DESIGN AND ENGINEERING OF POLY(LACTIDE) RESIN BASED BIOCOMPOSITES

By

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ABSTRACT

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Fiber reinforced composites are typically prepared using thermosetting polymeric resins derived from petroleum resources and involving hazardous chemicals. We present a vinyl-ester system utilizing a 100% renewably based polyester enabling the sequestration of carbon from the atmosphere into durable goods for decades. The biopolymer poly(*meso*-lactide) (PML) is synthesized using a strategy giving vinyl end groups. In place of potentially carcinogenic styrene which is predominantly used as a reactive diluent to reduce the thermoset viscosity, the new sustainable bioresin dissolved in methyl methacrylate (MMA), infused into various fibers, and cured to form the composite panels. Mechanical properties are excellent and comparable with less sustainable materials from fossil resources.

As homeowners adopt a lifestyle that is more responsive to environmental need, industry and academia are tasked with finding more sustainable solution for cast polymer products like countertops and sinks. Particulate fillers in the cast polymers are bound by either poly(methyl methacrylate)/methyl methacrylate (PMMA/MMA) or unsaturated polyester/styrene (UPR/Styrene) resin. For the first time ever, we have introduced biopolymer poly(lactide) (PLA) dissolved in MMA as a novel bioresin formulation which can be directly substituted for less sustainable PMMA/MMA and more carcinogenic UPR/Styrene counterparts. Mechanical properties of fabricated biorenewable solid surface and cultured marble composites are on par with commercially available products. This environmentally benign resin is also used to fabricate a prototype of a Drop-in-Bowl solid surface and preliminary calculations show a 24% reduction in greenhouse gas emissions (CO₂ equivalent) compared to PMMA/MMA acrylic resins available in the market.

Otherwise destined to landfills or incineration, recovery and recycling of composite materials not only improves the sustainability metrics but also opens the door to various end-of-life options. Recycling of sinks and countertops via solvolysis reduces the usage of new resources, prevents waste, and lowers the emission associated with their production and transportation. For the first time ever, Drop-in-Bowl solid surface sink was fabricated using fully recyclable resin PLA dissolved in MMA and is demonstrated that simple base solvolysis can be employed to recover the particulate filler material along with other end-of-life options including edible food ingredient, and superabsorbent polymer.

Chain transfer agents (CTAs) are conventionally used to regulate the polymer molecular weight during the free radical polymerization of acrylate polymers. Also, curing reaction of MMA undergoes a sudden temperature rise because of auto-acceleration known as Trommsdorff effect. These curing effects in the presence and absence of CTAs were investigated for MMA resin-based systems. One-dimensional (1D) mathematical model combining the reaction kinetics and heat transfer was extended to incorporate the effect of CTAs. Agreement between experimental findings at small scale (6 to 8 g) and simulation results indicate that in bulk polymerization of MMA based resins, presence of chain transfer not only controls the polymer properties but is also reduces the peak polymerization temperatures. Also, control of the in-situ polymerization of thick methacrylic composite parts is essential to minimize or avoid the monomer boiling. Above mentioned thermokinetic model was expanded considering of spatial geometry and experimentally validated to study the effect of CTAs to mitigate the temperature rise during ~kg quantities of bulk free radical polymerization and fabrication of thick MMA/PMMA resin composites.

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CHAPTER 1: INTRODUCTION

For centuries, mankind has exploited the renewable resources for shelter, clothing, tools, weapons, and coatings but research progress in the coal-based chemistry of 19th century followed by petrochemical revolution and population growth of 20th century led to the development of polymers from the fossil based nonrenewable resources which not only swamped the world with huge quantities of plastics but it is also threatening the marine life, food safety, quality of human health and contributing to adverse climate change. Nature produces approximately 170 billion tons of biomass annually out of which only 3.5% is currently utilized for the human needs[1]. Therefore, exploitation of macromolecular material from renewable resources became inevitable which led to growing interest in the bio-based polymers and bio-composites[2-5].

It is estimated that approximately 8.3 billion metric tons of virgin plastic has been produced till date out of which 6.3 billion metric tons of plastic waste had been generated from which only 9% has been recycled, 12% incinerated and 79% accumulated in the landfills. At this rate roughly 12 billion metric tons of plastic waste will be in landfills or in the natural environment by 2050[6]. Therefore, it is crucial to design eco-friendly polymers, reactive diluents, and products with high content of bio-based chemical compounds which can also be recycled from waste and scrap materials.

Polymer matrices can be classified into thermosetting and thermoplastic resins. Majority of thermoplastics can further divide into polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), poly(styrene) (PS), acrylonitrile butadiene styrene (ABS), polyamide (PA), polycarbonate (PC), polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES) and polyphenylene sulfide (PPS). Thermoset polymers can be also classified into epoxy, unsaturated polyesters (UPR), and vinyl ester (VER) resins. Epoxy is commonly used thermoset

polymeric matrix due to its excellent strength, adhesion to most fibers, little shrinkage upon curing but it tends to be expensive when compared to other thermoset alternatives. Epoxy resin also possesses relatively high viscosity limiting its suitability for various composite manufacturing process. UPR is another commonly used thermoset polymer matrix because of its relatively low cost, low viscosity, ease to work with and can be molded into relatively complex shape. However, their brittle nature prevents their use in the applications like bathroom fixtures and marine industry where high impact and loads are anticipated. VER is often considered to be the most well-balanced thermosetting polymer of choice having low viscosity, reasonably priced, tough, and possessing good chemical, and mechanical properties. VERs are most commonly used in chemical processing equipment, marine, automotive and military applications[7, 8].

Although majority of thermoplastics and thermosetting resins are obtained from petroleum feedstocks, "bio resins" or "green resins" that exhibit superior performance relative to petroleum incumbents should be used as a sustainable alternative to offset the fossil carbon use. Various biobased thermoplastic polymers such as poly(lactide) (PLA), poly(hydroxyalkanoate), poly(butylene succinate) and polyamide have been successfully commercialized[9]. Comparatively, research on bio-based thermosetting polymers is promising, with notable progress in the resins based on epoxies, polyurethanes (PU), UPRs and VERs derived from the plant oils, lignin, and other renewably sourced monomers[10-14]. Despite the increase in the production and usage of biopolymers in the commodity, packaging and biomedical industries, they still accounted for only 1% of the global polymer market in 2019[15].

1.1 Poly(lactide)

PLA is of great interest to us because it is 100% bio-based, biodegradable, commercially available at low cost, possesses excellent processability and characteristics like PE, PP, PET and

PS. However, the widespread use of PLA is limited because of poor toughness and low glass transition temperature (T_g) as compared to other commodity thermoplastics and lack of reactive side-chain groups like VERs. Bulk properties of PLA are greatly affected by the molecular weight, chain architecture, presence of copolymers and degree of crystallinity[16]. Nonetheless, the global PLA market size was ~ \$530 million in 2020 and expected to grow to \$1.7 billion by 2028 driven by the agriculture, textile and packaging sectors[17]. The basic building block of PLA is lactic acid (2-hydroxy propionic acid) with an asymmetric carbon atom and exists in two optically active configurations (Fig. 1). The L -isomer is produced in humans and other mammals, whereas both D and L enantiomers are produced in bacterial systems[18]. Majority of commercial production of lactic acid is done via fermentation of sugars from the glucose, maltose and dextrose obtained from corn or potato starch[19].



Figure 1.1: Stereoisomers of lactide[16].

PLA was first synthesized by William Carothers in 1932 at DuPont by heating lactic acid under vacuum while removing the condensed water, resulting in a low molecular weight (~4000 g/mol) polymer[20]. Figure 2 shows the routes for high molecular weight PLA synthesis[21, 22]. Presently, all the commercially available PLA is manufactured through a two-step process where the lactic acid is used to first produce oligomeric poly(lactic acid) chains which are then depolymerized to generate lactide.



Figure 1.2: Synthesis and methods for high-molecular weight PLA[21].

Ring opening polymerization (ROP) of lactide in the presence of tin catalyst yields high molecular weight PLA. This technology was pioneered by NatureWorks LLC (formerly a part of Cargill Inc.) and forms the basis of their manufacturing plant in Blair, Nebraska with an annual production capacity of 150,000 metric tons[23]. NatureWorks is also building its second PLA plant in Nakhon Sawan Province, Thailand which will add another 75,000 metric tons of capacity when it opens in 2024[24]. Crystallinity of PLA can be tuned by the relative proportions of L or D isomers in the polymer backbone. Tin(II) 2-ethylhexanoate catalyzed PLA prepared from any combination of the ROP of lactide isomers are random copolymers and with more than 92% of L-isomer are semi-crystalline whereas 8-50% of D-isomer yields amorphous polymer[25]. It is a known method to control the molecular weight of the PLA by the starting hydroxyl initiators (alcohols, lactic acid, hydroxyethyl methacrylate etc.) amount in the system[16].

1.2 Green Chemistry and Life Cycle Analysis (LCA)

The importance of 12 principles (prevention, atom economy, less hazardous chemical syntheses, designing for safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feedstocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention and inherently safer chemistry for accident prevention) of green chemistry[26], cradle to cradle design[27], pollution prevention[28], design for the environment[29] and LCA of products have increased over the past three decades with the creation of the United States Environmental Protection Agency (EPA) "Green Chemistry Program" in 1993 and similar programs in Europe which led to application and documentation of green chemistry principles for many case studies, including biopolymers and other biomaterials[30, 31]. Whether it is a drop-in replacement or a deeper innovation, the design stage of the new chemical or process is the most appropriate stage to incorporate the principles of green chemistry to minimize its environmental impact. As outlined by International Standards Organization (ISO), LCA is a well-defined framework for quantifying the resources used and the impact on the environment and

human health by a product, service, or system over its entire life cycle[32].

If polymer ends in the environment, we must have a biological system in place to deal with the polymer which is not the case for several non-renewable polymers. From design, PLA is benign from cradle-to-gate and its key value proposition can be seen from the Figure 1.3 where ecoprofile of NautreWorks PLA is compared with other non-renewable polymers[33]. This reinforces that PLA must be considered as part of a new solution for an increasingly recognized new biobased economy.



Figure 1.3: LCA analysis of climate change, non-renewable energy, water depletion for 1 kg of PLA and other commercial polymers [33].

1.3 Composite Materials

Composites are engineered materials having two or more components with unique physical and chemical properties that remains distinct at a macroscopic level in the finished part. Each composite material consists of reinforcement and a matrix component. The reinforcement provides the desired mechanical property whereas the matrix physically constrains the reinforcement part and may also protect it from the impact, abrasion, and exposure to chemical or water. These two components act together to produce a material with properties superior to those of the individual components.

Composite materials can be broadly classified into three categories: Firstly, polymer matrix composites (PMCs)- PMCs are most common type of composite materials due to the wide range of polymer matrices and reinforcement that can be combined, relative ease and low cost of manufacturing. Typical reinforcement for PMCs may be fibers, flakes, powder, or particles. Fibers are normally used to bestow strength in composites via dispersed form, chopped fiber mat, woven fabric, unidirectional or multidirectional cloth. When fibers (glass, carbon, aramid) are used as the reinforcement in polymer matrix, resulting material is referred to as fiber reinforced composite (FRPC). Powder or particles are generally used as a filler material to decrease the cost of the polymeric composites. Fillers like calcium carbonate (CaCO3), alumina trihydrate (ATH), mica and glass microspheres along with other additives like tougheners, colorants, adhesion agents, flame retardants and ultraviolet absorbers may also be added to composite matrix resin based on the specific application[8].

Secondly, metal matrix composites (MMCs) are those in which metal (steel, aluminum, copper, nickel, and titanium) is used as a matrix material and ceramic (alumina, silicon carbide, nickel oxide, zirconia, titanium carbide and silicon trinitride) is used a reinforcement material. Metal used in the matrix is processed through the powder metallurgy which involves the use of fine metal powders and mixed with reinforcement followed by sintering at high temperatures and pressure. Metal powder fuses into a continuous phase matrix around the reinforcement and unique aspect of MMCs is that the metal matrix is the load bearing component and the ceramic

reinforcement provides the wear resistance and hardness. Most common examples of MMCs include the brake pads and electronic components for the aerospace applications[34]. Thirdly, ceramic matrix composites (CMCs) employ ceramic (alumina and silicon carbide) as a matrix material which possesses a very high melting temperature and are processed into a powder through suspension in water or by compression and sintering. Components of jet exhaust nozzles and blades are often made from CMCs[35].

1.4 Vacuum Assisted Resin Transfer Molding (VARTM)

Composite materials are preferred for many applications because of their durability and superior strength and FRPCs are most used composites because their physical properties can be tailor to meet specific requirements. VARTM technique has become preferred method for the composite fabrication in recent years due to an interest in the reduction of volatile organic compound (VOC) emission and to lower the labor content in the production processes which rely on the open molding technology[36]. In the VARTM process, a flexible vacuum bag is sealed with a vacuum tape over a stack of flow media, breather cloth and fibers which are placed on a mould surface coated with a mould release agent. Inlet for resin and vacuum ports are strategically positioned to fill the desired part during infusion. Vacuum is pulled through the port(s) on one side of the part and the reactive resin is pulled through the inlet port(s). When the part is fully wetted out, gelling will be followed by curing to form a solid FRPC[37]. Figure 1.4 shows the fiberglass panel casting using in-house VARTM setup. Although most FRPCs uses thermoset resin as a polymer matrix, thermoplastics like poly(methylmethacrylate) (PMMA) based acrylic resin[38] and PLA based bioresin[14] have received significant attention because of improved recycling convenience and introduction of biorenewable polymer in the resin matrix.



Figure 1.4: VARTM setup for fiberglass composite panel fabrication.

When dedicated to construct the FRPCs using thermoset resins in VARTM, two important criteria related to the resin must be satisfied- 1) Ability to dissolve the cross-linker or prepolymer in reactive diluent and 2) Viscosity of the formulation (generally below 500 cP) such that it should be compatible with further processing with reinforcing composite material. Styrene is predominantly used as a reactive diluent to reduce the resin viscosity but there is a growing awareness about its health concerns and industry is actively looking for alternative solutions[39-42]. Our group previously demonstrated the viability of styrene-free, PLA and methyl methacrylate (MMA) based formulation suitable for composite panel fabrication by VARTM process[40, 43]. However, the low molecular PLA (Mw=16000 g/mol, Mn= 6700 g/mol) was obtained from the random cleaving of commercial high molecular weight PLA (Mw=83000 g/mol, Mn=65000 g/mol) which took more than 2 weeks for dissolution in MMA or ~18-24 hours at 50 °C. Origin of this research was to synthesize large quantity (>kg batch size) of vinyl terminated

poly(meso-lactide) (which was hypothesized to have an improved dissolution in MMA than previously obtained PLA counterpart) and investigate its viability in the fiber and particulate filled composite materials. Further introduction and technical details are provided in Chapter 2 and 3.

1.5 Recycling of Composite Materials

Plastics recycling has been steadily growing in recent years with regulation and industry initiatives arising from consumer awareness and adverse environmental impacts[9, 44]. Recycling and disposal of composite materials is an issue that is being increasingly addressed, as it should be with any widely used material[45, 46]. Fiber reinforced composite parts (for example, wind turbine blades, automobiles, and aircrafts) that have lived their useful life must be recovered and recycled to transform them into a beneficial output. Three prevalent routes of composite recycling are mechanical recycling, thermal recycling, and chemical recycling with energy demands of 0.1-4.8 MJ/kg, 23-30 MJ/kg, and 63-91 MJ/kg respectively[47]. Mechanical recycling consists of shredding and size reduction processes to reduce the waste into recyclates which are further separated into coarse pieces (higher fiber content) and fine particles (higher resin content)[48, 49]. Recyclates obtained from this method of recycling is mostly limited to the low-value applications such as filler or reinforcing materials because of the disruption in the physical and mechanical properties of the virgin fibers[50].

In thermal recycling, heat is used to separate fibers from the polymer matrix and can be further divided into pyrolysis[51], fluidized bed pyrolysis[52] and microwave pyrolysis[53] processes. Main advantages of thermal recycling include utilization of inherent energy in the composites for fuel and it preserves the structural value of the fibers for reuse. Disadvantages include the use of high temperature, lower quality of recovered fibers than chemical recycling and oxidization process is needed to remove the char deposition from the fiber surface. Chemical recycling is the process of converting polymers of a FRPC matrix to monomers or partially depolymerized to oligomers through chemical reaction by dissolution of composite in acids, bases or solvents[54]. Main advantages include low temperature solvolysis and good-quality recycled fibers compared to other composite recycling processes. However, some chemical solvents can be toxic to environment which will require further processing[55].

At the end-of-life, particulate filled composite parts like kitchen countertops or bathroom sinks inevitably produces waste. Some countertops are recycled into new building projects and home improvements, but majority ends up in the landfill[56]. If one 60 m windmill blade which weighs approximately 20 tons costs around \$200-250k to manufacture[57] then 20 tons worth of bathroom sinks (One 6 kg sink for \$100) will cost around \$300-350k. Therefore, it is wise to recycle and reincarnate the cast polymer products like countertops and sinks to recover the embedded energy, raw materials, and value-added products which is the major focus of Chapter 4 of this thesis.

1.6 Resin Transfer in Free Radical Polymerization

Bulk free radical polymerization has been extensively studied since its inception and substantial effort has been devoted to the development of mathematical models of free radical polymerization kinetics and to predict temperature evolution in a curing composite part[58-62]. The challenge for manufacturing thick thermoset composite is, however, to control the heat generated during the manufacturing. Thicker the part, more difficult it is to prevent the core from overheating which may lead to voids, resin degradation, uneven curing of the composite part which will ultimately affect its physical properties[63].

In free radical polymerization, chain propagation can not only be arrested by combination and disproportionation termination events, but also the radical can be involved in a chain transfer reaction when hydrogen atom is abstracted from a monomer, solvent, initiator, or polymer molecule in the system. Also, chain transfer agent (CTA) can be intentionally added to control and modify the resulting polymer properties[64-66]. However, the elucidation of the effect of CTAs in the PLA/MMA and PMMA/MMA composite resin formulation is lacking which is the basis for Chapter 5 and 6 of this thesis work.

1.7 Thesis Outline

Aim of this thesis is to develop novel biopolymer composite system having improved sustainability metrics with physical properties on-par to that of incumbent technologies, recycle end-of-life parts and augment the 1D and two dimensional (2D) mathematical model via simulation and experiments to incorporate the effect of chain transfer kinetics to simultaneously predict the temperature evolution in thick composite parts. Chapter 2 describes the synthesis of novel thermoset poly(meso-lactide) and its incorporation within various fibers to make composite panels followed by mechanical characterization to showcase its potential use as a biorenewable resin for FRCs. Chapter 3 further demonstrates the utility of our bioresin by direct substitution in the realm of cast polymers formulations. Chapter 4 introduces the novel way of recycling cast polymer products via chemical recycling through base hydrolysis to recover the filler and other value-added products. Chapter 5 presents the 1D mathematical model with experimental validation to include the chain transfer kinetics in the bulk free radical polymerization of PMMA/PLA/MMA resin-based composites. Chapter 6 advances the kinetic mathematical model of previous chapter to experimentally verify and control the temperature rise across thick composite part. Finally, Chapter 7 summarizes this work as a whole and discusses opportunities for future research.

CHAPTER 2: POLY(MESO-LACTIDE) THERMOSET RESIN BASED FIBER REINFORCED COMPOSITES

2.1 Introduction

Epoxy, UPR and VER based thermoset resins are widely used polymer matrices in the FRPCs with estimated global market of \$27 billion by 2026[67]. Due to their low density and high strength-to-weight ratio, they are utilized in a wide range of applications such as automotive, aerospace, electrical, adhesives, coatings, transportations, wind energy, sporting goods, and marine industry[8]. UPRs and VERs generally comprise of unsaturated oligomers dissolved in polymerizable diluent where they further react by free-radical polymerization to form the cross-linked network. Traditional VERs oligomers are synthesized by end-capping epoxy resins with unsaturated mono-caboxylic acids, and UPRs oligomers are the condensation products of unsaturated acids or anhydrides and diols with or without diacids[68]. The reactive diluent serves two main purposes; it reduces the resin viscosity to ensure good processability and complete fiber wetting, and it controls the cross-link density and average molecular weight between cross-links of the network so that robust bulk mechanical properties are attained[39].

Styrene is the most common reactive diluent in VERs and UPRs due to its low cost, low viscosity, favorable reactivity, and aromaticity, with lends to good compatibility with aromatic oligomers and high glass transition temperatures. However, Styrene is toxic, volatile compound that is listed as potentially carcinogenic by the U.S. Department of Health and Human Services[42, 69]. In addition to its health hazards in the workplace, particularly in certain composite manufacturing techniques that are open to the atmosphere, styrene is difficult to produce from renewable resources due to its high membrane toxicity to microbes[70]. Various bio-based reactive diluents have been reported in the literature. Methacrylated cardanol from cardanol oil was used

as a reactive diluent with bio-based maleic anhydride modified glycidyl methacrylate oligomers[71]. However, low T_g (40-50 °C) of such resin restricts its use in high temperature conditions. Wool *et al.*[72, 73] synthesized aromatic bio-based methacrylates from vanillin, eugenol and guaiacol from lignin but they were either solid or low volatile liquids with viscosity 25-40 times larger than styrene which limits their use in composite applications due to processing issues. In another study, lignin derived cinnaminic and methacrylic acid and renewably sourced fumaric acid and muconate were crosslinked in the presence of fiberglass reinforcement which exhibited properties similar to reinforced composites prepared with styrene[74]. In another study, miscibility with UPRs and viscosity and compared with MMA based systems. MMA based thermoset appeared to be the toughest of them all, but it was also the most volatile compound. Increasing regulatory pressures are also pushing the composite industry towards the methacrylate based resin and cross-linker system[75-77].

Another major component of thermoset resin is prepolymer or cross-linker that reacts with reactive diluent via free radical polymerization. In 2020, worldwide production volume of bioplastics was 4.2 million metric tons with bio-based epoxy resins and cellulose acetate being the market leaders followed by PLA and starch containing polymers[78]. Various PLA based thermoset resin have been prepared in the literature by end-capping lactic acid oligomers with methacrylic or acrylic groups which can further participate in the free-radical polymerization with or without reactive diluents. Xie *et al.*[79] synthesized glycolide/lactide based methacrylated polyester with compressive yield strength and modulus of about 20 MPs and 730 MPa respectively. Helminen *et al.*[80] synthesized methacrylic anhydride end functionalized linear and star-shaped lactic acid oligomers, which produced a resin with tensile strength and modulus of about 120 MPa

and 2800 MPa respectively. Wallach *et al.*[81] copolymerized methacrylate-terminated PLA with itaconic anhydride (ITA) to obtain 9000-70000 g/mol oligomers. Bakare *et al.*[82] synthesized and evaluated the performance of methacrylated glycerol, allyl alcohol and pentaerythritol based lactic acid resin with natural cellulose based (flax) fiber reinforced composites with tensile modulus and tensile strength of 4-10.3 GPa and 25-91 MPa respectively. Star shaped PLA oligomers, resulting from the condensation reaction of lactic acid with multifunctional hydroxyl core molecules have also been reported in the literature[83].

Recently, Moran *et. al*[43], formulated thermosetting resin with vinyl terminated PLA oligomers dissolved in MMA as a reactive diluent. Dylan *et al.*[40] further quantitatively characterized the fundamental solution properties of PLA in MMA through series of rheology and multiple angle light scattering experiments to show that Mark-Houwink exponent is 0.73 and Flory-Huggins interactions parameter is 0.4, indicating MMA is a good solvent for PLA. However, the adapted reaction scheme[84] by Moran *et. al* to make the PLA oligomers involved random cleaving via alcoholysis of high molecular weight polymer. This uncontrolled reaction can chop the polymer in such a way that the resulting low molecular weight chains may contain more L-isomer or D-isomer than the starting high molecular weight amorphous polymer. This resulted in semi-crystalline polymers with melting peak at ~120 °C[43] with long dissolution time in MMA.

ROP of *meso*-lactide or breakdown of high molecular weight poly(*meso*-lactide) (PML) is bound to give only amorphous PLA because *meso*-lactide is optically inactive and has one L and one D isomer in in the lactide ring. Also, the availability of commercial quantities[85] of *meso*lactide is encouraging the researchers to develop novel PML based biorenewable products. Witzke *et al.*[25] synthesized and characterized various copolymers of L-lactide and *meso*-lactide in bulk with stannous octoate catalyst and estimated the infinite T_g of PML to be 46 °C. Introduction and amount of meso-lactide depressed the melting point by PLA ~30 °C and PLA did not crystallize when the starting lactide mixture contained more than 15% of *meso*-lactide[25, 86]. Ovitt and Coates have made novel stereoregular PMLs using various chiral catalysts. However, due to high degree of stereoregularity, the resulting polymers were crystalline, and the molecular weights (M_n) were only between 10000 to 30000 g/mol[87, 88]. Okuda *et al.*[89] used group 4 metal bis(phenolate) complexes as catalysts to synthesize syndiotactic *meso*-lactide based polymers with maximum M_n of 47000 g/mol. In another study, Chen *et al.*[90] employed epimerization of *meso*lactide to racemic-lactide followed by stereoselective polymerization to obtain crystalline isotactic PLAs with M_n of 11000 g/mol.

To our knowledge, synthesis of completely amorphous high molecular weight (M_n >200000 /mol) PML and vinyl terminated poly(*meso*-lactide) (VE-PML) with controlled molecular weight ($M_n \sim 10000$ g/mol) and its incorporation in the FRPCs have not been reported in the literature. Here, we develop a low viscosity, styrene free bioresin from variable VE-PML content in MMA and PLA oligomers (obtained from the hydrolytic degradation of commercial amorphous PLA) with tri-acrylate cross-linker dissolved in MMA for FRPCs. If MMA commercially becomes available from biomass, then a resin system utilizing PML, and MMA is bound to give excellent sustainability metrices.

2.2 Experimental

2.2.1 Materials

meso-Lactide was obtained from NatureWorks and further recrystallized three times in ethyl acetate (Fisher Chemical, purity >99.9%). Benzyl alcohol (Sigma-Aldrich, Anhydrous, purity 99.8%), HEMA (Sigma-Aldrich, purity >99%, Monomethyl ether hydroquinone <50 ppm as inhibitor) and Itaconic anhydride (Sigma-Aldrich, purity >95%) were used as received. Tin(II)- 2-ehtylhexanoate (Sigma-Aldrich, purity 92.5-100%) was distilled under vacuum before use. ACS grade chloroform and methanol (VWR international) were used as received. MMA (Sigma-Aldrich, Purity 99%, Monomethyl ether hydroquinone <30 ppm as inhibitor) was stored in the refrigerator and used as received. N,N-Dimethyl-p-toluidine (DMT) (Sigma-Aldrich) and Benzoyl Peroxide (BPO) solution Luperox® AFR40 (Sigma-Aldrich) were stored in the refrigerator and used as received. Fiberglass (0°- 864 g/m² E-Glass, 90°- 79 g/m² E-Glass and 12 g/m² polyethersulfone stitching), Kevlar (plain weave), Carbon Fiber (2×2 twill weave) and yellow sealant tape were purchased from the Fibre Glast Developments Corp. Triacrylate cross-linker (SARET SR 517[®]) was provided by Sartomer. Amorphous grade commercial PLA pellets, named Ingeo 10361D, were provided by NatureWorks.

2.2.2 Methods

Small Scale High Molecular Weight PML Preparation: 15 g of *meso*-Lactide was loaded in the flame dried 50 ml flame dried RB flask with magnetic stirrer and dried under vacuum for 24 hours at 40 °C. After drying, the flask was sealed with a rubber septum and purged with argon for 10 minutes followed by melting of lactide in an oil bath at 130 °C under magnetic stirring. Tin(II) 2-ethylhexanoate (1 mol Tin(II) 2-ethylhexanoate per 2500 mol lactide) was added and polymerization was performed for 12 hours with adventitious water molecules acting as an initiators. The flask was quenched in an ice bath and chloroform was added to dissolve the polymer followed by precipitation in 10-fold excess of methanol. Resulting PML was dried in vacuum oven overnight at 40 °C and stored in argon purge glass bottle before use. Overall yield of reaction was ~95%.

Large Scale VE-PML Preparation: 1500 g of *meso*-Lactide was loaded in the 5L flame dried reaction vessel with stir bar and dried under vacuum for 2 days at 40 °C. After drying, the reaction

vessel was sealed with a rubber septum and purged with argon for 10 minutes followed by melting of lactide in an oil bath at 130 °C under magnetic stirring. HEMA (1 mol HEMA per 71 mol of lactide units) was added using syringe in the melted pool of lactide and stirred for 30 minutes followed by Tin(II) 2-ethylhexanoate (1 mol Tin(II) 2-ethylhexanoate per 2500 mol lactide) addition. HEMA initiated polymerization was carried out for 18 hours at 130 °C. The vessel was quenched in an ice bath and chloroform was added to make a 50 wt.% solution. Itaconic anhydride (2:1 molar excess) and Tin(II) 2-ethylhexanoate (1% w/w PLA) were added. The end-capping reaction, as shown in Scheme 2.1-B, was carried out on heating mangle with magnetic stirring and refluxed for 8 hours. A VARIAC was used to maintain a steady boiling rate so that a balloon covering the top of the condenser remained erect but not inflated. Polymer solution after both reactions were precipitated into 10:1 volume excess of methanol, dried in a vacuum oven overnight at 40 °C, crushed into powder with a mortar and pestle, and stored in plastic pails before use. Overall reaction yield was ~85%.

Large Scale Degraded PLA Oligomers Preparation: 400 g of 10361D pellets were taken in three 1-quart glass bottle to which 400 g of DI water was added. Glass bottles were capped with a metal lid followed by heating in the convection oven held at 90 °C and removed after 13 hours and water was discarded. Resulting degraded PLA oligomers were designated as DP-13. DP-13 pellets were transferred to a glass tray which were dried in the vacuum oven at room temperature for 48 hours followed by 72 hours drying at 40 °C. Similar procedures were used to obtain DP-18 and DP-24 oligomers which were degraded for 18 and 24 hours respectively.

Resin Preparation: VE-PML was dissolved in MMA at concentrations of 30, 40, 50 wt.%. Prior to exotherm measurement, BPO and DMT (1:1 mol ratio) were dissolved in amounts of 0.004, 0.008 and 0.013 mol BPO+DMT per mol of double bonds in the resin. For composite panels fabrication

0.004 mol BPO+DMT per mol of double bonds was used. DP-Mix [75:25 mixture of DP-18 and DP-13] was dissolved in MMA at 40 wt.% concentration to study the effect of cross-linker in the composite panel performance.

Curing Exotherm Measurement: 20 ml screw-cap scintillation vials were loaded with 6 g of resin followed by BPO+DMT addition. Thermocouples were inserted to the center of the resin through holes drilled in caps and sealed with yellow sealant tape. Vials were placed in an oil bath at room temperature. Temperatures of the centers of the reactions were recorded at 1 Hz sampling rate until the reactions reached completion.

Composite Panel Fabrication: 4 piles of fibers ($30 \text{ cm} \times 30 \text{ cm}$) were stacked parallel to each other and laid on a tempered glass plate with release wax followed by release cloth, resin flow media, bagging film and final sealing with a yellow sealant tape. 24" Hg of vacuum was applied to the fibers for 30 minutes. The resin was degassed in a vacuum chamber at 23" Hg for 2 minutes. The resin was slowly infused into the fibers at room temperature using 5" Hg of vacuum. Once all the fibers were completely wetted, the vacuum line and feed line was clamped shut. Panels were removed next day and cured in an oven at 90 °C to post-cure for 8 hours.

Nuclear Magnetic Resonance (NMR): ¹H-NMR spectra of 6.25 wt.% polymer solutions in CDCl₃ were obtained using Bruker Avance 300 MHz spectrometer. The spectra were analyzed using MNova NMR software.

Gel Permeation Chromatography (GPC): The GPC system contained an Agilent PLgel 5µm MIXED-C column, a Wyatt DAWN DSP Laser Photometer, and a Wyatt OPTILAB DSP Interferometric Refractometer. The light scattering detector was calibrated using toluene and normalized to the 90° detector using monodisperse poly(styrene) with 30 kg/mol molecular weight. The refractometer was calibrated by injecting various concentrations of polystyrene in

THF (dn/dc=0.185). PLA samples were measured in chloroform at 35 °C (dn/dc=0.024 mL/g). Solutions of approximately 10 mg/mL were filtered once through a 0.45 μ m poly(tetrafluoroethylene) syringe filter prior to injection.

Differential Scanning Calorimetry (DSC): The DSC of meso-lactide, PML, VE-PML, degraded PLAs and cured resins were performed using a Q20 TA DSC calibrated with an indium standard. To check the *meso*-lactide purity, ~1-3 mg of crystals were sealed in an aluminum pan in the glove box. The scanning protocol was: equilibrate at 20 °C, followed by heat from 20 °C to 110 °C at 1 °C/min. For rest of the samples: Approximately 10-15 mg of dried materials were sealed in aluminum pans. The scanning protocol was: hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min, hold for 5 min at 200°C, cool from 200°C to -40°C at 5°C per min, hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min. Glass transition temperatures (T_g) were assigned for the second heat scan using the half height method, which is the temperature at which a sample's heat capacity is halfway between the difference of its glassy and rubbery state heat capacities.

Thermal Gravimetric Analysis (TGA): TGA was performed using TGA Q500. Approximately 10 mg of samples were loaded in the platinum pan and heated under nitrogen from 25 °C to 600 °C at 20 °C/min.

Scanning Electron Microscopy (SEM): SEM samples (casted and polished in an epoxy resin) were coated with Pt and images were acquired using Zeiss Auriga Crossbeam microscope.

Tensile Testing: Tensile testing was performed according to ISO 527-5 using a MTS hydraulic load frame and 100 kN load cell, hydraulic wedge grips and MTS extensometer. Samples dimensions were approximately 250 mm \times 15 mm (length \times width) for fibers in the longitudinal direction for E-Glass and approximately 250 mm \times 25 mm for transverse directions E-Glass, Kevlar, and

Carbon fibers. Samples were gripped with end-tabs at 1000 psi. A pre-stress of 0.05 kN was applied followed by tensile strain at a rate of 1.5 mm/min.

Dynamic Mechanical Thermal Analysis (DMTA): DMTA was conducted using an ARES-G2 rheometer equipped with torsional rectangular fixtures. Rectangular specimen ($\sim 45 \times 10 \times 3 \text{ mm}^3$) were heated from 30 °C to 180 °C at 5 °C /min with fixed strain (0.03%) and frequency (1.0 Hz).

2.3 Results and Discussion

As shown in Scheme 2.1, Figure 2.1, and Table 2.1 large quantities of high molecular weight PML and vinyl terminated VE-PML were successfully synthesized from pure *meso*-lactide crystals (Figure 2S-1). ¹H-NMR spectra, shown in Figure 2.1a, were used to validate the reactions. As expected, the high molecular weight PML and commercial PLA (10361D) shows two peaks, a, and b, assigned to methylene and methine protons, respectively, along the backbone. End-groups are not visible due to high molecular weight. For VE-PML, HEMA and itaconic acid end-groups are visible by peaks c-g and peaks h-j respectively. Peak integrations of ¹H-NMR spectra are reported in Table 2S.1. As expected, peak a is 3 times larger than peak b. Integration of end-group protons showed equimolar amounts of end groups for VE-PML indicating almost all the chains were initiated and end-capped by the desired species instead of adventitious water. Also, >kg quantities of low molecular weight PLAs were obtained from the degradation of commercial high molecular weight PLA 10361D in DI water. Peak at 4.34 ppm for degraded PLAs is arising from the end group methine proton adjacent to -OH group of lactic acid and it becomes more prominent as molecular weight decreases.


Scheme 2.1: A) Ring opening polymerization of meso-Lactides by adventitious water molecules. B) End-capping with Itaconic anhydride to make VE-PML C) Room temperature free radical polymerization of VE-PML with MMA D) Degradation of 10361D PLA in DI water at various times and E) Room temperature free radical polymerization of MMA with DP-Mix with and triacrylate as a crosslinker.

Molecular weights were determined by both GPC chromatograms, shown in Figure 2.1c, and end-group analysis of the ¹H-NMR spectra integrations (for VE-PML) in Table 2S.1. Resulting molecular weights are reported in Table 2.1. PML had a M_w and M_n of 275000 g/mol and 220000 g/mol respectively which is the highest molecular weight reported for the poly(*meso*-lactide) based polymers so far. This also validates our synthesis capability to obtain high and controlled molecular weight poly(*meso*-lactide) polymers. The expected M_n of VE-PML according to the amount of HEMA added to the reaction is 10000 g/mol respectively. The M_n value reported in

Table 2S.1 from NMR is slightly higher, which could indicate slightly less than complete conversion of the first step of the reaction.



Figure 2.1: a) ¹H-NMR spectra b) DSC scans c) GPC d) TGA of PML, VE-PML, Commercial PLA (10361D) and Degraded PLAs b) Recrystallized pure *meso*-lactide crystals.

Polymer Type	M _w (GPC)	M _n (GPC)	ורו	M _n (NMR)	T_g	T_{peak}	<i>T</i> _{<i>d</i>-10}		
	(g/mol)	g/mol) (g/mol)		(g/mol) (g/mol)		(g/mol)	(°C)	(°C)	(°C)
PML	275000 ± 5000	222000 ± 16000	1.24 ± 0.07		41.6	303	262		
VE-PML	20800 ± 2900	10100 ± 800	2.08 ± 0.35	12700 ± 70	19.3	263	200		
10361D	65900 ± 3900	42800 ± 4100	1.54 ± 0.06		55	379	344		
DP-13	28100 ± 1400	15700 ± 600	1.79 ± 0.03		51	375	333		
DP-18	11200 ± 2400	6000 ± 800	1.87 ± 0.27		43.1	362	299		
DP-24	7800 ± 2100	3800 ± 600	2.08 ± 0.34		34.5	361	277		

Table 2.1: GPC, DSC, NMR and TGA data of PML, VE-PML, 10361D and Degraded PLAs

Thermal properties of the synthesized and degraded polymers were investigated using DSC

and TGA. Figure 2.1b shows the DSC scans upon the first and second heating steps. Table 2.1 shows the thermal properties of polymers where T_{peak} and T_{d-10} are the temperatures obtained from the TGA (Figure 2.1d) at peak degradation and weight loss at 10 wt.% respectively. TGA showed about 1 wt.% remaining after heating to 600 °C. DSC scans of both PML and VE-PML showed no melting peak in the first heating scan indicative of completely amorphous polymer which would be very well suited for the easy dissolution in the MMA. Low T_g of PML was expected because it increases with L-stereoisomer content and Mn. Also, the infinite molecular weight T_g of PML was estimated to be 46 °C[25]. Molecular weight measurement of 10361D and degraded PLAs were determined via GPC and confirms the reduction in molecular weight as the amount of hydrolysis time increases. Although, starting commercial PLA, 10361D was completely amorphous, degraded PLAs exhibited melting peak at around 115-120 °C. This is characteristic of semi-crystalline PLA. 10361D had sufficient D-stereoisomer to put it below the crystallization threshold but, its random cleaving by hydrolysis to obtain the degraded PLAs, did not have enough D-stereoisomer and resulting low molecular weight chains semi-crystalline.

VE-PML oligomers were dissolved in MMA at 30 wt.%, 40 wt.% and 50 wt.% concentrations to make 30 wt.% VE-PML, 40 wt.% VE-PML and 50 wt.% VE-PML resins respectively. DP-18 and DP-13 were mixed in 75:25 weight ratio (DP-mix) and dissolved in MMA at 40 wt.% which is termed as 0 wt.% x-linker resin. Further 0.3 wt.%, 0.7 wt.% and 1.1 wt.% of triacrylate cross-linker was added in the 40 wt.% DP-mix resin to make 0.3 wt.% x-linker, 0.7 wt.% x-linker and 1.1 wt.% x-linker resin respectively. Maintaining low resin viscosity is important for VARTM and should be less than 0.5 Pa.s[8]. The viscosities of 30 wt.%, 40 wt.% and 50 wt.% VE-PML in MMA and 40 wt.% DP-mix in MMA, shown by the shear sweep data in Figure 2.2, were determined to be 0.017, 0.062, 0.21 and 0.25 Pa.s respectively. These viscosities

indicate that resin is well suited for VARTM at room temperature, and it would also be acceptable for processes requiring lower viscosities like sheet molding compounding[91].



Figure 2.2: Measured viscosities (hollow shapes) of PLA/MMA solutions compared with predicted (solid line) $c[\eta]$ as a function of shear rate at 20 °C.

Dylan *et al.*[40] has showed that Mark-Houwink exponent for PLA/MMA system is 0.73 and the Flory interaction parameter is 0.4, which indicate that MMA is a good solvent for PLA. A semi-empirical equation was developed to estimate the concentration-molecular weight dependence of PLA/MMA solution viscosity[40]:

$$\log(\eta_{sp}) = C_1 (\log(c[\eta]))^3 + C_2 (\log(c[\eta]))^2 + C_3 (\log(c[\eta])) + C_4$$
(2.1)

where η_{sp} and $[\eta]$ is specific and intrinsic viscosity, respectively, $C_1 = 0.23$, $C_2 = 1.0$, $C_3 = 2.1$ and $C_4 = 0.38$. Solid line in Figure 2.2 represents the predicted viscosity using above parameters, equation 2.1, concentration of resin and measured molecular weights. Measured viscosity for 40 wt.% DP-mix agrees well whereas the measured viscosities of VE-PML based solutions were lower than the predicted values indicative of the higher overlap concentration (c*) (or smaller coil

volume) for *meso*-lactide based polymers.

To determine the infusion time, curing exotherms were measured in conditions mimicking the resin transfer molding process. That is, heat produced by the reaction was transferred to surroundings that remained at a constant temperature. The BPO/DMT (1:1 mol ratio) concentration was controlled relative to the total number of double bonds in the resin, as this represents the total amount of potential energy that can be converted to heat. The temperature profiles of various reaction mixtures measured during curing are shown in Figure 2S.2. Room temperature polymerization of MMA initiated by BPO/DMT system begins with a nucleophilic attack of DMT on peroxide bond of BPO followed by a redox reaction to generate two radicals[62]. As expected, the polymerization time decreased when initiator concentration increased. Also, the onset of Trommsdorff effect time (gel time) decreased with increasing VE-PML concentration. Temperature for all the initiator concentrations, did not exceed the boiling point of monomer. Initiator concentrations of 0.004 mol BPO+DMT/mol double bond were used for the composite panel fabrication.

Glass fiber reinforced panels (30 mm × 30 mm) were prepared from the 30, 40, 50 wt.% VE-PML and 0 wt.%, 0.3 wt.%, 0.7 wt.% and 1.1 wt.% x-linker based 40 wt.% DP-mix based resins using VARTM. Kevlar and Carbon fiber reinforced panels (30 mm × 30 mm) were prepared from the 40 wt.% VE-PML based resin using VARTM. After overnight curing, panels were post cured in the convection oven at 90 °C for 9 hours. Small piece of cured resin was used to measure the thermal properties shown in Figure 2.3 and Table 2.2. Glass transition temperatures of the cured resins were significantly higher than that of VE-PML and degraded PLAs alone due higher glass transition of polymerized PMMA. In general, glass transition temperature of the VE-PML thermoset resins decreased with higher VE-PML concentrations. T_g of 40 wt.% DP-Mix with 0

wt.% x-linker thermoplastic resin was 52.7 °C which increased to 66 °C and 68 °C with 0.3 wt.% and 0.7 wt.% x-linker amount respectively. Further improvement in T_g was not observed at 1.1 wt.% x-linker concentration. This shows the benefit of using cross linker to make a PMMA thermoset in the absence of vinyl terminated PLA. Also, only one T_g was observed for all the resin compositions indicative of single phase without micro/nano scale separation for the PLA/MMA based resins. The measured glass transition temperatures were ~5-10 °C lower than the predicted values from the Fox-Flory equation[92], indicating a slight depression in T_g exists in PLA/PMMA resin system, which is similar to the melt compounded PLA/PMMA blends reported from other works[93]. All the PLA/PMMA resin system, exhibited good thermal stability with degradation temperature in the range of 250 to 400 °C. Also, as shown in Figure 2.4, morphology of the polished surface of composites were characterized by SEM. This indicates that individual fibers were well wetted by the resin and good fiber/resin interface is achieved for all types of fibers without any phase separation.



Figure 2.3: a) DSC and b) TGA of cured resins.

Composite Resin Type	T_g	T _g (Fox-Flory eq.)	T_{peak}	<i>T</i> _{<i>d</i>-10}
	(°C)	(°C)	(°C)	(°C)
30 wt.% VE-PML	66.4	74	280, 408	256
40 wt.% VE-PML	58.2	65	280, 405	269
50 wt.% VE-PML	52.6	56.5	280, 408	258
40 wt.% DP-Mix w/ 0 wt.% x-linker	52.7		375	304
40 wt.% DP-Mix w/ 0.3 wt.% x-linker	66		379	316
40 wt.% DP-Mix w/ 0.7 wt.% x-linker	68.1	/8.5	379	327
40 wt.% DP-Mix w/ 1.1 wt.% x-linker	68		379	317

Table 2.2: Thermal properties of the cured resins



Figure 2.4: SEM images (10 μ m and 1 μ m resolution) of 40 wt.% resin based a) Glass fiber b) Kevlar fiber c) Carbon fiber reinforced composite.



Figure 2.5: Tensile properties of PLA/MMA resin with various fibers.

				Tensile	Tensile		Fiber	Normalized to Volume Fi	50% Fiber
-	Fiber	Polymer	Polymer		Strength	Elongation	Volume	Tensile	Tensile
Туре	Direction	Туре	(wt.%)	(GPa)	(MPa)	(%)	(%)	Modulus (GPa)	Strength (MPa)
			30	33 ± 4	659 ± 16	2.19 ± 0.1	46.5	37.3 ± 4	711 ± 17
		VE-PML	40	36 ± 2	713 ± 21	2.30 ± 0.2	48	37.7 ± 2	740 ± 22
			50	41 ± 3	846 ± 39	2.19 ± 0.2	55	37.9 ± 3	775 ± 36
	Longitudinal	DP-mix_0 wt% x-linker		38.7 ± 2	793 ± 31	2.29 ± 0.2	54.3	35.6 ± 3	744 ± 21
		DP-mix_0.3 wt% x-linker	40	41 ± 2	821 ± 65	2.41 ± 0.3	54	38.5 ± 3	765 ± 60
	DP-mix_0.7 wt% x-linke	40	41.4 ± 4	884 ± 35	2.69 ± 0.1	54.1	39.4 ± 3	813 ± 35	
E Class		DP-mix_1.1 wt% x-linker		42.1 ± 1	930 ± 15	2.51 ± 0.5	56.5	38.3 ± 4	844 ± 12
E-Glass			30	11.4 ± 1.2	72 ± 8	2.24 ± 0.2	46		
		VE-PML	40	12.8 ± 1.1	78 ± 4	2.31 ± 0.2	47		
			50	12.3 ± 1.2	86 ± 5	2.35 ± 0.1	55		
	Transverse	DP-mix_0 wt% x-linker		12.4 ± 1.3	80 ± 8	2.35 ± 0.1	54.3		
		DP-mix_0.3 wt% x-linker	40	12.7 ± 1.5	88 ± 4	2.69 ± 0.1	54		
		DP-mix_0.7 wt% x-linker	40	13.1 ± 2	91 ± 9	2.53 ± 0.3	54.1		
		DP-mix_1.1 wt% x-linker		12.9 ± 1.5	90 ± 6	2.70 ± 0.2	56		
Kevlar	Plain weave	VE-PML	40	27.5 ± 4	485 ± 19	2.42 ± 0.2	50		
Carbon	Twill weave	VE-PML	40	46 ± 2	701 ± 17	1.51 ± 0.1	46		

Table 2.3: Tensile properties of the fiber reinforced composites

The mechanical properties of fiber reinforced composites are crucial to determine their applications. The tensile properties of all the PLA/MMA resins are reported in Figure 2.5 and Table 2.3. For glass fiber composites, in the longitudinal direction, tensile modulus was was ~38 and 39 GPa for VE-PML and x-linker/DP-mix based polymers. Tensile strength and elongation at break and elongations for the bio-based composites were independent of PLA concentration and were between 700-850 MPa and 2.2 to 2.5% respectively. Within uncertainty of error, tensile properties of these bio-based resin are comparable to reported values for E-Glass/Acrylic and E-Glass/Epoxy system[94-96]. Also, mechanical properties of the bio-based Carbon fiber and Kevlar fiber composites are on par to that of the literature reported values[97, 98].



Figure 2.6: DMTA (torsional) of PLA/MMA fiber reinforced composites.

Fiber	Composite rein type	G' at 30 °C	G" at 30 °C	Tan δ Peak Temperature	G" Peak Temperature
		(GPa)	(GPa)	(°C)	(°C)
	30 wt.% VE-PML	3.3 ± 0.3	0.52 ± 0.02	94.6 ± 0.6	66.6 ± 0.9
	40 wt.% VE-PML	3.8 ± 0.02	0.58 ± 0.02	86.3 ± 0.2	62.3 ± 1.1
	50 wt.% VE-PML	4 ± 0.4	0.61 ± 0.03	80 ± 1.8	56 ± 6
E-Glass	0 wt.% x-linker	3.7 ± 0.5	0.58 ± 0.06	93.1 ± 4.5	50.3 ± 4.7
	0.3 wt.% x-linker	4.2 ± 0.4	0.64 ± 0.04	95.6 ± 3.2	62.7 ± 5
	0.7 wt.% x-linker	4.4 ± 0.4	0.67 ± 0.1	97.2 ± 1.7	65.5 ± 4
	1.1 wt.% x-linker	4.3 ± 0.6	0.67 ± 0.1	97.5 ± 0.4	66 ± 1
Kevlar	40 0/ VE DMI	1.72 ± 0.08	0.27 ± 0.01	86.9 ± 0.2	60 ± 0.1
Carbon	40 WI.70 VE-PML	3.71 ± 0.2	0.54 ± 0.05	100.8 ± 0.9	63.1 ± 0.6

Table 2.4: DMTA data of fiber reinforced composites.

Mechanical properties of the composites were also investigated by DMTA, and results are shown in Figure 2.6 and Table 2.4. Chain segmental mobility is enabled during the glass transition, which is indicated by the peak in the loss modulus (G") and drop in the storage modulus (G'). Also, G" peak temperature matches well with the T_g obtained by DSC and it depends on number of factors, but it is mainly related to the flexibility of the polymer chains. In cross-linked system, flexibility of the polymer chains is decreased, so T_g would be higher than if the same chains were not cross-linked. This can be clearly seen from the increase in the G" peak temperature, T_g , and Tan δ peak temperature when the cross-linking density increases for VE-PML, or DP-Mix/x-linker based composites. Effect of the cross-linking can also be seen from the plateau of the G' and G" at high temperatures. Composites with more cross-linking exhibit higher plateau modulus than those with less or no cross-linking.

2.4 Conclusion

These results demonstrate that bio-based, styrene-free, cross-linking resin can be formulated using vinyl functionalization to make thermoset PML or using a cross-linker with thermoplastic PLA with MMA as a reactive diluent. Physical properties reported here indicate that these resins are well-suited for preparing fiber reinforced composites. The physical properties of the composites can be further optimized by investigating different molecular weight polymers and comonomers. Additionally, 100% bio-based composites are imaginable by using natural fibers and pending the development of bio-based MMA. Bio-based thermoset resins offer promising potential for economic and environmental improvements.

APPENDIX



Figure 2S.1: a) DSC scan of *meso*-lactide b) Recrystallized pure *meso*-lactide crystals.

peak	ppm	PML	VE-PML	10361D	DP-13	DP-18	DP-24
a	1.53	3.02	501.71	3.04	3.04	3.05	3.06
b	5.14	1.00	166.68	1.00	1.00	1.00	1.00
c+d	4.33		4.79				
e	1.90		3.31				
f	6.08		0.96				
g	5.56		1.01				
h	3.38		2.16				
i	6.41		1.00				
j	5.84		1.01				

Table 2S.1: Peak integration areas of PML, VE-PML, 10361D and Degraded PLAs.



Figure 2S.2: Curing reaction exotherms of various VE-PML/MMA resin and initiator concentrations loaded in scintillation vials and immersed in an oil bath at room temperature.

CHAPTER 3: SUSTAINABILITY IN THE SINKS AND COUNTERTOPS. I. FORMULATION AND PHYSICAL PROPERTIES

3.1 Introduction

The conversation about the sustainable building, design and remodeling practices is an evolving one. Since the late 20th century, building occupants' expectations of a modern, ecofriendly, and comfortable lifestyle have increased the attention towards more sustainable cast polymers products. Cast polymers are artificially made, chemically bonded, mineral-filled polymeric materials that are casted and hardened to form solid materials of various shapes to meet the design requirements of end users. These products are utilized in the construction of vanity tops, kitchen slabs, countertops, bathtubs, exterior cladding and kitchen sinks[99, 100].

Cast polymers can be broadly divided into three categories- 1) Cultured Marble: It consists of ~24 wt.% unsaturated polyester resin (UPR) in styrene, ~74 wt.% Calcium carbonate (CaCO₃) and ~2 wt.% catalyst and pigments. Bathroom vanity tops, basins and shower surrounds are the most common applications due to its cost and ability to constructed in any desired shape. Gel coat is applied on the mold prior to cultured marble matrix curing to achieve waterproof, non-porous and durable surface. However, with age, gelcoat can crack, and exterior chemicals can sip into the product and can eventually extend throughout the porous material underneath[101]. 2) Engineered Stone: It is a man-made granite which includes quartz, polymer concrete and crushed marble stone. Majority of the engineered stone is made by Breton method[102] (compaction by vibrocompression vacuum process) which uses elastomeric molds in which a crushed stone/resin mix is cast on a moving belt. It constitutes 90-95 wt.% quartz and 5-10 wt.% resin. They are mostly used in kitchen countertops due to superior scratch and moisture resistance but integrated sink bowl options are limited[103]. 3) Solid surface: Materials feature of 30-40% acrylic or polyester resin and 58-68% Alumina trihydrate (ATH) filler and 2 wt.% catalysts/pigments. DuPont's Corian[®] material falls under this category and mainly used in bathroom, hospitals, schools, and offices[104]. Solid surface material is non-porous, easy to repair and can be fabricated to fit any space. Drawbacks includes poor heat resistance, and vulnerable to chemicals like nail polish remover or lacquer thinners.

It is understandable that there is no perfect surface material for every use and budget, but consumer's growing awareness of using eco-friendly products has made composite manufacturers to come up with countertops which are made from renewable and recycled materials. High pressure laminates (HPL) are one of the cheapest surface materials made from the kraft paper impregnated with melamine or phenol formaldehyde binders which are pressed under heat until it crosslinks and fuses into a thin thermoset plastic. HPL is then adhered to particle board or medium density fiber board. Baltix's Biosurf tabletop laminate uses polymer derived from soyabean and corn[105]. Like HPLs, PaperStone[®] and EcoTop[®] composite surfaces are made from post-consumer recycled paper, wood or bamboo fibers which are bound by the resin (50 wt.% of the final product) derived from the cashew-nut hulls and corn. These products require sealing and should be protected from the prolonged water exposure [106, 107]. Glass composites from Vetrazzo[®] use 100% recycled glass or porcelain along with epoxy and portland cement to provide stone like look to the countertops[108]. ECO[™] by Cosentino uses ~25% polyester resin derived from corn polyols along with recycled content that comes from the windshields, bottles, stone scrap and industrial byproducts[109].

Natural stone, such as granite, limestone, quartzie are still popular countertops due to its beauty and easy maintenance, but they are mined in an energy intensive process and known to crack under excessive heat and must be sealed regularly[110]. One of the bio based engineered

stone example where, 50 wt.% of the resin (epoxidized triglycerides and carboxylic anhydride) used was derived from the vegetable oil[111]. Durat[®] and Cristalplant[®] is a polyester-based solid surface material which contains about 30% recycled post-consumer plastics and 30% corn derived polyester resin respectively[112, 113]. Alkemi-acrylic is another solid surface alternative, made using pre-consumer aluminum and copper flake waste, solid surface scrap and recycled acrylic[114].

Styrene is the most common reactive diluent or hardener in the cultured marble and engineered stone-based resin due to its low cost and robust thermal and mechanical properties of PS. However, industry is striving for an alternative due to health-related issues associated with styrene[42]. Solid surface material is bound together by petroleum derived acrylic resin where major component is PMMA dissolved in MMA as a reactive diluent. Various bio-based reactive diluents have been reported in the literature. Methacrylated fatty acid monomers from soybean oil[115], methacrylated cardanol from cardanol oil[71], carbohydrate derived isosorbide[116], methacrylates from vanillin[73], eugenol[117] and guaiacol from lignin[72] and renewably sourced fumaric acid [74] are few examples but T_g , inadequate viscosity, low mechanical properties limit their use in composite applications. On the other hand, MMA is a ubiquitous monomer in the polymer, paint and adhesive industries, but it is produced through multistep, petroleum derived substrate with harsh reaction conditions[118]. Even though PMMA has the similar thermal and mechanical properties as that of PS, it is not commercially derived from the bio renewable sources. However, recent work shows the evidence of one-step synthesis of MMA from bio-mass itaconic acid and methanol using hexaaluminate catalysts[119].

Recently, Moran *et.al.*[43] formulated low viscosity bio-based thermosetting resin with vinyl terminated PLA oligomers dissolved in MMA as a reactive diluent. This novel styrene free,

bioresin was successfully utilized to make fiber reinforced composite (FRC) material and mechanical properties were on par to that of the incumbent resins. Dylan *et al.*[40] further quantitatively characterized the fundamental solution properties of PLA in MMA through series of rheology and multiple angle light scattering experiments to show that MMA is a good solvent for PLA. If MMA commercially becomes available from biomass, then a resin system utilizing PLA and MMA is bound to give excellent sustainability metrics.

Therefore, it is instinctive to explore the use of economically attractive, styrene free, PLA/MMA based biobased resin system other than FRCs. To the best of our knowledge, we are for the first-time introducing bio renewable resin system formulated using PLA and MMA in to cultured marble and solid surface formulation. Thermoset PLA was synthesized by ring opening polymerization of lactides by 2-hydroxyethyl methacrylate (HEMA)[120] followed by end-capping with itaconic anhydride (ITA) and thermoplastic PLA was obtained by degradation of high molecular weight commercial PLA. Formulation and physical properties of these novel bio composite cast polymers are provided. Finally, we have demonstrated the utility of our bio resin by fabricating a prototype of a "Drop-in-Bowl" by collaborating with a local cultured marble manufacturing company.

3.2 Experimental

3.2.1 Materials

L- and *meso*-Lactides were obtained from NatureWorks and further recrystallized in ethyl acetate (Fisher Chemical, purity >99.9%). HEMA (Sigma-Aldrich, purity >99%, Monomethyl ether hydroquinone <50 ppm as inhibitor) and Itaconic anhydride (Sigma-Aldrich, purity >95%) were used as received. Tin(II)-2-ehtylhexanoate (Sigma-Aldrich, purity 92.5-100%) was distilled under vacuum before use. ACS grade chloroform and methanol (VWR international) were used as

received. MMA (Sigma-Aldrich, Purity 99%, Monomethyl ether hydroquinone <30 ppm as inhibitor) was stored in the refrigerator and used as received. N,N-Dimethyl-p-toluidine (DMT) (Sigma-Aldrich) and Benzoyl Peroxide (BPO) solution Luperox® AFR40 (Sigma-Aldrich) were stored in the refrigerator and used as received. Amorphous grade commercial PLA pellets, named Ingeo 10361D, were provided by NatureWorks. ATH ($1.3 \text{ m}^2/\text{g}$, mean particle diameter 16 µm) and CaCO₃ ($0.21 \text{ m}^2/\text{g}$, mean particle diameter 60 µm) was donated by Huber Materials and used as received. Recycled PET flakes were donated by Clean Tech Inc. and were grinded in a blender with dry ice to produce ~250 µm to 1-2 mm size powder (rPET) (Figure 3S.5). BYK C-8002 as an adhesion additive between ATH and acrylic matrix was donated by BYK and used as received. Ethylene glycol dimethacrylate (EGDMA) (Sigma-Aldrich, Purity 98%, 90-110 ppm monomethyl ether hydroquinone as inhibitor) cross-linker was used as received. Fiberglass mold for "Drop-in-Bowl" was donated by Marshall Gruber company.

3.2.2 Methods

Large scale vinyl terminated poly(lactide) (VE-PLA) preparation: 1500 g of Lactide (60:40 weight ratio of L:*meso*) (80:20 L:D enantiomeric content) was loaded in the 5L flame dried reaction vessel with stir bar and dried under vacuum for 2 days at 40 °C. After drying, the reaction vessel was sealed with a rubber septum and purged with argon for 10 minutes followed by melting of lactide in an oil bath at 130 °C under magnetic stirring. HEMA (1 mol HEMA per 71 mol of lactide units) was added using syringe in the melted pool of lactide and stirred for 30 minutes followed by Tin(II) 2-ethylhexanoate (1 mol Tin(II) 2-ethylhexanoate per 2500 mol lactide) addition. HEMA initiated polymerization was carried out for 18 hours at 130 °C (Scheme 3.1A). The vessel was quenched in an ice bath and chloroform was added to make a 50 wt.% solution. Itaconic anhydride (2:1 molar excess) and Tin(II) 2-ethylhexanoate (1% w/w PLA) were added. The end-

capping reaction, as shown in Scheme 3.1B, was carried out on heating mantle with magnetic stirring and refluxed for 8 hours. A VARIAC was used to maintain a steady boiling rate so that a balloon covering the top of the condenser remained erect but not inflated. PLA solution after both reactions were precipitated into 10:1 volume excess of methanol, dried in a vacuum oven for room temperature for 48 hours followed by 40 °C for 72 hours. Finally, dried polymer was crushed mortar and pestle, and stored in plastic pails before use. Overall yield of the reaction was ~90%. Large Scale Degraded PLA Oligomers Preparation: As mentioned in Chapter 2, 1200 g of commercial 10361D PLA pellets were hydrolyzed in 1200 g of DI water at 90 °C in convection oven for various times. DP-13, DP-18 and DP-24 were hydrolyzed for 13, 18 and 24 hours, respectively (Scheme 3.1D). These hydrolyzed or degraded PLAs were dried in the vacuum oven at room temperature for 48 hours followed by 40 °C for 72 hours.

NMR: ¹H-NMR spectra of 6.25 wt.% polymer solutions in CDCl₃ were obtained using Bruker Avance 300 MHz spectrometer. The spectra were analyzed using MNova NMR software.

GPC: The GPC system contained an Agilent PLgel 5µm MIXED-C column, a Wyatt DAWN DSP Laser Photometer, and a Wyatt OPTILAB DSP Interferometric Refractometer. The light scattering detector was calibrated using toluene and normalized to the 90° detector using monodisperse poly(styrene) with 30 kg/mol molecular weight. The refractometer was calibrated by injecting various concentrations of polystyrene in THF (dn/dc=0.185). PLA samples were measured in chloroform at 35 °C (dn/dc=0.024 mL/g). Solutions of approximately 10 mg/mL were filtered once through a 0.45 µm poly(tetrafluoroethylene) syringe filter prior to injection.

DSC and TGA: DSC was performed using a Q20 TA DSC calibrated with Indium standard. Approximately 2-3 mg of Lactide crystals were sealed in aluminum pan in N₂ filled glove bag and purity was measured by scanning at 1 °C/min. Approximately 10-15 mg of dried polymers or 3040 mg of powder filled composites were sealed in an aluminum pan. Scanning protocol for DSC was- hold for 5 min at -40 °C, heat from -40 °C to 200 °C at 10 °C/min, hold for 5 min at 200 °C, cool from 200 °C to -40°C at 5 °C/min, heat from -40 °C to 200 °C at 10 °C/min. Glass transition temperatures were assigned using the half height method, which is the temperature at which a sample's heat capacity is halfway between the difference of its glassy and rubbery state heat capacities. TGA was performed using TGA Q500. Approximately 10 mg of samples were loaded in platinum pan and heated under nitrogen from 25 °C to 600 °C at 20 °C/min.

Resin Preparation: DP-13 and DP-18 were dissolved in MMA to make 20 wt.% and 40 wt.% of the thermoplastic PLA in MMA solutions. VE-PLA was dissolved in MMA to make 40 wt.% of the thermoset PLA in MMA solution.

Viscosity Measurement: PLA/MMA resin and powder filled slurry viscosities were measured using Anton Paar MCR 302 equipped with 25 mm, 2° cone and with Peltier cooling plate. Steady rotational shear sweeps were executed at 20 °C.

Cast Polymer Samples Acquisition, Fabrication and Curing Exotherm Measurement: Commercial granite and cultured marble samples were donated by Marblecraft Company. Commercial Corian[®] solid surface and Quartz sample were donated by Mica Crafter Inc. and Lowe's respectively. Slurry of ATH or CaCO₃ or ATH + rPET filled composites were prepared in two step mixing. In the first overhead mixing step, ATH or CaCO₃ or ATH+rPET powder was added slowly in the thermoplastic or thermoset PLA/MMA solution (with predissolved amount of 0.08 wt.% DMT) and mixed at 200 to 800 rpm at room temperature along with 0.6 wt.% addition of BYK C-8002. After one minute, mixing was stopped, and sample container was transferred to vacuum mixing set up where pressure was reduced by 25″ inHg and mixed at 1200 rpm to remove air bubbles from the slurry. After 30 to 45 seconds of mixing, 0.14 wt.% BPO was added in the slurry and mixed

for one minute at 1500 rpm under vacuum before casting it in the custom-made 8"×8"×1" rectangular mold made from Al angle bars on a PET film. Finally, mold was covered with 0.1 mm PET film and Al plate. After overnight curing, casted plates were post cured in the convection oven at 90 °C for 8 hours. For solid surface formulation, 39 wt.% resin, 60 wt.% ATH and 1 wt.% of catalyst, cross-linker and adhesion additives were used. For solid surface with recycled PET (rPET), 39 wt.% resin, 50 wt.% ATH, 10 wt.% rPET and 1 wt.% of catalyst, cross-linker and adhesion additives were used. For solid surface mixtures made from 40 wt.% VE-PLA, 20 wt.% DP-13 and 40 wt.% DP-18 are denoted as SS (40 wt.% VE-PLA), SS (20 wt.% DP-13) and SS (40 wt.% DP-18) respectively. Cultured marble mixture made from 40 wt.% DP-18 will be denoted as CM (40 wt.% DP-18).

Tensile Testing: Tensile testing was performed according to ISO-D638 using a UTS electromechanical frame with 1000 lb. load cell, wedge grips and UTS extensometer. Samples were cut from $\frac{1}{2}$ inch thick plates. Sample dimensions were approximately 165 mm × 12.5 mm × 6 mm and ends were tabbed with $\frac{1}{16''}$ thick garolite sheet. A pre-stress of 5 lb. was applied followed by crosshead speed of 0.05 inches/min.

DMTA: Dynamic mechanical thermal analysis (DMTA) was conducted using an ARES-G2 rheometer equipped with torsional rectangular fixtures. Polished rectangular specimen (~ $60 \times 12 \times 2 \text{ mm}^3$) were heated from 25 °C to 180 °C at 5 °C /min with fixed strain (0.03%) and frequency (1.0 Hz)

Boiling Water Resistance (BWR): BWR test was conducted using NEMA LD 3.5 where flat bottom Aluminum (Al) vessel (90 mm diameter \times 76 mm high \times 2.4 mm thick) was filled up to $\frac{1}{2}$ from the rim and heated till water boiled vigorously. With tongs, hot Al vessel was removed

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carefully and ~ 10 ml of boiling water was poured on the horizontal surface of the test specimen. Then hot Al vessel containing the remainder of the boiling water is set on top of the 10 ml puddle for 20 minutes.

SEM: SEM samples (casted and polished in an epoxy resin) were coated with Pt and images were acquired using Zeiss Auriga Crossbeam microscope.

3.3 Results and Discussion

As shown in scheme 3.1, >kg quantities of vinyl terminated VE-PLA were successfully synthesized from pure (>99.4 %) recrystallized lactide crystals (Figure 3S.1). Also, >kg quantities of low molecular weight PLAs were obtained from the degradation of commercial high molecular weight PLA 10361D in DI water. ¹H-NMR spectra in Figure 3.1A, were used to validate the polymer structure. Commercial PLA 10361D shows the two peaks, a, and b, assigned to methylene and methine protons, respectively, along the backbone. For VE-PLA, HEMA and itaconic acid end-groups are visible by peaks c-g and peaks h-j respectively. Peak integrations of ¹H-NMR spectra are reported in Table 3S-1. Integration of end-group proton (peak g) indicates ~6% of PLA chains in VE-PLA were monofunctional and were initiated by adventitious water molecules.



Scheme 3.1: A) Ring opening polymerization of Lactides by HEMA. B) End-capping with Itaconic anhydride to make VE-PLA. C) Room temperature free radical polymerization of VE-PLA with MMA. D) Degradation of commercial 10361D PLA in DI water at various times and E) Room temperature free radical polymerization of MMA with degraded PLA and EGDMA as a cross-linker.

As shown in Figure 3.1, molecular weights were determined by both GPC and ¹H-NMR and reported in Table 3.1. Thermal properties were investigated using DSC and TGA. Commercial PLA 10361D and synthesized VE-PLA were completely amorphous because presence of 8-50% of D-isomer in the backbone which prevents the PLA chains from crystallizing[16]. Even though 10361D was amorphous, first heating scan of degraded PLAs exhibited melting peak around 115 °C. This is a characteristic of low molecular weight semi-crystalline PLA. This phenomenon could be arising from the random hydrolysis of high molecular weight PLA by water such that lower molecular weight chains do not have enough D-isomer to prevent it from crystallizing.



Figure 3.1: a) ¹H-NMR b) DSC c) GPC and d) TGA of VE-PLA, 10361D and Degraded PLAs.

PLA type	Mw (g/mol)	Mn (g/mol) by GPC	Mn (g/mol) by NMR	PDI	<i>Tg</i> (°C)	<i>T</i> _{peak} (°C)	<i>T</i> _{<i>d</i>-10} (°C)
VE-PLA	9900 ± 1500	6000 ± 700	4200 ± 100	1.64 ± 0.10	30.6	244	
10361D	65900 ± 3900	42800 ± 4100		1.54 ± 0.06	55	379	344
DP-13	28100 ± 1400	15700 ± 600		1.79 ± 0.03	51	375	333
DP-18	11200 ± 2400	6000 ± 800		1.87 ± 0.27	43.1	362	299
DP-24	7800 ± 2100	3800 ± 600		2.08 ± 0.34	34.5	361	277

Table 3.1: GPC, DSC, NMR and TGA data of VE-PLA, 10361D and Degraded PLAs

The viscosity of the polymerizable mixture is important in cast polymers manufacturing because it can affect the processing conditions, solids loading, and physical properties of the final product. For ATH filled solid surfaces, preferable viscosity of the PMMA/MMA polymer solution

is ~0.05-5 Pa.s[121]. 40 wt.% of VE-PLA, 20 wt.% of DP-13 and 40 wt.% of DP-18 polymers were dissolved in MMA and solution viscosities by the shear sweep data in Figure 2 were determined to be 0.051, 0.11 and 0.098 Pa.s respectively. A semi-empirical equation developed by our group was also used to predict the viscosities of the above three PLA/MMA solutions as a function of product of polymer concentration (c) and intrinsic viscosity ([η])[40] which shows good agreement between the measured and predicted viscosity values. Also, the temperature evolution during curing of one of the solid surface formulations was measured as shown in Figure 3S.2.



Figure 3.2: Measured viscosities (circled) of PLA/MMA solutions compared with predicted (line) $c[\eta]$ as a function of shear rate at 20 °C.

As shown in Figure 3.3, the morphology of the polished cast polymer samples was characterized by SEM. Granite is a natural igneous stone formed by the slow cooling of hot lava

below the earth's crust which is quarried directly from the mountains. Grain boundaries and some voids can be seen in the Figure 3.3a. For quartz (Figure 3.3b), tight packing of filler having particle size from 0.5 µm to 50 µm can be observed. Cultured marble sample obtained from Marblecraft [CM (Marblecraft)] (Figure 3.3c), also had a wide distribution of particles but some voids and gap between the CaCO₃ particles and UPR/polystyrene matrix can be seen indicating lack of adhesion between CaCO₃ and UPR/Styrene matrix. Cultured marble made from our resin (Figure 3.3f) also has interfacial separation between CaCO₃ and PLA/PMMA resin. Corian[®] solid surface (Figure 3.3d) appears to have ATH particles with round/etched edges. Like Corian[®] sample, our solid surface material (Figure 3.3e, 3.3g, 3.3h, 3.3i) do not have any voids and has well dispersed ATH particles with excellent adhesion between PLA/PMMA matrix.



Figure 3.3: SEM images of a) Granite b) Quartz c) CM (Marblecraft) d) SS (Corian[®]) e) SS (20 wt.% DP-13) f) CM (40 wt.% DP-18) g) SS (40 wt.% VE-PLA) h) SS (40 wt.% DP-18) i) SS (40 wt.% DP-18 w/rPET)

Thermal properties and SEM images of filler material used in this study is shown in Figure 3S.3 and 3S.4 respectively. 66.2 %. 99.6 % and 12.3 % material remaining at the end of TGA run for ATH, CaCO₃ and rPET respectively. T_g (Figure 3.4a) and thermal stability (Figure 3.4b) of granite and cast polymers were measured by DSC and TGA and summarized in Table 3.2. As expected, the absence of glass transition in the DSC scan and the lack of degradation in TGA run,

granite is 100% natural stone without any resin. Both Quartz and CM (Marblecraft) has UPR/Styrene resin with a T_g of 47.4 °C and 45.5 °C respectively. Also, 89.5 % of material was left at the end of the TGA run for Quartz indicating 10.5% resin. Corian[®] solid surface had a good thermal stability with T_g of 107.6 °C and 43.6 % material remaining at 560 °C. Our PLA/MMA resins also exhibited good thermal stability with T_g of 89.8 °C, 70 °C, 72.2 °C, 69.9 °C and 40.2 %, 40.9 %, 40.4 %, 34.3% material remaining at 560 °C for SS (20 wt.% DP-13), SS (40 wt.% DP-18), SS (40 wt.% VE-PLA) and SS (40 wt.% DP-18 w/rPET) respectively. Even though inclusion of 10 wt.% rPET increased the recycled content in the solid surface matrix, we did not observe any noticeable difference in the T_g or thermal stability. BWR test (Figure 3S.6) on PLA/MMA solid surface with 40 wt.% DP-18 formulation, did not show any visible change on the casted surface after 20 minutes contact of hot Al container filled with boiling hot water.



Figure 3.4: a) DSC and b) TGA of granite and cast polymers.

The mechanical properties are important to determine the feasibility of the granite and cast polymers in various household applications. Inclusion of powders in the resin improves the compression of the composite, but it is also important to improve the interfacial adhesion between the resin and particulates as fine particles are only mechanically embedded in the resin matrix. Figure 3.5 shows the tensile properties of the cast polymers. It is evident that granite had the lowest tensile strength and elongation of them all as it do not have any resin. It was not feasible to measure the tensile modulus of granite due its brittle nature and sensitivity limit of the UTS testing machine. It is intriguing to observe that Quartz having a highest tensile strength among all the cast polymers with just 10.5% resin as opposed to Corian material which has ~38% acrylic resin. Tensile performance of our cultured marble and solid surface is on par to that of the commercial counterparts.



Figure 3.5: a) Tensile Strength b) Elongation c) Tensile Modulus of granite and cast polymers.



granite and cast polymers from DMTA tests. The room temperature storage modulus is function of solid loading in the material with granite (no resin) having the highest value of 12.9 GPa followed by 10.4 GPa for Quartz (10.5 wt.% resin), 5.9 GPa for CM (Marblecraft) (24 wt.% resin), 5.2 GPa for CM (SS 40 wt.% DP-18) (26 wt.% resin) and 3.4 GPa for SS (Corian[®]) (38 wt.% resin). Solid surface made from our PLA/MMA resin had a comparable room temperature modulus to that of Corian[®] with a value of 3.3 GPa, 3.1 GPa and 3.5 GPa for 20 wt.% DP-13, 40 wt.% VE-PLA and 40 wt.% DP-18 based resins respectively.



Figure 3.6: DMTA of granite and cast polymers.

Material	Tensile Modulus	Tensile Strength	Tensile Elongation	Tg	<i>Td</i> -10	Tpeak-1,2,3	G' 30 °C	G" Peak Temperature	Tan δ peak Temperature
1,14,001141	(GPa)	(MPa)	(%)	(°C)	(°C)	(°C)	(GPa)	(°C)	(°C)
Granite	-	5.4 ± 1	0.04 ± 0.02	-	-	-	12.9	-	-
Quartz	26.3 ± 3.7	37.5 ± 2.6	0.15 ± 0.02	47.4	386.9	339.1	10.5	53	80
CM (Marblecraft)	14.4 ± 1.1	21.8 ± 0.5	0.14 ± 0.02	45.5	326.4	332.5	5.9	52	76.4
SS (Corian [®])	9.5 ± 2.1	30.4 ± 2.7	0.35 ± 0.08	107.6	250.6	264.4, 313.3, 350.9	3.4	97	120.4
SS (20 wt.% DP-13)	9.8 ± 2.2	27.1 ± 2.3	0.3 ± 0.1	89.8	241.5	256.3, 338.7	3.3	77	113.3
CM (40 wt.% DP-18)	12 ± 1.1	20.3 ± 1.8	0.15 ± 0.04	69.9	268.9	244.7, 349.8	5.2	65	101.2
SS (40 wt.% VE-PLA)	9.6 ± 2.3	27.5 ± 2.6	0.3 ± 0.1	72.2	242	255.2, 367.5	3.1	62	88
SS (40 wt.% DP-18)	9.9 ± 2.2	20.9 ± 0.2	0.2 ± 0.1	70	252.9	257.4, 308.9, 347	3.5	61	101.2
SS (40 wt.% DP-18 w/rPET)	7.4 ± 2.4	15.2 ± 1.2	0.18 ± 0.07	69.9	254	256.3, 303.9, 344.3, 406	2.2	60	101.3

Table 3.2: Summary of Tensile, Thermal and DMTA results of cast polymers

Figure 3.7a shows that economically it is advantageous use PLA/MMA based resin because PLA is commercially available at ~\$1.87/kg which is cheaper than PMMA (\$2.76/kg), UPR (\$2.65/kg) and VER (\$4.19/lb). However, on the reactive diluent side, styrene (\$0.91/kg) is cheaper than MMA (\$1.15/kg). But, when formulated to make 40 wt.% resin, PLA/MMA turns out to be a cost-effective option than incumbent resins used in cast polymer composition.



Figure 3.7: a) Per kg price of 40 wt.% resins from the average of process of economic program and alibaba.com. b) Impact categories as available in Ecoinvent 3.2 and reported using SimaPro 9.3 with IMPACT 2002+ V2.15 midpoint indicator for 1 kg of 40 wt.% resin with world as a geographical location.

	Climate Change	Carcinogens	Non-renewable Energy		
For 40 wt.% Kesin	(kg CO ₂ eq.)	(kg C ₂ H ₃ Cl)	(MJ Primary)		
PLA/MMA	4.737	0.060	88.679		
PMMA/MMA	6.205	0.068	123.665		
UPR/Styrene	2.889	0.204	89.353		
VER/Styrene	3.253	0.223	95.397		
PLA/Styrene	2.690	0.158	69.915		

Table 3.3: LCA impact assessment results obtained from SimaPro

Figure 3.7b and Table 3.3 shows the general information about the environmental impact of selected resin formulations. Such comparison is effective only if formulation condition of the resins is similar. Climate change (kg of CO₂ eq.) impact of PLA/MMA is ~24% lower than that of

PMMA/MMA based formulation but \sim 39% and 31% higher than that of UPR/Styrene and VER/Styrene based formulations. This is primarily because the environmental impact (kg of CO₂ eq.) of MMA has a higher than that of styrene. However, in the case of carcinogens (kg C₂H₃Cl) emission and use of non-renewable energy, PLA/MMA based resin is superior to other options.



Figure 3.8: Fabricated Drop-in-Bowl from the PLA/MMA bioresin at Marblecraft

Figure 3.8 shows the picture of Drop-In-Bowl casted at a local cultured marble manufacturing company Marblecraft in Fowlerville, MI with final formulation of 15.86 wt.% PLA,

23.80 wt.% MMA, 60.28 wt.% ATH and 0.05 wt.% BPO/DMT (1:1 mol ratio). Owners of Marblecraft were excited to observe that gel coat was not required on the mold prior to fabrication which would ultimately save the time and resources at manufacturer's end. Cured bowl was demolded next day and to owner's surprise it turned out to be an excellent useable sink in the first attempt.

3.4 Conclusion

This research showcases one of the ways to create sustainable countertops and sinks by understanding the need to become steward of the environment in present times. Tensile properties of novel PLA/MMA bioresin cast polymers were comparable with commercial resin system. Thermal stability can be tuned with the molecular weight of PLA, cross-linking, formulation, and amount of resin used in the system. For the first time ever, we have incorporated bio renewable PLA into cast polymer composition and demonstrated its utility by fabricating a prototype of a relevant commercial product which not only improves the sustainability metrics, but our composite resin can also enable material circularity which prevents wasting of embodied energy at the end of products life.
APPENDIX



Figure 3S.1: DSC of recrystallized *meso-* and L-Lactides.

peak	ppm	VE-PLA	10361D	DP-13	DP-18	DP-24
а	1.53	173.72	3.04	3.04	3.05	3.06
b	5.14	57.43	1.00	1.00	1.00	1.00
c+d	4.33	3.74				
e	1.90	2.96				
f	6.08	0.88				
g	5.56	0.94				
h	3.38	2.16				
i	6.41	1.00				
j	5.84	1.12				

Table 3S.1: ¹H-NMR spectra integration areas of peaks a-j



Figure 3S.2: Temperature rise during room temperature curing of ATH filled SS (40 wt.% DP-18) with BPO/DMT catalyst system.



Figure 3S.3: a) DSC and b) TGA of ATH, CaCO₃ and rPET.



Figure 3S.4: a) and b) Raw CaCO₃ powder. c) and d) Raw ATH powder.

~15-20 mm PET Flakes



1-2 mm

<250 µm

PET Powder





Figure 3S.6: a) $8" \times 8" \times 0.5"$ solid surface plate from 40 wt.% DP-18 PLA/MMA resin b) DI water boiled in an Al container then placed on the solid surface plate for 20 min c) PLA/MMA solid surface plate after 20 min d) Bottom surface of the Al container after the test.

CHAPTER 4: SUSTAINABILITY IN THE SINKS AND COUNTERTOPS. II. CHEMICAL RECYCLING THROUGH BASE SOLVOLYSIS

4.1 Introduction

Polymer composites combine resins and epoxies with reinforcing fibers or minerals to create indispensable materials that has transformed our everyday lives. We take the advantage of durability, design flexibility, resilience, and superior specific mechanical properties of polymer composites in automotive, aerospace, construction, marine, sports equipment, and energy sectors as these materials improve strength, stiffness, impact resistance and corrosion resistance along with long lifespan[8, 122, 123]. However, in recent years, sociotechnical awareness for developing sustainable composite recycling solution is growing[45]. Major contributing factors like composite wind turbine blades reaching their end-of-life[124], decommissioning of aircrafts[125], mass production of increased electric composite cars driven by zero-emission goals[126] are pushing the researchers to develop green chemistries and to recycle and reuse the high value composite parts. Architects and homeowners are also championing the benefits of green building design as construction of residential and commercial buildings accounts for almost 40% of the U.S. CO₂ emission[127].

Glass is most used fiber type in fiber reinforced composite (FRC) materials due to its cost, mechanical strength, thermal stability, chemical and wear properties[128]. In particulate filled composites (PFC), CaCO₃ is the most widely used organic filler followed by carbon black, kaolin or clay, talc, silica, and alumina trihydrate or ATH (Al₂O₃.H₂O). Fillers are added in the composites to reduce cost, reduce shrinkage during polymerization or molding, reduce flammability, improve dimensional stability, increase compressive strength and stiff resistance[129, 130]. Thermosetting resin such as epoxy, vinyl ester (VER), unsaturated polyester

(UPR) and poly(urethane) dominate the composite materials market but, use of thermoplastics like polyethylene, polypropylene, polyamides, polyether ether ketone, polysulfone, polyphenylene sulfide and acrylic resins are also prevalent due to ease in processing, welding of composite parts, recovery of fibers and polymer matrix[38, 131-134]. Polymer matrix apart from imparting the chemical, abrasion, and moisture resistance, holds the fiber or particulate reinforcement together in place and transfers load to them. Whether it is fibers, minerals, or polymer matrix, an "end-oflife" solution for composite material is necessary to minimize the environmental impacts.

Various recycling options has been demonstrated for FRCs[45, 135]. 1) Mechanical recycling or grinding is chopping and reusing the recovered materials with or without fiber/matrix separation. Usually recovered fibers are most valuable but polymer matrix can also be beneficial if recycling cost is lower than the cost of raw materials[136]. 2) Pyrolysis employs high temperatures (450-600 °C) to recover fibers from thermoset or thermoplastic matrix[51]. Although recovered fibers from pyrolysis have lower mechanical properties as compared to composites made from virgin counterparts, recovered oil and hydrocarbons can be used to provide the energy for the reaction[137]. 3) Solvolysis involves breaking of covalent bonds of polymer matrix using reactive solvent at elevated temperature and pressure[138]. Compared to pyrolysis, solvolysis avoids the formation of char contamination on the recycled fiber surface which can prevent the good interaction with new polymer matrix[139].

Recovery and recycling from the filled polymer composites sound to be sensible and straightforward but, there are hurdles which prevents it to be a commercial success as bulk particulate fillers are available at low cost and recycled powders do not meet the specific characteristics as that of virgin raw materials[129]. However, recovery and recycling of carbon black via pyrolysis is receiving much attention because it is relatively expensive filler and in elastomer applications, especially tires consume 30% of worldwide carbon black production[140, 141]. It can be argued that while not renewable, common minerals like CaCO₃ and ATH are available in abundance and thus depletion is not an immediate concern. However, environmental impact of their extraction and quarrying cannot be overlooked. For example, limestone (composed mostly of CaCO₃) is often mined from quarry and environmental hazards from mining operations depends on location, characteristics and extent of mining operations.[142] Multiple adverse impacts observed are leakage of CaCO₃ in groundwater, habitat loss, noise pollution, dust emission and changes in aquifer regimes[143]. ATH is manufactured during Bayer process where bauxite is digested with alkali solution followed by purification and crystallization of ATH from a liquor rich in dissolved aluminum and one of the major environmental issue is the disposal of bauxite residue commonly called red mud[144, 145]. Globally, ~3 billion tons of red mud are stored in waste ponds or dry mounds contaminating nearby rivers and ecosystems by poisoning the soil and ground water through leaching of residual alkaline chemicals[146].

Remodeling of kitchen or bathroom inevitably also produces waste. According to environmental protection agency (EPA), in 2018, approximately 600 million tons of construction and demolition waste was generated in the United States[147]. Some of the waste like sinks and countertops which are still valuable and rather than putting them in landfill, we must explore the recycling options and try to recover the embedded energy from such articles. This research proposes one of such option where the solid surface drop-in-bowl sink was fabricated using a completely recyclable bio renewable poly(lactide) resin with MMA as a reactive diluent and ATH as a filler. Raw materials were recovered via mild solvolysis (40 °C) method using a simple base bath which is usually a solution of water, isopropanol (IPA) and potassium hydroxide (KOH). Utility of this approach was further demonstrated by conversion of recovered components into edible food ingredients and superabsorbent polymer.

4.2 Experimental

4.2.1 Materials

MMA (Sigma-Aldrich, Purity 99%, Monomethyl ether hydroquinone <30 ppm as inhibitor) was stored in the refrigerator and used as received. N,N-Dimethyl-p-toluidine (DMT) (Sigma-Aldrich) and Benzoyl Peroxide (BPO) solution Luperox® AFR40 (Sigma-Aldrich) were stored in the refrigerator and used as received. Methanol, Isopropanol (IPA) and Potassium hydroxide (KOH) were purchased from VWR and used as received. Ethylenediamine (EDA) was purchased from Sigma-Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide was purchased from TCIchemicals. Amorphous grade commercial PLA pellets, named Ingeo 10361D, were provided by NatureWorks. ATH ($1.3 \text{ m}^2/\text{g}$, mean particle diameter 16 µm) was donated by Huber Materials and used as received. Fiberglass mold for "Drop-in-Bowl" was donated by Marshall Gruber company. Solvolysis bath had a composition of 4L IPA:1L DI water:250 g of KOH.

4.2.2 Methods

Degraded PLA (DP-24) Oligomers Preparation: As mentioned in Chapter 2, 1200 g of commercial 10361D PLA pellets were hydrolyzed in 1200 g of DI water at 90 °C in convection oven for 24 hours. These were dried in the vacuum oven at room temperature for 48 hours followed by 40 °C for 72 hours.

NMR: ¹H-NMR spectra were obtained using Bruker Avance 300 MHz spectrometer. The spectra were analyzed using MNova NMR software.

GPC: The GPC system contained two Agilent PLgel 5µm MIXED-C column in series, a Wyatt DAWN DSP Laser Photometer, and a Wyatt OPTILAB DSP Interferometric Refractometer. The light scattering detector was calibrated using toluene and normalized to the 90° detector using

monodisperse poly(styrene) with 30 kg/mol molecular weight. The refractometer was calibrated by injecting various concentrations of polystyrene in THF (dn/dc=0.185). PMMA and PLA samples were measured in chloroform at 25 °C (dn/dc=0.06 mL/g and 0.024 mL/g for PMMA and PLA respectively). Solutions of approximately 10 mg/mL were filtered once through a 0.22 μ m poly(tetrafluoroethylene) syringe filter prior to injection.

DSC and TGA: DSC was performed using a Q20 TA DSC calibrated with Indium standard. Approximately 10-15 mg of dried polymers or 30-40 mg of powder or powder filled composites were sealed in an aluminum pan. Scanning protocol for DSC was- hold for 5 min at -40 °C, heat from -40 °C to 200 °C at 10 °C/min, hold for 5 min at 200 °C, cool from 200 °C to -40°C at 5 °C/min, heat from -40 °C to 200 °C at 10 °C/min. Glass transition temperatures were assigned using the half height method, which is the temperature at which a sample's heat capacity is halfway between the difference of its glassy and rubbery state heat capacities. TGA was performed using TGA Q500. Approximately 10 mg of samples were loaded in platinum pan and heated under nitrogen from 25 °C to 600 °C at 20 °C/min.

DP-24 resin preparation: DP-24 was dissolved in MMA to make 40 wt.% of the thermoplastic PLA in MMA solution.

Casting of Drop-In-Bowl and small discs of solid surface: Drop-In-Bowl was casted at a local cultured marble manufacturing company in Fowlerville, with 39.66 wt.% of 40 wt.% DP-24 in MMA, 60.28 wt.% ATH and 0.05 wt.% BPO/DMT (1:1 mol ratio). Leftover slurry was used to cast solid surface discs in 90 mm diameter glass petri dishes and cured overnight followed post curing at 90 °C for 8 hours.

DMTA: DMTA was conducted using an ARES-G2 rheometer equipped with torsional rectangular fixtures. Polished rectangular specimen ($\sim 60 \times 12 \times 2 \text{ mm}^3$) were heated from 25 °C to 180 °C at

5 °C /min with fixed strain (0.03%) and frequency (1.0 Hz).

SEM: Powders for SEM samples were coated with Pt and images were acquired using Zeiss Auriga

Crossbeam microscope.

4.3 Results and Discussion



Figure 4.1: a) Fabricated PLA/MMA based biorenewable solid surface Drop-In-Bowl b) Casting of Drop-In-Bowl and solid surface discs at Marblecraft c) Solvolysis of solid surface disc in the base bath d) Leftover base bath e) Recovered ATH f) Recovered PMMA

As shown in picture 4.1a and b, PLA/MMA based Drop-In-Bowl was casted at a local marble manufacturing company. Leftover slurry was used to cast the 90 mm discs of solid surface which were used for the solvolysis study. 5L of solvolysis bath was used to digest one 165 g of cured thermoplastic solid surface disc at 40 °C. As we can see in the picture 4.1c, almost half of the disc was digested in 30 days. After two months, entire disc was fully digested, and ATH powder (Figure 4.1e) was filtered and washed thoroughly with water and dried at 80 °C in vacuum oven for 3 days. The collected solution (Figure 4.1d) was cooled down to room temperature and PMMA (Figure 4.1f) layer was removed by vacuum filtration which was further washed thoroughly with water and dried under vacuum at 80 °C for two days.



Figure 4.2: a) GPC of recovered PMMA b) Spartan gummy candies from the recovered potassium lactate c) NMR spectra of i) DP-24 ii) Recovered PMMA iii) PMAA iv) Recovered potassium lactate v) Commercial potassium lactate vi) Recovered IPA.



Figure 4.3: a) DSC and b) TGA scans of powders, polymers and solid surface.

Table 4.1: Molecular	weights and thermal	properties of various	polymers/materials
	0	1 1	

Material/Polymer	M _w (GPC)	M _n (GPC)	זרוק	T_g	Tpeak-1, 2	<i>Td</i> -10
Туре	(g/mol)	(g/mol)	ΓDΙ	(°C)	(°C)	(°C)
DP-24	7800 ± 2100	3800 ± 600	2.08 ± 0.34	34.5	361	277
SS-24				47.5	288, 347	246
Recovered PMMA	1166000 ± 28300	891200 ± 60300	1.31 ± 0.06	130	398	228
PMAA				238	73, 455	333

The filtrate was first neutralized using lactic acid solution and then distilled at 85 °C to recover IPA and potassium lactate. Alkaline solvolysis of PLA/PMMA composite degrades PLA into the salt of lactic acid, (such as potassium lactate when potassium hydroxide is used). Figure 4.2a, b and c show the GPC chromatogram of recovered PMMA, ¹H-NMR spectra of polymers/materials used/recovered and spartan gummy candies made from the recovered potassium lactate. The obtained potassium lactate is ultra-pure, which is comparable with commercial food grade potassium lactate and was used to prepare Spartan gummy candies (Figure 4.2c) using recipe described in the Appendix. Table 4.1 and Figure 4.2 show the molecular weight and thermal properties of the materials of interest. As confirmed by ¹H-NMR, GPC, DSC and TGA, high molecular weight PMMA was recovered with T_g of 130 °C and peak degradation temperature of 398 °C.



Figure 4.4: SEM images of a-c) Virgin ATH powder d-f) Recovered ATH powder.

Figure 4.4 shows the SEM images of the virgin and recovered ATH powder after solvolysis. Particles of various sizes were found in both the powders and TGA analysis (Figure 4.3b) revealed ~5% of polymer remained on the recycled ATH. PMAA is a water-soluble polymer

which can act as a poly(electrolyte) and is used in hydrogels for drug delivery and other biomedical applications[148-150]. Further solvolysis of PMMA at 140 °C for 24 hours completely hydrolyzed the ester bonds of the PMMA chain to convert it to poly(methacrylic acid) (PMAA). T_g of 238 °C was measured by DSC and is similar to the reported (extrapolated) value of 230 °C[151].

Using carbodiimide chemistry[152] as shown in Figure 4.5 and described in Appendix, crosslinked PMAA gel as a water absorbent material was created which can absorb as much as 60 times of its original weight. Recovery efficiency (Table 4S.1), of ATH, PMMA, PLA and IPA were 98%, 80%, 53% and 65% respectively. Figure 4.6 shows the DMTA of the samples made from the virgin and recycled ATH. Similar mechanical performance was observed for both the samples showing the viability of using the recycled ATH to prepare such biorenewable solid surface.



Figure 4.5: a) PMAA gel before and after water intake b) Effect of ethylenediamine concentration on swelling of cross-linked PMAA.



Figure 4.6: DMTA of solid surface casted from the virgin and recycled ATH powders.

4.4 Conclusion

This research showcases one of the ways to create sustainable countertops and sinks by understanding the need to become steward of the environment in present times. Solvolysis of PLA/MMA based solid surface yielded multiple recycled components for value-added products, including pure edible food ingredient and superabsorbent polymer. Mass recycling efficiency was 85 % and thermomechanical property of the solid surface made from the recycled ATH was similar to that of the virgin ATH.

APPENDIX

Total		ATH	PMMA	PLA	IPA
Feedstock (g)	165	99.5	39.3	26.2	3945
Recovered (g)	143	97.5	31.5	13.9	2564
Recovery efficiency (%)	86.7	98	80.2	53	67.3

Table 4S.1: Recycled mass from the solvolysis of the solid surface disc

Recipe for Spartan gummy candies: Potassium lactate is recognized as a food ingredient (21CFR184.1639), used as a flavor enhancer, pH control agent or potassium resources for muscle health. Spartan candies with potassium lactate were prepared following a common recipe. Typically, 70 g gelatin was first gradually dissolved in 140 g water at 65 °C for 30 minutes, and then 30 mg potassium lactate (recycled from the solvolysis), 15 g tartaric acid, 10 g sugar, 20 g sorbitol powder, 200 g glucose syrup and various food colorings were added with gently stirring. Subsequently, the mixture was casted into a Spartan S silicone mold and refrigerated until very firm.

Preparation of super-absorbent PMAA gel: 1 gram of recycled PMMA was further hydrolyzed to PMAA in 40 ml alkaline solution at 140 °C for 24 hours in 50 ml PTFE vessel enclosed in the hydrothermal autoclave reactor. Obtained PMAA was washed thoroughly with DI water and vacuum dried for 24 hours at 50 °C. 5 % of ethylenediamine in methanol solution (10 mg/ml) and 10 % of 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide in methanol solution (80mg/ml) were added into PMAA/methanol solution (85 mg/ml) and polymerized for 30 min at 20 °C. The obtained gel was washed twice using distilled water and dried under vacuum at 40 °C for 24 hours. The water absorbance test was measured by recording the mass changes of crosslinked PMAA before and after soaked in water for 8 hours at 20 °C.

CHAPTER 5: EFFECT OF CHAIN TRANSFER IN COMPOSITES. I. 1D-MODEL DEVELOPMENT

5.1 Introduction

In 1932, Röhm and Bauer were first to polymerize methyl methacrylate (MMA) into rigid transparent sheets of Poly(methyl methacrylate) (PMMA)[153]. Worldwide PMMA production is expected to reach around 2.3×10^6 t/a by the end of 2023 with end-use in automotive, construction, electronics, signs, and display sectors[154]. Attributes that make PMMA an attractive industrial polymer are low cost, light weight, optical clarity, mechanical strength, weather and UV resistance supplemented by thermoformability, surface modification by coatings, pigmenting, treatment with flame retardants and composites[155]. Free radical polymerization of MMA can be carried out by thermal decomposition of peroxide or azo initiators at 60 to 90 °C. Alternatively, benzoyl peroxide in the presence of tertiary amine[156] or the hemi-perester of peroxymaleic acid promoted with heavy metal bases in conjunction with mercapto ester[121] can be used to achieve room temperature curing. PMMA bound thick composites like fiber reinforced wind turbine blades[14] or alumina trihydrate (ATH) filled solid surface countertops[104] are cured at room temperature due to fabrication challenges associated with molding and casting of large design specific composite parts. However, thermal management during curing of such thick composite part needs to be addressed as the heat of polymerization of MMA to PMMA is 57.8 kJ/mol[157], which is around three times higher than a typical epoxy resin.

In bulk free-radical polymerization, conversion of MMA is governed by the gel (Trommsdorff) effect[158]. This phenomenon arises from sudden increase in viscosity of the reaction medium during polymerization which hinders the diffusion of the macroradicals considerably which results in an instant drop of the bimolecular chain termination rate[159]. As a

result, concentration of trapped growing radicals increases by several orders of magnitude along with sharp increase in the polymerization rate and molecular weight[160]. This causes surrounding MMA to get consumed in a very short period and temperature of the system increases dramatically. This auto acceleration of a free radical polymerization system has been noted in many bulk polymerization systems[161]. In the absence of adequate heat dissipation and safety measures, auto acceleration could result in reaction vessel failure or explosion[162]. Thus, to prevent a runaway reaction, monomer boiling and to control the molecular weight, chain transfer agent (CTA) is incorporated in to the polymerization composition[163]. The term chain transfer was first coined by Paul J. Flory to attribute a phenomenon that average molecular weight of polymers in the free radical vinyl polymerization were lower than the predicted by rate considerations alone[164].

Chain transfer reaction is the interaction of the radical site of a growing chain with a nonradical species to produce a dead polymer chain and a new radical. Chain transfer may occur due to side reactions with various components during polymerization like initiators, solvent, monomers, polymers, or it can be introduced deliberately by use of CTAs[64, 165-167]. Importance of chain transfer can be realized in the functionalization of polymers[168], control of polymer chain branching[169], control the molecular weight[170] and to control polymerization exotherm[171]. Mercaptans and halocarbons have been recognized to be one of the most used CTAs in polymerizations that produce poly(styrene), polyacrylates, latexes and other vinyl type polymers[157, 166, 172-174]. The presence of weak S—H and C—Cl, Br or I bond in CTAs promotes the abstraction of hydrogen or halogen to form dead polymer chain and a new radical.

Experimental and modeling efforts has been devoted in past to investigate the kinetics[61, 62, 159, 175] and to incorporate the effect of CTAs in the solution and bulk polymerization of

MMA[166, 172, 176-180]. However, to our knowledge, the elucidation of CTA effect in curing of thick composite system is lacking. Based on the existing methodologies, part I of this work is to further advance the 1-dimensional (1-D) reaction kinetics heat transfer model[61] with inclusion of chain transfer kinetics to simultaneously predict the temperature evolution in the gram scale MMA composite resin.

5.2 Experimental

5.2.1 Materials

MMA (Purity 99%, Monomethyl ether hydroquinone <30 ppm as inhibitor), *N*,*N*-dimethyl*p*-toluidine (DMT) and benzoyl peroxide (BPO, Luperox[®] AFR40) were purchased from Sigma-Aldrich as used as received. Chain transfer agent Ethylene Glycol Bis(3-mercaptopropionate) was donated by Thiochem.com and used as received. K-Type thermocouples and 4-Ch SD card data logger were purchased from Amazon.com. PMMA was obtained from Polysciences, Inc. Commercial poly(lactide) (Ingeo[®] 10361D by NatureWorks, M_w=65 kg/mol, PDI=1.5) was degraded to DP-13 (PLA) as described in Chapter 2. Various amount of BPO:DMT (1:1 mol ratio) were used as an initiator for the bulk polymerization of MMA, 20 wt.% PMMA in MMA and 20 wt.% PLA in the absence and presence of CTA. Polymerized samples were post-cured in the convection oven at 120 °C for 10 hours for molecular weight and T_g measurement.

5.2.2 Methods

Temperature Measurement Using Thermocouples: Temperature as a function of time was measured using thermocouples and data logger. For small scale experiments, resin (6 g MMA alone or 6 g MMA with 1.5 g PMMA or PLA), and various amounts of initiator (1:1 mol ratio of BPO:DMT) were well mixed in a 20 ml scintillation vial. A hole was drilled in the plastic cap with aluminum backing, and a thermocouple was inserted through the hole. Gap between the lid and

thermocouple was closed using a vacuum bag sealant tape. After initiating the reaction, scintillation vials were placed in a constant temperature stirred oil bath. For characterization, the scintillation vials were broken with a hammer and sample was taken from the bottom using a wire cutter.

GPC: The GPC system contained two Agilent PLgel 5μm MIXED-C column in series, a Wyatt DAWN DSP Laser Photometer, and a Wyatt OPTILAB DSP Interferometric Refractometer. The light scattering detector was calibrated using toluene and normalized to the 90° detector using monodisperse poly(styrene) with 30 kg/mol molecular weight. The refractometer was calibrated by injecting various concentrations of polystyrene in THF (dn/dc=0.185). PMMA and PLA samples were measured in chloroform at 25 °C (dn/dc=0.06 mL/g and 0.024 mL/g for PMMA and PLA respectively). Solutions of approximately 10 mg/mL were filtered once through a 0.22 μm poly(tetrafluoroethylene) syringe filter prior to injection.

DSC: The DSC of polymerized samples were performed using a Q20 TA DSC calibrated with an indium standard. Approximately 10-15 mg of dried materials were sealed in aluminum pans. The scanning protocol was: hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min, hold for 5 min at 200°C, cool from 200°C to -40°C at 5°C per min, hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min. T_g was assigned for the second heat scan using the half height method, which is the temperature at which a sample's heat capacity is halfway between the difference of its glassy and rubbery state heat capacities.

Simulation technique for model: The coupled equations of curing kinetics and heat transfer were solved numerically using Wolfram Mathematica (version 12.2). Detailed model parameters are available in Appendix.

5.3 Results and Discussion

Figure 5.1 shows the example of the temperature evolution during curing reaction of MMA based resin in the presence and absence of CTAs using equimolar amounts of BPO and DMT. The redox reaction between BPO and DMT generates two radicals at room temperature[62]. Temperature of the mixture gradually increases up to certain point during induction time followed by a sudden rise in temperature within tens of seconds because of the auto acceleration known as the Trommsdorff effect[158].



Figure 5.1: Temperature profiles during bulk free-radical polymerization of MMA at room temperature in the absence of and presence of CTA.



Figure 5.2: a) to e) Diffusion and reaction steps during the termination of two PMMA (red) macroradicals f) Trapped very high molecular weight PMMA macroradicals g) to i) Effect of chain transfer agent on the reaction and termination of active PMMA chains.

During induction time, the termination rate of the growing macroradicals was governed by the ability of the radical chain ends to diffuse and orient to each other. Figure 5.2 a) to e) describes this phenomenon where at certain point in time t > 0, there will be small molecular weight chains of PMMA who can diffuse easily in the reaction medium, whose chain ends can orient to each other via segmental diffusion. Also, in the beginning of the reaction, viscosity of the medium is low and entire macroradical can move through the solution known as a Translational diffusion. As reaction proceeds, molecular weight of the PMMA chains increases and solution becomes concentrated enough such that termination rate is limited by translational diffusion (Figure 5.2f). During this period, temperature of the solution begins to display discernible increase and within couple of minutes temperature of the medium increases rapidly leading to auto-acceleration of the reaction kinetics. This sudden temperature rise arises because entire macroradical and its chain ends being trapped in the viscous and entangled solution. At this point, the rate of termination drops dramatically, and MMA molecules are still mobile enough to diffuse through the viscous liquid gets consumed quickly. Therefore, the overall reaction rate and temperature increases rapidly. But, when the CTAs are present in the system (Figure 5.2 g to i), who are also mobile molecules, mitigates the situation by scavenging the active center from the trapped molecules and diffusing out by starting a new chain or terminating it with another active center and thus lowering the peak exotherm.



Figure 5.3: a) Experimental setup to measure the temperature evolution during the curing reaction of MMA and 20 wt.% polymer resins. b) Temperature profiles as function of time for bulk free radical polymerization of MMA at various initiator concentrations.

As shown in Figure 5.3a, the temperature evolution was monitored using thermocouples in 20 ml scintillation vials with resin placed in a constant temperature oil bath. The gap between the thermocouple and the hole drilled in the lid was sealed with yellow vacuum tape to prevent the monomer evaporation. As seen in Figure 5.3b, temperature profiles strongly depend on the initiator concentrations. Induction time for the bulk polymerization of MMA for 0.6, 1.1, 2.1 and 3.1 wt.% initiator was ~40, 60, 90 and 160 minutes respectively. Also, maximum temperature tends to become higher and peak width tends to become sharper with higher initiator concentrations. These

temperature profiles also depend on the surface to volume ratio, heat transfer coefficient of the container and surrounding environment.



Figure 5.4: a) Temperature evolutions during the bulk free-radical polymerization reaction of MMA at various initiator concentrations b) ¹H-NMR spectra of MMA and PMMAs c) GPC chromatograms of PMMAs d) T_g vs M_n of PMMAs at various initiator concentrations.

Figure 5.4 a) to d) and Table 5.1 shows the temperature evolution of MMA to PMMA, ¹H-NMR spectra, GPC chromatograms, and T_g /Mn vs initiator wt.% of the polymerized PMMAs respectively. Although, 0.6 wt.% PMMA had the lowest exotherm peak it had the highest molecular weight and T_g of the series. Also, molecular structure of the synthesized PMMAs were verified by ¹H-NMR and numerous proton peaks around 7.5-8, 6.1, 4.3 and 2.5-3 ppm can be seen. Those peaks arises from the end groups resulting from termination/transfer due to primary BPO radicals, termination of the propagating radicals through disproportionation and combination[181]. Also, strong but expected dependence of T_g on the M_n can be observed for these PMMA samples. At lower initiator concentration, few MMA chains get initiated and large molecular weight chains are being formed over a long period before getting pinned in space or getting terminated by other radicals. As initiator concentration increases, peak exotherm time decreases and shorter molecular weight chains are formed. Also, PDI and yellow color (Figure 5S.1 top) of PMMAs increases as the initiator concentration increases. This can also be seen by the increase in ¹H-NMR peaks ~7.5-8 ppm resulting from the termination of chains by the increased concentration of the BPO radicals.



Figure 5.5: a) Temperature evolutions during the bulk free-radical polymerization reaction of MMA at various CTA concentration with 2.1 wt.% initiator concentration b) ¹H-NMR spectra of CTA, MMA and PMMAs c) GPC chromatograms of PMMAs d) T_g vs M_n of PMMAs at various CTA concentrations.

In next series of MMA to PMMA experiments (Figure 5.5, Table 5.1), 2.1 wt.% initiator was kept constant and CTA amount was varied. As seen from figure 5.5a, peak exotherm

temperature and molecular weight decreases, as the CTA concentration increases. Also, PDI and yellow color (Figure 5S.1 bottom) of the PMMAs decreases as CTA concentration increases. For a given amount of initiator, CTAs are effectively taking away the active reaction center from the trapped PMMA chains and lowering and broadening the peak exotherm.



Figure 5.6: a) Comparison of simulated and experimental temperature evolutions during the bulk free-radical polymerization reaction of 20 wt.% PMMA based resin at various initiator concentrations b) ¹H-NMR spectra of MMA and PMMAs c) GPC chromatograms of PMMAs d) T_g vs M_n of PMMAs at various initiator concentrations.



Figure 5.7: a) Comparison of simulated and experimental temperature evolutions during the bulk free-radical polymerization reaction of 20 wt.% PMMA and 1 wt.% CTA based resins at various initiator concentrations b) ¹H-NMR spectra of MMA, CTA and PMMAs c) GPC chromatograms of PMMAs d) T_g vs M_n of PMMAs at various initiator concentrations.

Polymerization of PMMA or PLA based MMA resin and prediction of exotherm is of particular interest to us as pure MMA alone is not utilized to fabricate the fiber or particulate filled composites. Figure 5.6 and Table 5.1 shows the data of initiator and CTA variation during the polymerization of 20 wt.% PMMA (M_w=74300 g/mol, M_n=42100 g/mol) dissolved in MMA based solutions (6 g MMA and 1.5 g PMMA). It can be noticed from Figure 5.4a, 5.5a, 5.6a and 5.7a that introduction of 20 wt.% of PMMA shortened the onset of the Trommsdorff effect due to increased viscosity of the matrix. For a given initiator concentration, slightly lower molecular weights were observed for the 20 wt.% PMMA based solutions as compared to the PMMAs

obtained from the polymerization of MMA alone. This could be due to the introduction of low molecular weight PMMA in the system lowering the overall molecular weight as compared to MMA alone. Resulting polymers were also characterized by ¹H-NMR and similar trend in the T_g vs M_n was observed. As shown in Figure, 5S.3, 5S.4 and Table 5.1, similar experiments were also performed for the 20 wt.% of PLA (M_w=27680 g/mol, M_n=16300 g/mol) in MMA based solutions. One-dimensional heat transfer model:

Adopted kinetic scheme[61] for the polymerization initiated by BPO/DMT is presented in Scheme 5.1a. In addition to the main reactions of decomposition, initiation, propagation, chain transfer reactions by initiators, monomer, radicals, and specifically chain transfer agents are also considered. Balance equations were illustrated in Scheme 5.1b.

a)	b)		
Decomposition	Balance Ec	luations	
$I + A \xrightarrow{f \times k_d} I^* + A^*$	1. Initiator $\frac{d[I]}{dt} = -f$	$\mathbf{k}_{d} \cdot [\mathbf{I}] \cdot [\mathbf{A}] - \mathbf{k}_{tr,\mathbf{I}} \cdot [\mathbf{I}] \cdot [\mathbf{P}^{*}]$	
Initiation $I^*/A^* + M \xrightarrow{k_i} P_1^*$	2. Amine $\frac{d[A]}{dt} = -$	$f \cdot k_d \cdot [I] \cdot [A] - k_{tr,A} \cdot [A] \cdot [P]$	P*]
$CTA^* + M \xrightarrow{k_{i,CTA}} P_1^*$	3. Initiator radicals $\frac{d[I^*]}{dt} = f$	$\mathbf{k}_{d} \cdot [\mathbf{I}] \cdot [\mathbf{A}] - \mathbf{k}_{i,\mathbf{I}} \cdot [\mathbf{I}^{*}] \cdot [\mathbf{M}]$	$ +k_{tr,I} \cdot [I] \cdot [P^*] - k_{tp} \cdot [I^*] \cdot [P^*]$
Propagation	4. Amine radicals $\frac{d[A^*]}{dt} =$	$\mathbf{F} \cdot \mathbf{k}_{d} \cdot [\mathbf{I}] \cdot [\mathbf{A}] - \mathbf{k}_{i,\mathbf{A}} \cdot [\mathbf{A}^{*}] \cdot [\mathbf{M}]$	$A] + k_{tr,A} \cdot [A] \cdot [P^*] - k_{tp} \cdot [A^*] \cdot [P^*]$
$\mathbf{P}^* + \mathbf{M} \xrightarrow{\sim} \mathbf{P}_{n+1}^*$	5. Monomer $\frac{d[M]}{dt} = -$	$-(k_{i,I} \cdot [I^*] + k_{i,A} \cdot [A^*]) \cdot [M] -$	$- k_{i,CTA} \cdot [CTA^*] \cdot [M] - k_p \cdot [P^*] \cdot [M] - k_{tr,M} \cdot [M] \cdot [P^*]$
Termination $P_n^* + P_m^* \xrightarrow{k_{t_c}} P_{n+m}$	6. Polymer radicals $(k_{tr,l} \cdot [I])$	$\frac{d[P^*]}{dt} = (k_{i,I} \cdot [I^*] + k_{i,A} \cdot [A^*] + k_{tr,A} \cdot [A]) \cdot [P^*] - k_{tr,M} \cdot [N]$	$\begin{split} \big] \big) \cdot [M] + k_{i,CTA} \cdot [CTA^*] \cdot [M] - (k_{tc} + k_{td}) \cdot [P^*]^2 - \\ M] \cdot [P^*] - (k_{tp} \cdot [I^*] + k_{tp} \cdot [A^*]) \cdot [P^*] - k_{tr,CTA} \cdot [CTA] \cdot [P^*] \end{split}$
$P_n^* + P_m^* \xrightarrow{k_{td}} P_n + P_m$	7. CTA radicals $\frac{d[CTA^*]}{dt}$	$= -k_{i,CTA} \cdot [CTA^*] \cdot [M] + k_{tr,C}$	$_{CTA} \cdot [P^*] \cdot [CTA]$
Side reactions $I/A + P_n^* \xrightarrow{k_{tr,A/I}} I^*/A^* + P_n$	8. CTA $\frac{d[CTA]}{dt} =$	$-k_{tr,CTA} \cdot [CTA] \cdot [P_n^*]$	
$M + P_n^* \xrightarrow{k_{tr,M}} M^* + P_n$	Heat Transfe	er Equation	
$I^*/A^* + P_n^* \xrightarrow{\leftarrow P} P_n$	1-Dimension	nal	2-Dimensional
$CTA + P_n^* \xrightarrow{k_{tr,CTA}} CTA^* + P_n$	$\frac{dT}{dt} = \frac{\Delta H_{PMMA}}{\rho \cdot C_p} \cdot \left(-\frac{dM_{MMA}}{dt}\right) -$	$\frac{h \cdot A}{m \cdot C_p} \left(T(t) - T_{cold} \right)$	$\frac{\mathrm{d}\mathrm{T}}{\mathrm{d}\mathrm{t}} = \frac{\Delta\mathrm{H}_{\mathrm{PMMA}}}{\rho \cdot \mathrm{C}_{\mathrm{p}}} \cdot \left(-\frac{\mathrm{d}\mathrm{M}_{\mathrm{MMA}}}{\mathrm{d}\mathrm{t}}\right) - \frac{\kappa}{\rho \cdot \mathrm{C}_{\mathrm{p}}} \left(\frac{\partial^{2}\mathrm{T}}{\partial x^{2}}\right)$

Scheme 5.1: a) Kinetic scheme for free-radical polymerization initiated by BPO/DMT b) List of coupled balance equations. The superscript * indicates radicals.

where, I=Initiator, A=Amine, M=Monomer (MMA), P=Polymer, CTA=Chain transfer agent, f=Efficiency of initiation reaction, kd, ki, ki,CTA, kp, ktc, ktd, ktr,A/I, ktr,M, ktp, ktr,CTA=Decomposition, Initiator Initiation, CTA Initiation, Propagation, Termination by combination, Termination by disproportionation, Transfer coefficient to Initiator, Monomer, Initiator/Monomer radicals and CTA coefficient respectively. Prediction of pot life and maximum temperature during the cure cycle enables better applications for the resin. Heat evolved during polymerization is proportional to the monomer consumed and is dissipated to the surrounding by the heat transfer. Simple 1-D heat transfer equation of scheme 5.1 describe the temperature (T) change as a function of time (t) by chemical reaction[61] where ΔH_{PMMA} , m, v, CP, M_{MMA}, h and T_{cold} is the heat of polymerization of PMMA, total mass, total volume, heat capacity, mass of the monomer (MMA), heat transfer coefficient and temperature of the surroundings respectively. First and second term on the right side of 1D heat transfer equation is the heat generated by the MMA polymerization reaction and heat dissipation by heat transfer to the surroundings which acts as a heat sink.

Determination of first term of 1D heat transfer equation is a non-trivial task where kinetic parameters of MMA polymerization are functions of both conversion and temperature in a complex manner [182, 183]. Based on a previously developed model[175], Achilias *et al.* demonstrated a mathematical model for an acrylic resin initiated with BPO and amine for the field of dentistry[182]. Zoller *et al.*[62] and Suzuki *et al.*[61] reported the mathematical model of MMA polymerization initiated by BPO and DMT. In this study, we followed these two approaches and model of Suzuki *et al.* was adopted and modified to incorporate the effect of CTAs. Detailed kinetic parameters are summarized in Table 5S.3. One empirical statement in the model is the termination rate constant (k_t), which is described by the four different regions depending on the conversion[59, 184]. These equations were entered in Wolfram Mathematica and numerically calculated.

One parameter that needs to be obtained from the experiment is the heat transfer coefficient

which depends on the material, geometry, and the surrounding environment of the reaction system. Here we used one of the experimental data and adjusted the heat transfer coefficient so that the peak temperature of the experiment and mode agree. The obtained heat transfer coefficient was fixed for the rest of the simulation in this study. The efficiency parameter (Table 5S3, Eq. S6) of the initiation reaction was adjusted and held constant to capture the experimental result. The simulated results for 20 wt.% PMMA and 20 wt.% PMMA with 1 wt.% CTA are presented in Figure 5.6a and Figure 5.6b (dotted line). The model reasonable captures the induction time and the maximum temperature when the initiator and CTA concentrations are changed.



Figure 5.8: Conversion as a function of time with different initiator concentrations predicted by the model in the absence and presence of CTAs. The onset of Trommsdorff effect (red line) correlates with the conversion.

The model also provides the profile of all the parameters as a function of time. Figure 5.8

depicts the conversion as a function of time. Because of 20 wt.% of pre-dissolved PMMA was added, the conversion (x[t]) was defined as an equation 1 of Table 5S3. Because of the definition, the conversion starts at 0.2. Final conversion decreases as the initiator concentration decreases. In the presence of CTAs, even though experimentally lower molecular weights are obtained, higher conversion was observed at high initiator concentrations as compared to cases where no CTAs were present. Model also implies that the Trommsdorff effect starts at a conversion 0.35-0.4.

		M_{w}	M_n		
Variation Information		(g/mol)	(g/mol)	PDI	T_g
		by G		(°C)	
	0.6	764700 ± 36400	$\frac{110}{202000 \pm 32000}$	38 ± 0.42	112.5
Initiator	1 1	704700 ± 30400 328400 ± 25000	202900 ± 52000 165200 ± 61100	3.8 ± 0.42 2.1 ± 0.62	100.0
(xyt 9/2)	2.1	328400 ± 23000	103200 ± 01100	2.1 ± 0.03	04.9
(wt.70)	2.1	239000 ± 19000	82000 ± 39000	3.2 ± 1.3	94.8
	3.1	162000 ± 33200	70000 ± 41700	2.7 ± 1.11	68./
СТА	0.5	198600 ± 1700	76900 ± 15300	2.63 ± 0.05	90.6
(wt.%)	1	63705 ± 2750	43300 ± 3200	1.5 ± 0.05	82.9
(2.1 wt.%	1.5	37400 ± 2050	25700 ± 2300	1.47 ± 0.05	71.3
Initiator)	2	25700 ± 800	17800 ± 1400	1.45 ± 0.05	61.5
	2.5	20500 ± 200	15200 ± 500	1.36 ± 0.03	51.8
75k PMMA		74300 ± 2500	42100 ± 1200	1.78 ± 0.21	89.1
DP-13		27680 ± 7500	16300 ± 4800	1.52 ± 0.45	51
	20 wt% PMMA	702900 ± 20700	144000 ± 10900	4.9 ± 0.22	105.5
0 6 wet 0/ Initiator	20 wt% PLA	1123000 ± 218000	638800 ± 292000	1.88 ± 0.52	85.6
0.0 wt.76 Initiator	20 wt% PMMA_1 wt% CTA	41700 ± 2600	26500 ± 4500	1.59 ± 0.17	82.6
	20 wt% PLA_1 wt% CTA	36800 ± 2100	26600 ± 5300	1.4 ± 0.2	64.8
	20 wt% PMMA	377100 ± 36300	91600 ± 20000	4.17 ± 0.52	95.5
	20 wt% PLA	563050 ± 45800	310000 ± 102700	1.9 ± 0.48	76.8
1.1 wt.% Initiator	20 wt% PMMA 1 wt% CTA	44000 ± 900	29600 ± 1400	1.5 ± 0.04	86.5
	20 wt% PLA $\overline{1}$ wt% CTA	37200 ± 1000	26600 ± 1100	1.4 ± 0.02	69.1
	20 wt% PMMA	203000 ± 13700	77400 ± 7700	2.63 ± 0.08	78.3
0 1	20 wt% PLA	227000 ± 19000	78800 ± 5700	2.89 ± 0.03	63.6
2.1 wt.% Initiator	20 wt% PMMA 1 wt% CTA	47100 ± 900	28800 ± 1400	1.66 ± 0.23	76.9
	20 wt% PLA $\overline{1}$ wt% CTA	43800 ± 1500	28200 ± 1100	1.56 ± 0.13	70.8
	20 wt% PMMA	148300 ± 1900	79500 ± 7500	1.87 ± 0.20	60.6
	20 wt% PLA	198000 ± 11200	67500 ± 11900	2.97 ± 0.36	55
3.1 wt.% Initiator	20 wt% PMMA 1 wt% CTA	56800 ± 1100	35000 ± 3000	1.63 ± 0.11	71.1
	20 w/t% PLA = 1 w/t% CTA	53500 ± 500	27800 ± 2500	1.03 ± 0.11 1.93 ± 0.18	63.4
	20 wt/01 L/1_1 wt/0 CIA	55500 ± 500	27000 ± 2300	1.75 ± 0.10	0.5.4

Table 5.1: Molecular weights and T_g of various polymer formulations and compositions

5.4 Conclusion

Reaction kinetics and temperature evolution during the bulk polymerization of MMA, 20 wt.% PMMA or 20 wt.% PLA in MMA in the absence and presence of CTAs were investigated. Due to Trommsdorff effect, the temperature of the reaction medium increases rapidly after an induction time. The presence of CTAs not only reduces the peak temperature by transferring the active radical site from the pinned reaction center, but it also regulates the molecular size, distribution and color which may be necessary so that the resulting polymers have good processability and have specific properties required for intended applications. A mathematical model based on the reaction kinetics and heat transfer equations with CTA effect was developed to simulate these behaviors. Furthermore, it was observed that for the 1 wt.% CTA amount, even though the peak exotherm time increased slightly, higher conversion was achieved at higher initiator concentrations which was not the case for the polymerization in the absence of CTAs. Combination of scintillation vial experiments and chain transfer model can be used as a basis for designing and screening of PMMA or PLA based resin formulations.

APPENDIX



Figure 5S.1: Scintillation vials picture of polymerization of MMA at various Initiator and CTA concentrations.


Figure 5S.2: a) Experimental temperature evolutions during the bulk free-radical polymerization reaction of 20 wt.% PLA based resin at various initiator concentrations b) ¹H-NMR spectra of MMA, PLA and PLA/PMMAs c) GPC chromatograms of PLA/PMMAs d) T_g vs M_n of PLA/PMMAs at various initiator concentrations.



Figure 5S.3: a) Experimental temperature evolutions during the bulk free-radical polymerization reaction of 20 wt.% PLA and 1 wt.% CTA based resin at various initiator concentrations b) ¹H-NMR spectra of MMA, PLA, CTA and PLA/PMMAs c) GPC chromatograms of PLA/PMMAs d) T_g vs M_n of PLA/PMMAs at various initiator concentrations.



Figure 5S.4: DSC curves of polymers for a) MMA to PMMA at various initiator concentrations b) MMA to PMMA at various CTA concentrations at fixed initiator concentration of 2.1 wt.% c) 20 wt.% PMMA d) 20 wt.% PLA e) 20 wt.% PMMA and 1 wt.% CTA f) 20 wt.% PLA and 1 wt.% CTA based formulation at various initiator concentrations.

Number	Symbol	Name	Units	Value	Ref.
1	ΔH_{PMMA}	Heat of polymerization of MMA	kJ/mol	28.5	[61]
2	T _{g,MMA}	Glass transition temperature of MMA	Κ	147	[62]
3	T _{g,PMMA}	Glass transition temperature of PMMA	K	387	[62]
4	$ ho_{ m MMA}$	Density of MMA	g/cm ³	0.936	[185]
5	$ ho_{ m PMMA}$	Density of PMMA	g/cm ³	1.190	[185]
6	C _{P, MMA}	Heat capacity of MMA	kJ/kg/k	1.91	[185]
7	C _{P, PMMA}	Heat capacity of PMMA	kJ/kg/k	1.42	[185]

Table 5S.1 Physical constants for MMA and PMMA.

Table 5S.2 Constants used for the mathematical model. Monomer, polymer, and amine refer to MMA, PMMA, and DMT respectively. We calibrated heat transfer coefficient and adjustable parameter for initiator efficiency using the experimental data for 2.1 wt.% initiator system so that the induction time and the maximum temperature obtained from the model agreed with the experimental data. The parameters calibrated to this one experiment were then fixed and used verbatim for all other simulations. For CTA based experiments, k_{i,CTA} was adjusted to fit the 2.1 wt.% initiator based experimental data and was kept constant for other cases.

No.	Symbol	Name	Units	Value	Ref.
1	h	Heat transfer coefficient	J/kg	0.0085	
2	Mo	Initial monomer concentration	mol/l	9.3	
3	Ι _ο	Initial initiator concentration	mol/l	0.023	
4	Ao	Initial amine concentration	mol/l	0.023	
5	CTAo	Initial CTA concentration	mol/l	0.039	
6	CI	Coefficient of the transfer reaction of initiator		0.06	[61]
7	C _A	Coefficient of the transfer reaction of amine		0.3	[61]
8	C _M	Coefficient of the transfer reaciton of monomer		5×10^{-5}	[61]
9	C _{CTA}	Coefficient of the transfer reaction of CTA		0.7	[185]
10	r _p	Reaction radius	nm	0.69	[61]
11	D _{m o}	Monomer diffusion coefficient	cm ² /s	3×10^{-1}	[61]
	11,0			т 1 0 м	L' J
12	k _{i,BPO}	Initiation coefficient by BPO	l/(mol.s)	1.8×10^{-8}	[61]
13	k _{i,Amine}	Initiation coefficient by Amine	l/(mol.s)	9.7×10^{5}	[61]
14	k _{i,CTA}	Initiation coefficient by CTA	l/(mol.s)	0.07	
15	V _{g,M}	Free volume of monomer at glass transition temperature		0.025	[61]
16	с.	Volume expansion coefficient of monomer	K ⁻¹	$5 \times 10^{-10^{-10^{-10^{-10^{-10^{-10^{-10^{-$	[61]
10	ссM		IX.	4	
17	V _a p	Free volume of polymer at		7.5 ×	[61]
10	8,1	glass transition temperature	T7 1	10-5	[01]
18	∝ _P	Volume expansion coefficient of polymer	K-1	0.025	[61]
19	t _o	Initiator efficiency coefficient		0.2	
20	С	Adjustable parameter for initiator efficiency		6.9 ×	
21		Overlanning factor of the redical		10 ~	[61]
21	Υı	Overlapping factor depending on the size of the		0.41	[01]
21	γ_{m}	molecule		0.6	[61]

Table 5S.3 List of equations used for kinetic parameters[61]. In first equation, M[0], M[t], P_0 indicates initial monomer concentration, monomer concentration at time t, and weight percent of pre-dissolved polymer, respectively. Other constants correspond to the constants in Table 5S.1 and 5S.2.

No.	Name	Equation
1	Conversion x[t]	$x[t] = \frac{\frac{M[0]}{(1 - P_0)} - M[t]}{\frac{M[0]}{(1 - P_0)}}$
2	Free volume of the resin V _f [t]	$V_{f}[t] = V_{f,m} \times \left(1 - \frac{0.8 \times x[t]}{1 - 0.2 \times x[t]}\right) + V_{f,p} \times \left(1 - \frac{0.8 \times x[t]}{1 - 0.2 \times x[t]}\right)$
3	Free volume of the monomer $V_{\rm f.m}$	$V_{f,m} = V_{g,m} + \alpha_{M} \cdot (T[t] - T_{g,m})$
4	Free volume of the polymer $V_{f,p}$	$V_{f,p} = V_{g,p} + \propto_P \cdot (T[t] - T_{g,P})$
5	Diffusion coefficient of monomer D _m [t]	$D_{m}[t] = V_{f,m} \cdot \exp\left(-\frac{\gamma_{m}}{V_{f}[t]}\right)$
6	Efficiency of initiation reaction f[t]	$f[t] = \frac{t_0}{1 + \frac{C}{\exp\left(-\frac{\gamma_I}{V_c[t]}\right)}}$
7	Decomposition coefficient kd	$k_{d} = 832 \times \exp\left(\frac{26 \times 1000}{8.3 \times T(t)}\right)$
8	Propagation coefficient $k_p[t]$	$\begin{split} k_{p,0} &= 2.7 \times 10^8 \times \exp\left(-\frac{22.4 \times 1000}{8.3 \times T(t)}\right); \frac{1}{k_p[t]} \\ &= \frac{1}{k_{p,0}} + \frac{1}{4\pi N_A r_p D_m[t]} \end{split}$
9	Termination coefficient	$k_{t} = k_{t,c} + k_{t,d}$ $x[t] < 0.35; k_{t} = k_{t,0} \times (1 - x[t])$ $0.35 \le x[t] < 0.5; \ln(k_{t}) = 27.5 - 35 \times x[t]$ $0.5 \le x[t] < 0.78; \ln(k_{t}) = 15 - 10 \times x[t]$ $0.78 \le x[t] < 1; \ln(k_{t}) = 28 - 26.6 \times x[t]$
10	Transfer coefficient to initiator $k_{tr,I}$	$\mathbf{k}_{\mathrm{tr},\mathrm{I}} = C_{\mathrm{I}} \cdot \mathbf{k}_{\mathrm{p}}$
11	Transfer coefficient to Amine ktr,A	$\mathbf{k}_{\mathrm{tr},\mathrm{A}} = \mathbf{C}_{\mathrm{A}} \cdot \mathbf{k}_{\mathrm{p}}$
12	Transfer coefficient to Monomer ktr.M	$\mathbf{k}_{\mathrm{tr},\mathrm{M}} = \mathrm{C}_{\mathrm{M}} \cdot \mathbf{k}_{\mathrm{p}}$
13	Transfer coefficient to CTA ktr.CTA	$\mathbf{k}_{tr,CTA} = \mathbf{C}_{CTA} \cdot \mathbf{k}_{p}$
14	Transfer coefficient to initiator radicals $k_{tp}[t]$	$\begin{aligned} k_{tp,0} &= 2.7 \times 10^8 \times \exp\left(-\frac{5.9 \times 1000}{8.3 \times T(t)}\right); \frac{1}{k_{tp}[t]} \\ &= \frac{1}{k_{tp,0}} + \frac{1}{4\pi N_A r_p D_m[t]} \end{aligned}$

CHAPTER 6: EFFECT OF CHAIN TRANSFER IN COMPOSITES. II. APPLICATION TO THICK COMPOSITE PARTS

6.1 Introduction

Compared to traditional construction materials, fiber or particulate reinforced polymer matrix composites offer enhanced performance and flexibility due to their high specific mechanical and superior chemical properties. Fabrication of these composite materials is accomplished using either hand-lay-up, open molding or various resin infusion molding techniques like resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), filament winding, pultrusion, compression and injection molding[8]. Although majority of the research has been focused on the manufacturing and processing of thin (< 0.5-1 inch) composite laminates, exploration of thick-sectioned (> 1 inch) composites for structural and defense applications has been growing rapidly [186]. Deep water exploration submersible vehicle hull made from the 6 inch thick carbon fiber/epoxy wall[187], 5-inch-thick E-glass fiber reinforced composite structure carrying two 35-ton trucks[188], 100-m glass fiber/epoxy composite wind turbine blade with 6.3 inch thick root[189] are few examples of thick fiber reinforced composites utilized in commercial applications. For particulate filled composites in the realm of cast polymers, quartz (5-7% unsaturated polyester resin with 95-93% SiO₂ filler) and solid surfaces (35-40% acrylic resin with 60-65% ATH) are popular choices for the kitchen countertops, where industry standard is $\frac{1}{2}$ " to $\frac{3}{4}$ ", but new trend can be spotted with many homeowners moving up to 2" thick countertops [190].

Typically epoxy, unsaturated or vinyl ester based thermoset matrix is used in various composite formulations. But, dedicated thermoplastic resins derived from methyl methacrylate (MMA) which are also recyclable is getting significant attention to fabricate the fiber reinforced composite part for wind turbine blade application[191]. Curing is one of the most critical steps in

the composite manufacturing where polymerization of reactive resin is initiated at room or at elevated temperature to form a structurally rigid component. High quality thick composite parts require an understanding of the challenges associated with the heat generation during polymerization and thermal conductivity of the composite matrix. Exothermic heat of reaction will not dissipate as quickly as in thin sections which can lead to non-uniform cure, residual thermal stress, and matrix degradation[61, 192-194]. In-situ free radical polymerization of MMA exhibits Trommsdorff effect[158] where beyond gel point, exothermic reaction self-accelerates due to limited motion of the trapped macro radicals whose rate of termination reduces by several orders of magnitude leading to formation of high molecular weight PMMA chains. To prevent monomer boiling and subsequent cavitation in the high value thick composite parts, it is imperative to control the temperature evolution during this run-away phase. Inclusion of chain transfer agent (CTA) in the polymerization composition is one way to control the molecular weight and temperature rise due to exothermic reaction [170, 171, 195]. Chain transfer reaction involves a propagating polymer chain reacting with a transfer agent to terminate one polymer chain and produce a radical that initiate a new chain.

There have been several studies to predict the cure behavior of thick thermoset matrix composites. Loos and Springer experimentally validated the one-dimensional (1D) model coupling a heat equation and cure kinetics of an epoxy matrix[196]. Bogetti *et al.* developed a two - dimensional (2D) cure simulation analysis and predicted the temperature and degree of cure distributions within an arbitrary cross-sectional geometry[192]. Behzad *et al.* used three-dimensional (3D) heat transfer and cure model based on the finite element procedure to predict the thermo-physical properties of a composite block and compared with experimental results[197]. Similar models have been developed for the curing of thick thermoset composites[198-200], but

limited number of publications has been devoted to the curing of thick thermoplastic composites. Borzacchiello *et. al.*[201] used differential scanning calorimetry (DSC) data for the quantitative determination of the rates of polymerization which combined with heat transfer equation to predict the temperature profiles for polymerization of a methacrylic dental cement. However, a simple pseudo autocatalytic expression was used to predict the gel effect which did not consider various diffusion controlled free radical polymerization and termination reactions[202]. Teuwen *et. al.*[203] also used similar approach to simulate the 1D and 2D temperature evolution in 24 mm thick-walled polyamide 6/glass fiber composites. Suzuki *et al.*[61] combined the diffusion controlled polymerization model[62, 182] with 1D heat transfer equation to predict the temperature evolution and degree of conversion during polymerization of $\sim 7"-20"$ thick MMA/Glass fiber composite part. Recently, Gayot *et al.*[204] used similar method to predict the temperature profiles and degree of conversion during in-situ polymerization of $\sim 3"$ thick fiber-reinforced MMA composites.

In previous models, although chain transfer reactions to monomer, initiator and polymers were incorporated, evaluation of CTA to mitigate the temperature rise during bulk free radical polymerization and fabrication of thick MMA composites was not explored. Goal of this work is to advance the curing kinetics model of Chapter 5 to 2D and experimentally verify and control the temperature rise across the thick MMA based composite parts.

6.2 Experimental

6.2.1 Materials

MMA (Purity 99%, Monomethyl ether hydroquinone <30 ppm as inhibitor), *N*,*N*-dimethyl*p*-toluidine (DMT) and benzoyl peroxide (BPO, Luperox[®] AFR40) were purchased from Sigma-Aldrich as used as received. CTA Ethylene Glycol Bis(3-mercaptopropionate) was donated by Thiochem.com and used as received. ATH was donated by Huber Materials and used as received. K-Type thermocouples and 4-Ch SD card data logger were purchased from Amazon.com. $4.75 \times 4.75 \times 3.75$ inches³ Aluminum boxes (AL-75P) with lid were purchased from polycase.com PMMA was obtained from Polysciences, Inc. BPO:DMT (1:1 mol ratio) were used as an initiator for the bulk polymerization of MMA and 20 wt.% PMMA in MMA based resin absence and presence of CTA.

6.2.2 Methods

Temperature Measurement in 20 ml Vials: Temperature as a function of time was measured using thermocouples and data logger. For scintillation vial-based experiments, resin (6 g MMA or 6 g MMA with 1.5 g PMMA/PLA or 6 g MMA with 1.5 g PMMA/PLA and 11.2 g ATH), and 1.1 wt.% of initiator (1:1 mol ratio of BPO:DMT) were well mixed in a 20 ml scintillation vial. A hole was drilled in the plastic cap with aluminum backing, and a thermocouple was inserted through the hole. Gap between the lid and thermocouple was closed using a vacuum bag sealant tape. After initiating the reaction, scintillation vials were placed in a constant temperature stirred oil bath. For characterization, the scintillation vials were broken with a hammer and sample was taken from the bottom using a wire cutter.

Temperature Measurement in Thick Aluminum Box: Holes were drilled in the lid of the Al boxes at 5 positions (9 mm, 33 mm, 57 mm, 81 mm, 105 mm). Thermocouples were inserted in the Al box such that it remained in the middle height of the box. They were sealed with the yellow vacuum sealant tape at the top. Two large plastic containers with water were used a heat sink to dissipate heat of the reaction from the Al box. Submersible pumps were used to regulate water from one container to another.

DSC: The DSC of polymerized samples were performed using a Q20 TA DSC calibrated with an

indium standard. Approximately 10-15 mg of dried materials were sealed in aluminum pans. The scanning protocol was: hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min, hold for 5 min at 200°C, cool from 200°C to -40°C at 5°C per min, hold for 5 min at -40 °C, heat from -40 °C to 200°C at 10°C per min. T_g was assigned for the second heat scan using the half height method, which is the temperature at which a sample's heat capacity is halfway between the difference of its glassy and rubbery state heat capacities.

6.3 Results and Discussion

Figure 6.1 shows the temperature profiles during curing reactions of MMA, 20 wt.% PMMA, 20 wt.% PLA and 20 wt.%PMMA or PLA with 60 wt.% ATH based resins at 1.1 wt.% initiator concentrations. When compared to just MMA alone, amount of predissolved PMMA or PLA can be used to control the induction and cycle time as it increases the viscosity of the resin shortens the peak exotherm time from ~110 min to ~65 min. Presence of 1 wt.% CTA not only increases the induction time, but it also lowers the peak exotherm temperature by ~20 °C. Another important trend to notice is the ability of ATH to suppress the exotherm as it not only dilutes the solution by acting as a heat sink, but it also has higher thermal conductivity of 21.3 (W/m.K)[205] than 0.2 (W/m.K) PMMA.

Figure 6.2 and Table 6.1 shows the DSC scans and T_g 's of polymers and composites prepared in Figure 6.1. Even though lower peak exotherm temperatures exhibited, the in-situ polymerization in the presence of ATH showed ~7-10 °C increase in T_g of 20 wt.% PLA and PMMA based samples as compared to when ATH was not present in the mixture. This indicates that ATH particles are obstructing the polymer chain mobility which leads to higher T_g of the polymer composite matrix.



Figure 6.1: Temperature profiles during the cure of MMA, 20 wt.% PMMA or PLA (with and without 1 wt.% CTA) based resins at 1.1 wt.% initiator concentration in the absence (Top) and presence (Bottom) of 60 wt.% ATH.



Figure 6.2: a) T_g and b) DSC scans of PMMA and PLA based polymers cured at room temperature using 1.1 wt.% initiator in the absence and presence of ATH

Table 6.1: T_g of PLA/PMMA based polymers and composites with and without ATH. Initiator concentration was kept constant at 1.1 wt.%.

	T_g (°C)				
	MMA to	20 wt.%		20 wt.%	
	PMMA	PMMA		PLA	
			1wt.% CTA		1wt.% CTA
No ATH	109.9	95.5	86.5	76.5	69
with 60 wt.% ATH		106.4	95.4	83.1	80



Figure 6.3: a) Top view, b) Side view of the experimental set-up to measure the curing exotherm in 120 mm thick aluminum box. c) Location of thermocouples at various positions in the aluminum box (1-9 mm, 2-33 mm, 3-57 mm, 4-81 mm, 5-105 mm).

Figure 6.3 shows the experimental setup to measure the temperature evolution during polymerization of ~kg scale MMA or 20 wt.% PMMA based resin in 120 mm thick Al box. To evaluate the homogeneity of the set-up, temperature evolution in the four quadrants were measured and shown in Figure 6S.1. Also, Figure 6S.3 and 6S.4, shows the temperature profiles as a function of time and thickness during the polymerization of pure MMA and temperature of the water bath during that time respectively. Maximum temperature is observed at the center of the block and peak temperature decreases for the location closer to the wall (heat sink). The developed model of Chapter 5 was expanded to 2D by considering spatial geometry and temperature profile can be written as[61]:

$$\frac{\mathrm{dT}}{\mathrm{dt}} = \frac{\Delta \mathrm{H}_{\mathrm{PMMA}}}{\rho \mathrm{C}_{\mathrm{p}}} \cdot \left(-\frac{\mathrm{dM}_{\mathrm{MMA}}}{\mathrm{dt}}\right) - \frac{\kappa}{\rho \mathrm{C}_{\mathrm{p}}} \left(\frac{\partial^{2} \mathrm{T}}{\partial \chi^{2}}\right)$$
(6.1)



Figure 6.4: a) 2D and b) 3D representation of the temperature evolution during polymerization of 20 wt.% PMMA based resin at various CTA concentration in the thick Al box.



Figure 6.5: Simulation results of temperature evolution as a function of time and box thickness for a) 0 wt.%, b) 0.5 wt.%, c) 1.5 wt.% and d) 2 wt.% CTA concentration.

where, parameters κ and χ denotes the thermal conductivity and distance between two walls. Equation 6.1 was coupled with balance equations of scheme 5.1 of chapter 5 and were mathematically solved using Mathematica. Due to stiff nature of the employed differential equations, kinetic parameters were fixed at 323 K and simulation results for polymerization of 20 wt.% PMMA resin are presented in Figure 6.5. Other kinetic parameters were kept constant as that of the previous chapter. Thermal conductivity was adjusted to match the peak exotherm temperature. Because of the simplified kinetics, the induction time and maximum temperature are not precise; however, the computation captures the qualitative temperature profiles as a function of time and position for 120 mm thick Al box. Also, the important outcome is that the effect of CTAs to lower the peak exotherms were effectively incorporated and showcased via experiments and simulation for such thick PMMA blocks.

Figure 6.6 a-b) and c-n) shows the temperature evolution of 1.4 kg of composite resin comprising of 60 wt.% ATH and 40 wt.% acrylic resin (20 wt.% PMMA in MMA) measured using thermocouples across the thickness and IR camera across the exterior surface of the box respectively. Similar trend to that of small vial experiments of Figure 6.1, lower peak exotherm was observed as compared to non-ATH resin of Figure 6.4a. Also, less amount of MMA was polymerized in Figure 6.6 because addition of 845 g of ATH in 563 g resin completely occupied the entire volume of the box. Thermal images of Figure 6.6 c-n) were captured at various stages during the polymerization of acrylic slurry having above formulation. Maximum temperature of 39.6 °C was observed during peak of the polymerization period and seems to be reasonably matching with the extrapolated value of temperature measured on the surface of the Al box in the Figure 6.6 a-b.



Figure 6.6: a) 2D and b) 3D representation of the temperature evolution during polymerization of 20 wt.% PMMA based resin with 60 wt.% ATH at 1.1 wt.% initiator concentration c) to n) Thermal images captured by an IR camera tracking the heat evolution during polymerization of the same

formulation as that of a).

6.4 Conclusion

Temperature evolutions during ~kg scale bulk polymerization of MMA, 20 wt.% PMMA (in the absence and presence of 1 wt.% CTA) and 20 wt.% PMMA with ATH were experimentally measured. 2D mathematical model was implemented to predict the temperature field across the length of the thick composite part and demonstrate the effect of CTA to control the curing of resin without reaching the boiling point of the monomer with fixed chemical formulation. Learning from this work will be advantageous to manufacture thick composite materials with PMMA matrix having geometries of variable thicknesses.

APPENDIX



Figure 6S.1: a) Temperature evolution measurement setup and b) profile for the 4 quadrants of the Al box during polymerization of MMA.



Figure 6S.2: a) 2D and b) 3D representation of the temperature evolution during polymerization of MMA at various CTA concentration in the thick Al box.



Figure 6S.3: Temperature of the water in two containers used in the experimental setup during the polymerization of MMA in the thick Al box.

CHAPTER 7: CONCLUSIONS AND FUTURE OUTLOOK

This thesis was focused on the engineering and advancement of valued added biorenewable products to expand the portfolio of commercial applications for PLA. Findings of this work can be highlighted in five points- 1) Chapter 1 demonstrated the use of simple reaction process for large-scale vinyl terminated PML synthesis which were readily soluble in MMA to fabricate the FRPCs having excellent mechanical properties. 2) Chapter 2 showed that our novel PLA/MMA bioresin can be used as a direct substituent for incumbent styrene and acrylic based resin in the realm of cast polymer products. 3) Chapter 3 exhibited the feasibility of solvolysis of biorenewable solid surface in alkaline solution to recover the constituent materials and other value-added products. 4) Chapter 4 revealed the importance of chain transfer agents and 1D kinetic model to tailor and control the physical properties and temperature evolution in PLA/MMA and PMMA/MMA composites. 5) Chapter 5 augmented the model of previous chapter to 2D, to control and predict the curing of thick composite parts in the presence of chain transfer agents.

Characteristics like amorphous nature and lower T_g of PML and VE-PML should be investigated for other acrylic reactive diluents like methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate to investigate its performance in the applications of medical, coatings, paints, hydrogels, elastomers, adhesives, rubber, and emulsions. Apart from acrylates, compatibility, and properties of VE-PML with other reactive monomers and polymers needs to be explored. Many mechanical properties like fatigue resistance, hardness, and impact strength of PLA based FRPCs are of particular interest, needs to be investigated in the future. Also, apart from investigating the fabrication and properties of PLA based engineered surfaces, chemical, and physical properties of PLA cast polymers like toughness, scratch, stain, heat cycle, and microbial resistance should be studied extensively. Presently, a central thrust in today's product development is to utilize modeling and machine learning to predict the performance of various engineering materials[206-208]. The computationally comprehensive model along with machine learning can not only be used to predict the mechanical properties, cure of the resin, residual stress in the composite part but it can also be used to predict the material properties from the composite geometries and to find optimal designs to discover the patterns that may inspire further discovery. Various simulation techniques and software will be required to achieve this goal. But most importantly, the fundamental material properties and kinetic data will be needed as inputs for these simulation tools. Inclusion of chain transfer kinetics in our thermochemical model will provide a valuable guidance to generate such data. Furthermore, such kinetic model should be extended to predict 3D temperature evolution while curing of commercial composite part.

In conclusion, this thesis presents scalable, application-oriented, novel biorenewable material system with improved sustainability metrics and mathematical chain transfer thermokinetic model with experimental evidence to design and optimize the manufacturing of thick, large-scale composite parts. Also, we need to promote reduction, reuse and recycling of waste, as well reprocessing waste into raw materials. This type of value delivery can only be achieved through exceptional solutions and extraordinary collaboration.

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