dissertation research work helped in better understanding the toughening mechanism of PLLA, PLLA-MOF interface and the effect of the MOF content on the functional properties of these composites. This work also helped in understanding the stability of the $Cu_3(BTC)_2$ MOF crystal structure during extrusion processing. Mass transfer properties indicated that the presence of Cu_3BTC_2 MOF improved tran-2-hexenal permeability and CO_2/O_2 perm-selectivity of PLLA-20% MOF composites.

7.2 Recommendations for future work

7.2.1 Chemical modification of metal organic framework

Depending on the chemistry of the functional groups present in a MOF the permeability and selectivity of the membranes is strongly influenced. Post synthesis modification of MOF is one of the possible routes which can help in further improving the mass transfer properties and perm-selectivity and high separation efficiency of membranes.

7.2.2 Modeling mass transfer properties

The work described in chapters 4 and 5 improved the scientific understanding of the morphology and interface of MOF and PLLA mixed matrix membranes. Chapter 6 helped in understanding the mass transfer properties of PLLA-MOF MMMs. However, the mechanism of mass transfer is still poorly understood. Thus, additional work in this area by evaluating the mass transfer properties of these membranes to other compounds and utilizing theoretical models to understand the mass transfer properties can further improve the scientific understanding of these MMMs.

7.2.3 Environmental impact

Metal organic frameworks consists of transition metal ions bridged together using organic linkers. The environmental impact of the use of these compounds has not been evaluated or understood as a packaging material. Due to the presence of metal ions, these microporous materials can have negative impacts on the environment. Further work is needed to study their impact if used for packaging applications. Comparative studies with other metal free microporous species such as microporous organic polymers (MOPs), MOFs synthesized using alkali metals can be conducted.

7.2.4 Shelf life studies

Further, work is needed to understand and determine if such composites can be utilized in real life packaging applications. Designing an actual package and running shelf life studies in the lab on relevant products can be helpful in evaluating and understanding the performance of these materials for real packaging applications.