

# Master Thesis

## DEVELOPMENT OF BIO-BASED THERMOSETTING RESINS

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## **Objective**

The aim of the study is to investigate the possibility of developing bio-based unsaturated polyester resins from renewable monomers such as lactones and lactides. Different bio-based initiators will also be used. Further, the thermal properties of the produced unsaturated polyester resins will be measured.

## Abstract

Thermoset polymers are widely used polymers in the world, but Increase in global plastic pollution and lack of fossil fuel stimulates intense research towards environmentally sustainable materials. Bio-based unsaturated polyesters (UPs) would be an excellent solution to replace oil-based synthetic polyesters. Most of the unsaturated polyesters have been synthesised by ring opening polymerisation (ROP) of cyclic esters or lactides.

In this study, different resins were developed using different initiators such as isosorbide (IS), 1,4 butanediol (BD), and cis-2 butene 1,4 diol (C2BD) with monomers like lactide (L) and alpha angelica lactone (AAL) through the ring opening polymerisation process. The produced resins were further characterised by using Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimeter (DSC), and Dynamic Mechanical Analysis (DMA).

Synthesis of resin with lactone monomer was not successful while with lactide monomer it was successful. IS-based resin showed better thermal properties compared to other obtained resins. Tg value of IS containing resin was 63°C, thermal stability up to 235°C and Storage modulus about 3841 MPa. These values are comparable with other bio-based resins produced using the same monomer.

**Key words:** Bio-based polymer, Resin, lactide, lactone, isosorbide, butanediol, polymerisation, characterisation, FTIR, NMR, TGA, DMA

## **Acknowledgements**

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I would also like to thank lab technicians and my classmates who have helped me directly or indirectly during the course of this project.

This work would not have been possible without the priceless help and support of my husband Mr Gaurangkumar Mistry. He helped me a lot during my entire thesis work. He motivated me whenever I was feeling down.

**Snehaben G. Mistry**

## **Limitations of the Thesis Project**

Numerous bio-based monomers are used to produce bio-polymers, but in this research only thermosetting will be produced. The bio-based lactide and lactone monomers will be solely used.

# TABLE OF CONTENTS

<b>Chapter 1. Introduction</b>	<b>1</b>
<b>1.1 Brief information about Polymers</b>	<b>1</b>
<b>1.2 Types of polymerisation process</b>	<b>1</b>
1.2.1 Addition Polymerisation	1
1.2.2 Step growth polymerisation	2
<b>1.3 Commercial Polymers</b>	<b>2</b>
<b>1.4 Bio-based resins</b>	<b>3</b>
<b>1.5 Bio-based resins applications</b>	<b>4</b>
<b>1.6 Literature reviews on bio-based resins</b>	<b>4</b>
1.6.1 Itaconic acid-based resins	4
1.6.2 Vegetable oil-based resins	7
1.6.3 Furan-based resins	8
1.6.4 Isosorbide-based resins	9
1.6.5 Lactic acid or lactide-based resins	11
<b>Chapter 2. Experimental Methodology</b>	<b>13</b>
<b>2.1 Materials</b>	<b>13</b>
<b>2.2 Apparatus</b>	<b>13</b>
<b>2.3 Synthesis Process</b>	<b>13</b>
2.3.1 Condensation Reaction	17
2.3.2 End-functionalization	17
2.3.3 Curing of the resin	19
<b>Chapter 3. Characterisation</b>	<b>21</b>
3.1 Nuclear Magnetic Resonance Spectroscopy (NMR)	21
3.2 Fourier Transform Infrared Spectroscopy (FTIR)	21
3.3 Differential Scanning Calorimeter (DSC)	22

3.4 Thermogravimetric Analysis (TGA) .....	22
3.5 Dynamic Mechanical Analysis (DMA) .....	23
<b>Chapter 4. Result and Discussion .....</b>	<b>24</b>
4.1 NMR Analysis .....	24
4.2 FTIR Analysis.....	27
4.3 DSC Analysis.....	29
4.4 TGA Analysis .....	31
4.5 DMA Analysis .....	33
❖ Summary of findings .....	35
<b>Chapter 5. Conclusion.....</b>	<b>36</b>
<b>Chapter 6. Recommendation for Future Work.....</b>	<b>37</b>
<b>Chapter 7. References</b>	

# **Chapter 1: Introduction**

## **1.1 Brief information about Polymers**

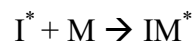
Polymer is a material which consists of macromolecules, composed of many repeating units called monomers. The repeating units are linked together via covalent bonds. There are two types of polymers; Natural and synthetic polymers. Natural polymers are wool, silk, cellulose, DNA, proteins etc. while synthetic polymers are polyethylene, polypropylene, polystyrene, Polyvinyl chloride, synthetic rubber etc.

## **1.2 Types of polymerisation Process**

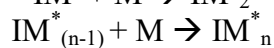
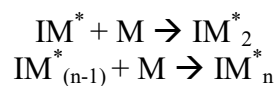
### **1.2.1 Addition Polymerisation or Chain growth polymerisation**

In Addition polymerisation process, the unsaturated monomer is added onto the active centre of the growing polymer chain at once. This process contains three steps: Chain initiation, chain propagation and chain termination. In the first step, chain carrier is generated through different ways of energy dissipation; Thermal initiation, high energy initiation and chemical initiation. In the second step, the chain starts to propagate as the active centre on the polymer molecule adds one monomer molecule to form a new polymer molecule with a new active centre. In the last step, the active centre disappears and the chain termination occurs. In this entire process no small molecule losses so no by product will be formed at the end. Types of chain growth polymerisation processes are: Radical polymerisation, Ring opening polymerisation, ionic polymerisation, coordination polymerisation etc. (See, Fig.1.1)

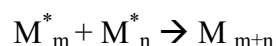
#### **Initiation**



#### **Propagation**



#### **Termination**

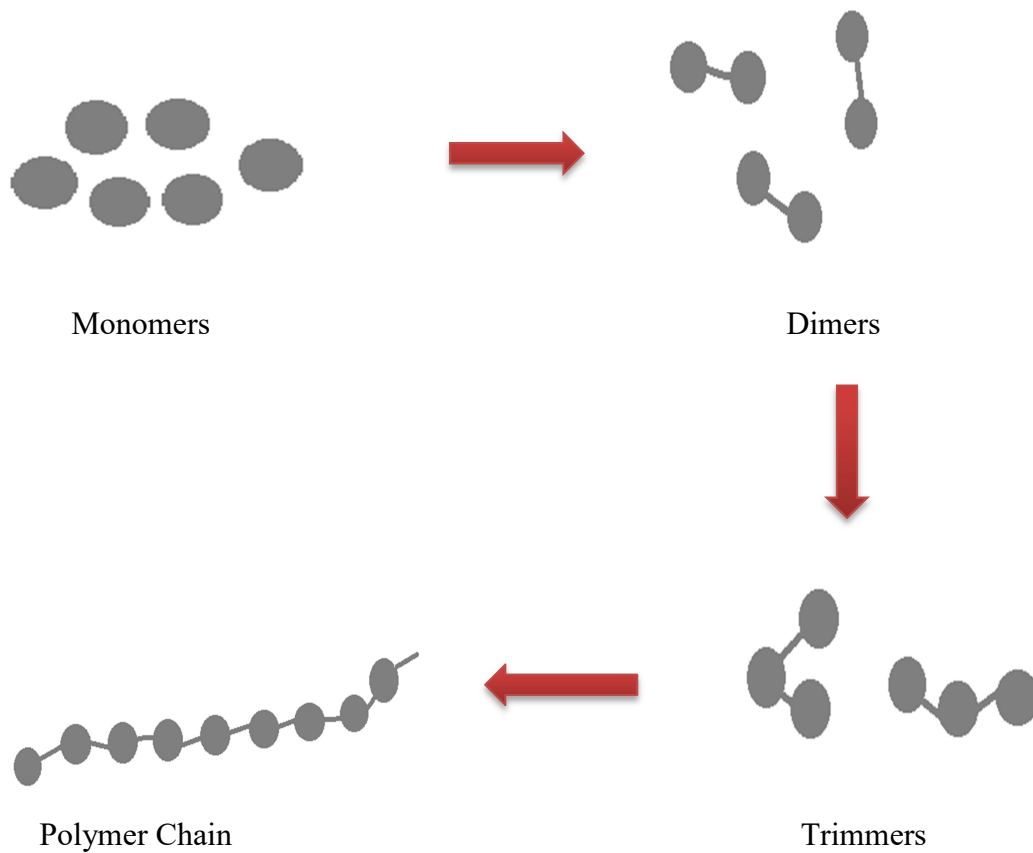


**Fig. 1.1** Addition polymerisation or Chain growth polymerisation



### 1.2.2 Step growth polymerisation

In the step growth polymerisation process, monomers having bi-functional or multifunctional properties start to react and first form dimers, then trimmers, then longer oligomers and at last the long polymer chain (Fig.1.2). In this process, two different monomers combine and a small molecule will lose, usually water. There is no requirement of initiator in this process.



**Fig. 1.2** Step growth polymerisation

### 1.3 Commercial polymers

The rapid modernisation has increased the demand of polymeric materials due to its excellent mechanical and thermal properties. There are two kinds of polymers according to thermal response, thermoplastic and thermoset. Thermoplastic can melt on application of heat and therefore they are recyclable while thermoset will deform when heat is applied due to its crosslink structure.

The thermosetting polymers are one of the most widely used synthetic polymers in the world. The commercial thermosetting resins are obtained from fossil fuel-based raw materials. The examples of thermosetting resins are epoxies, vinyl esters, polyurethanes, formaldehydes and unsaturated polyesters (UPs).

Unsaturated polyester (UP) is a linear polymer containing ester bonds and carbon-carbon (C-C) double bonds. Unsaturated polyester resin (UPR) is usually synthesised from petrochemical products such as UPs and reactive diluents (Malik et al., 2000; Ahamad et al., 2001). Currently, UPs are synthesised by polycondensation of dibasic organic acid with diols. Generally, the viscosity of the UP is high and to reduce the viscosity reactive diluent is required. The most adapted reactive diluent for UPs is styrene, which is a highly reactive solvent with lower viscosity. Styrene can be miscible with UPs that reduces the viscosity of resin and further it enhances the fiber impregnation. The participation of the C-C double bond of styrene in free radical polymerisation increases the cross-link density of the material, thus improving the final properties of material (Kandola et al., 2015). The UPs are highly in demand class of traditional thermoset polymers.

However, the large use of fossil fuel-based materials is becoming a major issue globally due to depletion of fossil fuels; fluctuations in the oil price, plastic pollution and due to several environmental concerns such as CO<sub>2</sub> emission, recyclability, and sustainability. These concerns have stimulated scientific efforts to find sustainable green alternatives to traditional synthetic plastics. To overcome these issues the researchers have concentrated on the renewable resources to be used as raw materials to develop bio-based thermosetting resin.

### 1.4 Bio-based resin

Currently, a class of biopolymers significantly attracted much attention of researchers is bio-based resins which can be produced from the renewable raw materials. Bio-based resins can be used in thermoplastic as well as thermoset polymers. Bio-based thermoset are widely used as matrices in fiber reinforced composite due to its outstanding properties such as heat and chemical resistance, excellent mechanical properties, easy processability, low density, good electrical conductivity and low cost (Penczek, 2005; Haq, 2007).

According to the German Nova institute, the production volume of bio-based polymers reached 7.5 million tonnes in 2018 which was just 2% of the production volume of fossil fuel-based polymers. However, the production of bio-based polymers is expected to grow up to 9.6 million tonnes by 2023. Further, the report stated that Asia is leading region when it comes to global

production of bio-based polymers by region by 2023 followed by Europe region ([Chinthapalli et al., 2019](#)).

The bio-based thermoset resin can be produced by two step reactions. In the first step, the incompletely reacted pre-polymer is produced while in the second step the final cross-linked polymer is produced ([Cowie, 2008](#)). Thus, bio-based thermoset resin is converted into non-recyclable resin by curing reaction which is unable to melt again on application of heat ([Ma, 2016](#)).

## **1.5 Bio-based resins application**

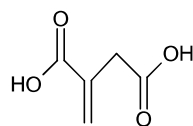
Most of the bio-based polymers possess excellent film forming properties which is suitable for traditional applications as well as high performance applications. It can be used in food containers, agriculture film and waste bags. Bio-based resins also found to be used in medical applications ([Yousaf et al., 2010](#); [Guo et al., 2011](#); [Tang et al., 2013](#)). According to the German Nova institute report, bio-based polymers were highly used in consumer goods manufacturing sector with 28% from actually produced bio-based polymers in 2018. The main polymers were epoxy resins, Polyurethane (PUR) and polyamide (PA). The Building and construction sector used 21%, the automotive and transport sector used 19%, the packaging sector used 15% and the textile sector used 11 % (woven and non-wovens). The significant growth in the application of these resins by different sectors is not expected to increase by 2023 ([Chinthapalli et al., 2019](#)).

## **1.6 Literature reviews on bio-based resins**

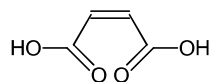
Over the past few years, lots of researches have been done for development of bio-based resins. In this section several bio-based resins produced from different renewable raw materials are reviewed.

### **1.6.1 Itaconic acid-based resins**

The molecular structure of IA contains carbon-carbon double bond and two carboxyl groups. This structure is close to the structure of maleic acid (MA) (Fig.1.3) hence, IA can replace traditional maleic acid or maleic anhydride in the synthesis of bio-based UPs. IA is also known as methylene succinic acid and it is usually prepared from renewable sources such as straw, sugar beet, sugar cane, starch etc. IA-based polymers are used in coatings, composites, elastomers and medical field ([Thomas et al., 2019](#)).



Itaconic Acid



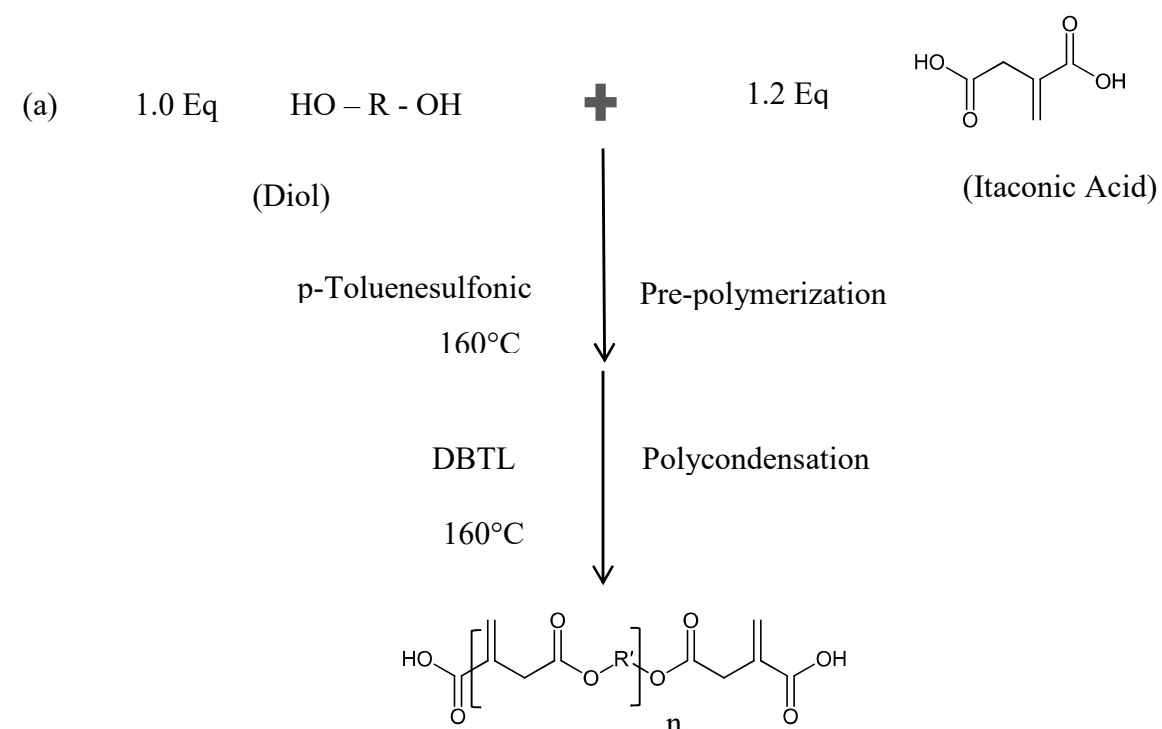
Maleic Acid

**Fig 1.3** IA and MA structure

The radically curable resins can be replaced by IA-based UPRs. However, the biggest problem of IA-based UPRs is complicated synthesis process under industrial scale. The unsaturated double bond of IA is prone to side reaction during polycondensation reaction which will lead to gel formation of polyester resin. Studies show that the choice of catalyst affects the side reaction during the polycondensation reaction ([Yang et al., 2012](#)).

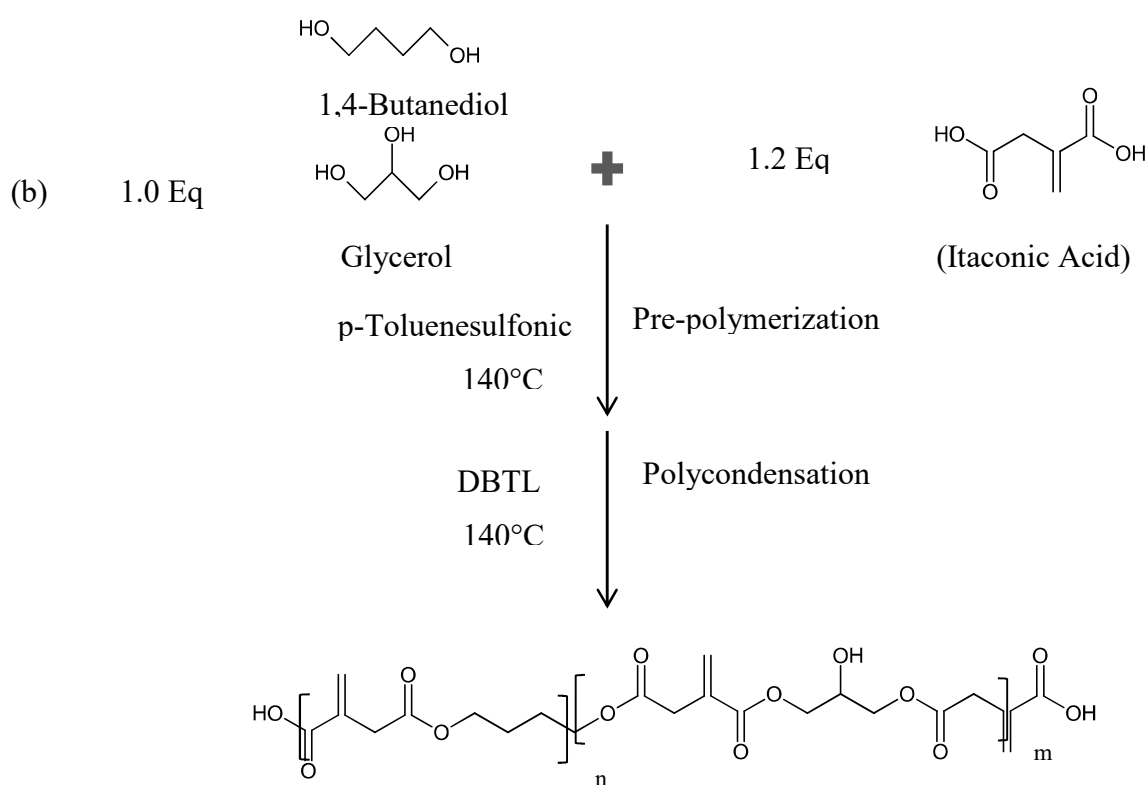
According to study of Robert et al., the polycondensation reaction with IA would not lead gel formation of UP. Water resistant Lewis acid ( $\text{Zn}(\text{OAc})_2$ ) had been used as catalyst for the polycondensation reaction of IA with 1,3-propanediol and 1,4 butanediol. The target products were obtained with >99% without any gel formation ([Robert et al., 2017](#)).

Dai et al, investigated synthesis process of UPs using Itaconic acid and different diols such as ethylene glycol (EG), 1,4 butanediol and 1,6-hexaediol (HDO) by pre polymerisation and polycondensation reactions (Fig.1.4). p-toluenesulfonic acid monohydrate was used as catalyst. The obtained resin was further copolymerised with acrylated soybean oil (AESO). The synthesised resin structure was verified using FTIR and  $^1\text{H-NMR}$ . Further, the mechanical and thermal properties were studied with the help of DSC, DMA and tensile testing. They found that polyesters obtained from Itaconic acid were significantly effective comonomers. They obtained glass transition temperature ( $T_g$ ) of  $32.2^\circ\text{C}$ , tensile strength of  $2.9\text{ MPa} \pm 0.6$ , young's modulus of  $33.3\text{ MPa} \pm 1.1$  and elongation at break  $12.4\% \pm 2.2$  ([Dai et al., 2015](#)).



(Bio-based Content Unsaturated Polyester)

R = -CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-



(Bio-based Content Unsaturated Polyester)

**Fig. 1.4** Synthesis of IA-based polyester (reaction scheme adopted from [Dai et al., 2015](#))

Itaconic acid-based UPs can also be prepared by enzymatic catalysis instead of using traditional chemical catalyst. Jiang et al. synthesised UPs using succinic acid (SA), Itaconate and 1,4-butanediol in the presence of CaLB (lipase B from *Candida Antarctica*) catalyst. The obtained UPs had high molecular weight of up to 13,000 g/mol and in addition the Tg and thermal stability of the obtained UPs did not change (Y. Jiang et al., 2013). Brannstrom et al., also confirmed that enzymatic catalyst CaLB can also be used for the synthesis of Itaconic acid-based UPs (Brännström et al., 2018).

### 1.6.2 Vegetable oil-based resins

Vegetable oil is an easily available, low cost and environment friendly renewable raw material. The structure of vegetable oil gives it biodegradable property. Numerous researches have been done on vegetable oil and researchers have developed various plant-based thermoset resins, thermoplastic resins and elastomers. Physical and chemical properties of vegetable-based products are close to the traditional fossil fuel-based polymers. Vegetable oil is composed of triglycerides of fatty acid, fatty alcohol, linoleic acid, aliphatic hydrocarbons, phospholipids and others (L. Espinosa and M. Meier, 2011).

The structure of vegetable oils composed of carbon-carbon double bonds, ester bonds and aliphatic chains. It can be polymerised into crosslinked UPs without any modification. To enhance reactivity of vegetable oil, modification is required to be done to introduce other kind of carbon – carbon bonds. There are several researches have been done to modify the vegetable oils.

Adekunle et al. reported the synthesis of epoxidized soybean oil with methacrylic acid, methacrylic anhydride and acetyl anhydride. The purpose of the study was to synthesis reactive soybean oils to be used as thermoset resin in structural natural fiber composite. First, they modified epoxidized soybean oil with methacrylic acid. This methacrylated soybean oil (MSO) was further modified with methacrylic anhydride and acetic anhydride. The obtained resins were successfully modified. The methacrylated soybean (MSO) and methacrylic anhydride modified soybean oil (MMSO) showed lower viscosities of 0.2 and 0.48 Pas, respectively. Further, resins were crosslinked with the help of t-butyl peroxybenzoate at 160°C for 24 h and characterised by FTIR as well as TGA. The FTIR result confirmed that there was no change in the structure of crosslinked resin despite of long curing time. The MSO sample showed single degradation TGA curve between 320-480°C. The lower viscosity and thermal properties of the obtained resins was acceptable to be used as matrix in composites (Adekunle et al., 2009).

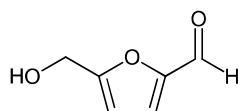
Chen et al. reported synthesis of acrylated sucrose (AS) to enhance the properties of UV (Ultraviolet irradiation) curable coatings composed of commercial hyperbranched acrylates (HBAs)-modified acrylated epoxidized soybean oil (AESO). They incorporated synthesized AS and HBAs to AESO. The obtained coatings showed improved mechanical properties,

tensile moduli, impact strength, elongation at break and T<sub>g</sub> while water resistivity and thermal stability decreased (Chen et al., 2011).

To enhance low rigidity of vegetable oil coatings, Díez-Pascual et al. has incorporated inorganic nanomaterial such as TiO<sub>2</sub> into acrylated vegetable oil. They synthesised AESO from epoxidized linseed oil and crosslinked it with an acrylic monomer. Further, TiO<sub>2</sub> nanoparticles were added as reinforcement and then subjected to UV radiation to produce nanocomposite coatings. The incorporation of nanoparticles enhanced thermal stability by increasing the decomposition onset temperature. It also improved resin barrier performance by decreasing water uptake, oxygen and water permeability. The obtained mechanical properties such as storage modulus, Young's moduli, indentation and pencil hardness were excellent. The obtained T<sub>g</sub> ranged from 33°C to 41°C and hardness was 75 MPa.

### 1.6.3 Furan-based resin

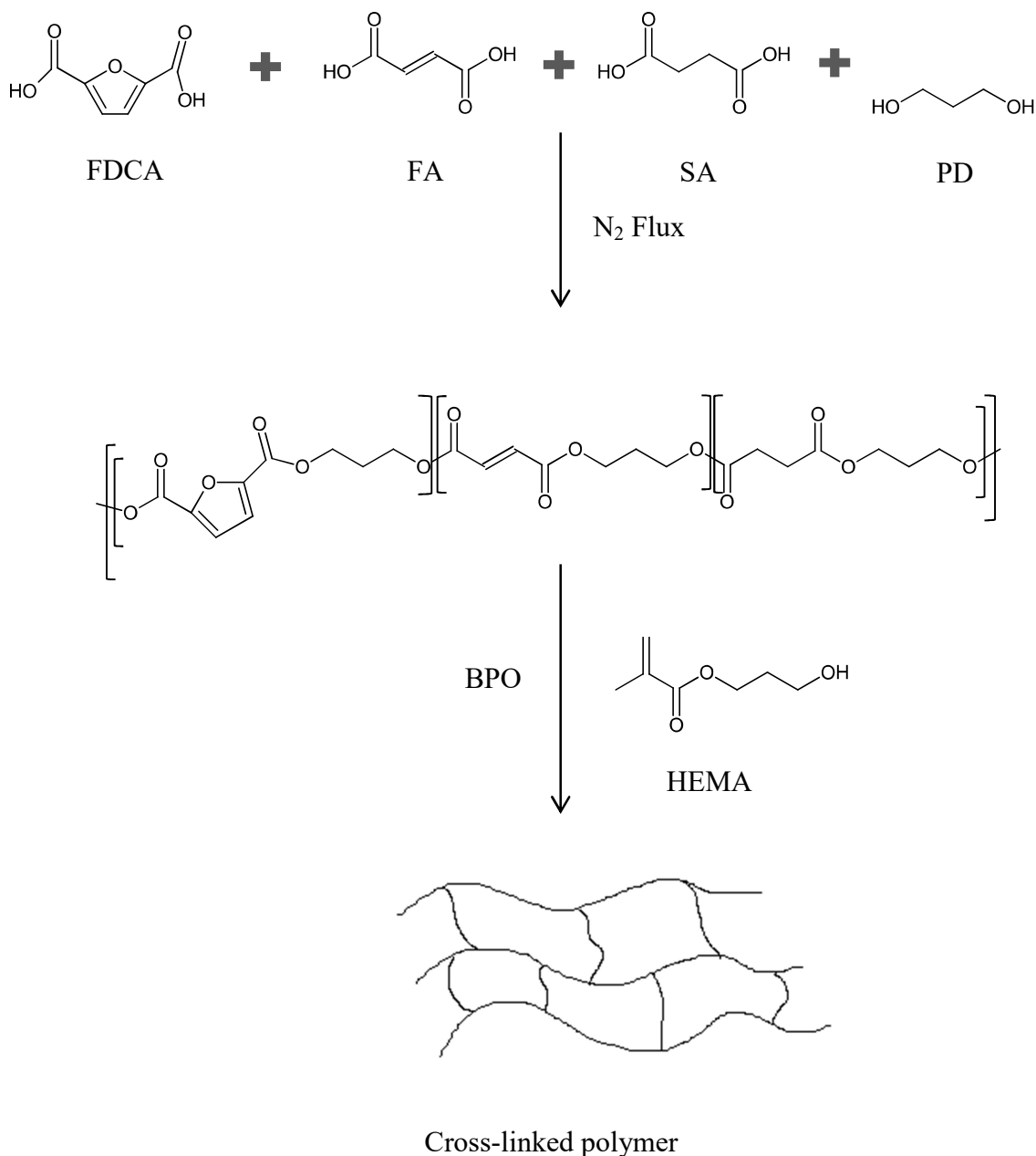
Furan chemical such as 5- Hydroxymethylfurfural (5-HMF) (Fig.1.5) can be produced from renewable resource like sucrose, glucose, fructose, cellulose and inulin. Over the past few years, Furan-based polymers have gained a lot of attention of researchers. Furan ring contains rigidity close to the benzene ring and acquire better properties compared to benzene ring.



**Fig 1.5** 5- Hydroxymethylfurfural (5-HMF) Structure

Sousa et al. reported furan-based UPs from 2,5 furandicarboxylic acid (FDCA), fumaric acid (FA), SA and 1,3 propanediol (PD) in the absence of catalyst via melt polycondensation reaction. Without purification the obtained UPs were cured by adding 2-hydroxyethylmethacrylate (HEMA) as a reactive diluent and benzoyl peroxide (BPO) as a thermal initiator (See, Fig. 1.6). The resulted crosslinked UPs showed thermal stability up to 230°C, T<sub>g</sub> between 87°C - 104°C and storage modulus at 25°C between 390 – 614 MPa (Sousa et al.,2015)

Chen et al., reported new furan-based UP which is synthesised from furfural dimethacrylate through proton-transfer polymerization. The obtained UP had a self-curing ability to crosslink and it can undergo Diels-Alder reaction based curing to produce strong polyester (Chen et al., 2016).



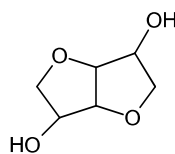
**Fig. 1.6** Synthesis of Unsaturated polyester from FDCA and its network structure of cross-linking product with HEMA (Sousa et al., 2015)

#### 1.6.4 Isosorbide-based resin

Isosorbide (IS) is a solid diol containing bicyclic rigid structure. It is produced from renewable resources using different methods such as catalytic dehydration of sorbitol and the enzymatic hydrolysis of starch. Hydrogenation of starch, glucose or sucrose will produce sorbitol (Wang et al., 2016). The structure of IS (Fig.1.7) contains two tetrahydrofuran rings which are connected with each other at 120 degree in V type shape and forms chiral diol

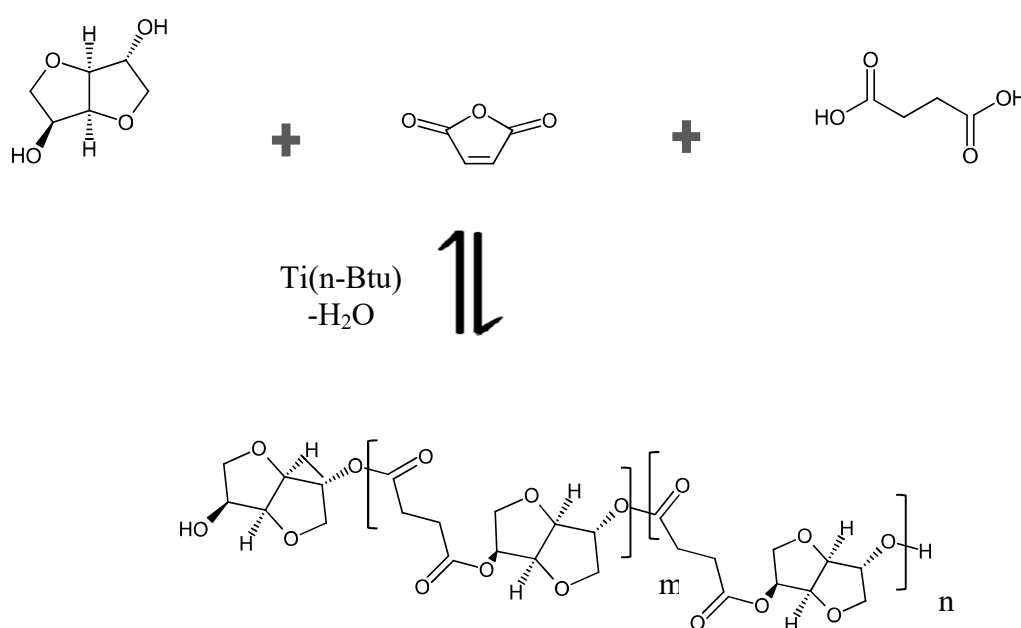


structure with two hydroxyl functional groups. Therefore, the polymers prepared from isosorbide possess excellent thermomechanical properties (Sadler et al., 2015).



**Fig.1.7** Isosorbide structure

Jasinska and Koning tried to synthesis series of bio-based UPs from isosorbide, succinic acid and maleic anhydride (See, Fig.1.8). Further, it was crosslinked with N-vinyl-2-pyrrolidinone, 2-hydroxyethyl methacrylate, acrylic acid, and methacrylamide in the presence of a peroxide initiator (2-butanone peroxide) and an accelerator (cobalt ( $\alpha$ ) 2-ethylhexanoate). After crosslinking they got high Tg up to 103°C, but thermal stability of obtained resin was poor. Though, it was still promising for coating applications (Jasinska and Koning, 2010).



**Fig. 1.8** Synthesis of poly (isosorbide maleate-co-succinate)s (Jasinska and Koning, 2010)

Sadler et al. synthesised resin through direct esterification of isosorbide utilizing methacrylic anhydride with base catalyst. The resulted isosorbide-methacrylate (IM) resin showed glass transition temperature higher than 240°C and main degradation temperature of ~400° C. It also showed better mechanical properties such as modulus of ~4 GPa and strength of 85 MPa. The thermal and mechanical properties of the obtained IM resin indicate that the resin has good potential to be used as matrix in composite applications at moderate temperature (Sadler et al., 2013).

### 1.6.5 Lactic acid or Lactide-based resin

Lactide-based thermoset resin has also earned attention of researchers. Lactide is produced from the lactic acid which is renewable resource. Lactide-based thermosetting resin can be produced by introducing reactive group into the oligomers of lactide i. e. by end capping lactide oligomers with acrylic group or methacrylic group etc. (Bakare et al., 2016). to start free radical polymerisation of the lactide oligomers. Åkesson et al. succeeded in end capping lactic acid oligomer with methacrylate groups and crosslinked them by free radical polymerisation for composite application. They synthesised thermoset resin by condensation of pentaerythritol, Itaconic acid and lactic acid. The obtained molecules were star shaped which were end capped by methacrylic anhydride. The resin showed good mechanical properties but it was highly viscous and that was its drawback (Åkesson et al., 2009). Highly viscous resin requires reactive diluent to lower its viscosity.

Bakare et al. studied probability of producing bio-based resin from lactic acid and glycerol. Glycerol was synthesised with lactic acid oligomers of three different chain lengths (n=3, 7 and 10) via direct condensation followed by end-functionalization using methacrylic anhydride. After end-functionalization, the product was submitted to a rotary evaporator to remove the remaining toluene and the by product (methacrylic acid) from it. Further, the resin was cured by mixing 2 wt. % dibenzoyl peroxide as an initiator and 0.5 wt. % N, N-dimethylaniline as the accelerator at room temperature for 1 h and then in oven at 150°C for 20 min. The cured sample was then characterised by using FTIR, DSC, DMA and TGA. TGA analysis result showed better thermal stability for chain length of 3 (See, Table 1.1). Bakare concluded that it was possible to produce bio-based resin using lactic acid and Glycerol. The chain length of 3 showed better rheological mechanical and thermal properties compared to chain lengths of 7 and 10 (Bakare et al., 2014).

**Table 1.1** Thermal characterisation results of the resin (F.O. Bakare et al., 2014)

Resin	<u>DSC</u>		<u>DMA</u>				<u>TGA</u>		
	Heat of exotherm for uncured resin (J/g)	Heat of exotherm for cured resin (J/g)	Tg (°C)	Standard Deviation	Standard modulus (MPa) at 25°C	Loss modulus (MPa) at 25°C	Degradation temperature at 10 wt. % loss (°C)	Maximum degradation (°C)	Second derivative peak (°C)
n=3	227.4	0	97	352	4314	353.8	258	375	438
n=7	162.2	0	80	215	3766	228.6	248	366	436
n=10	94.3	0	54	59	1736	481.8	202	357	433

Esmaeili et al., synthesised a set of bio-based star shaped thermoset resins via ring opening polymerization of lactide with different multi hydroxyl core molecules such as glycerol (GL), ethylene glycol (EG) and erythritol (ER). The obtained uncured resin was further characterised by using modular compact rheometer to measure rheological properties. Further, the uncured resin was crosslinked by mixing 2 wt.% dibenzoyl peroxide in pre-heated oven at 160°C for 15 min. The thermal properties of the cured resin were analysed by using DSC, DMA and TGA. FTIR results confirmed that the end-functionalization and curing reaction had taken place. The melt viscosity of the erythritol-based resin found lower and thermomechanical properties found superior compared to the glycerol-based resin. The obtained resins showed desired characteristics to be used as matrix for structural composites. Thermomechanical properties of the obtained resins were compared with commercial polyester resin (CPE). The result indicated that higher number of hydroxyl group containing core molecule showed better thermomechanical properties (Esmaeili et al., 2014).

**Table 1.2** thermal characterisation results of the resins (Esmaeili et al., 2014)

Resin	<u>DSC</u>		<u>DMA</u>				<u>TGA</u>
	Heat of exotherm for uncured resin (J/g)	Heat of exotherm for cured resin (J/g)	Tg (°C)	SD	Standard modulus (GPa) at 25°C	SD	Degradation temperature at 5 wt. % loss (°C)
ER	143.9	0	94	0.54	3.567	0.32	265
GL	130.5	0	66.11	0.69	3.478	0.039	260
EG	178.8	0	60.22	2.25	2.517	0.015	240
CPE	-	-	84.37	1.27	2.935	0.048	-

In this research study, the possibility of producing bio-based unsaturated polyester resins will be investigated. Monomers such as lactide and lactones will be tried to synthesise with different diols. The synthesis of the resins will be carried out via direct condensation reaction followed by end-functionalization reaction (Fig.2.1-2.4). Further, the crosslinked resins will be characterised for the thermal properties.

## **Chapter 2 : Experimental Methodology**

### **2.1 Materials**

3,6-Dimethyl-1,4-dioxane-2,5 dione (99%, Sigma Aldrich) and Alpha Angelica lactone (98%, Sigma Aldrich) were used as a main monomers. Different initiators such as 1,4 Butanediol ( $\geq 99\%$ , Merck KGaA), Isosorbide (98%, Acros Organics), Cis-2 butene-1,4-diol (97%, Acros Organics) were used. Toluene ( $\geq 99.9\%$ , Sigma Aldrich) was used as solvent. Tin (II)-ethylhexanoate ( $\sim 95\%$ , Sigma Life Science) and Methanesulfonic acid (98+%, Alfa Aesar) were used as catalysts in the reaction. Hydroquinone ( $\geq 99\%$ , Sigma Aldrich) was used as an inhibitor or stabilizer during end functionalization reactions. Methacrylic anhydride (94%, Sigma Aldrich) was used as a reagent for end-functionalization. Dibenzoyl peroxide (2 wt %) and N-N Dimethyl aniline (99%, Sigma Aldrich) were used as initiators for crosslinking of the obtained resin.

### **2.2 Apparatus**

Three neck round bottom flask  
Glass Condenser  
Magnetic Stirrer  
Stir Bar  
Thermometer  
Molds  
Oven  
N<sub>2</sub> Gas Inlet  
Cold Water Connection

### **2.3 Synthesis Process**

A most powerful strategy to synthesise polyesters is ring opening polymerisation (ROP). It is generally carried out in bulk or in solution (i.e., using Dioxane, THF, Toluene, etc.), emulsion or dispersion. The ROP process employs a metal catalyst and initiator for the polymerisation of cyclic ester monomers or lactones into linear polyesters. The polyesters can be derived from Glycolide (GA), Lactide (LA), Lactones etc. ([Albertsson and Varma, 2003](#)). There are three major reaction mechanisms for polymerisation such as anionic, carbocationic and coordination-insertion and this mechanism depends on the type of initiator used. However, anionic and coordination insertion mechanism will give high molecular weight polyesters.

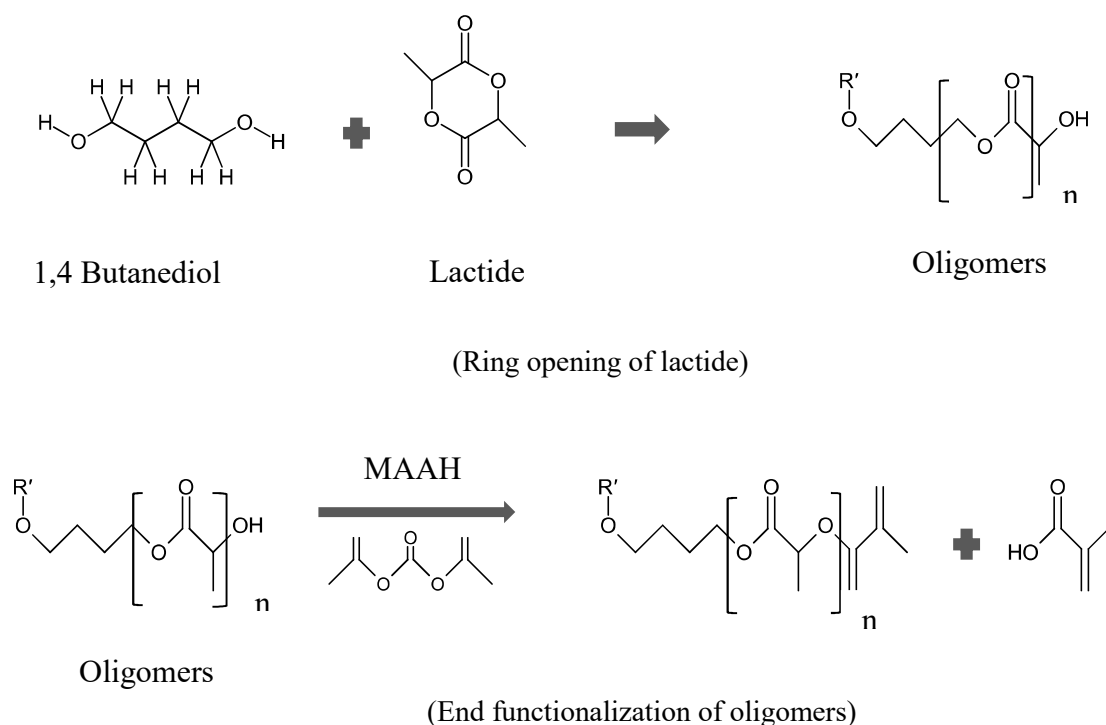
The average chain length can be regulated by adjusting the ratio between the monomer and the initiator. Moreover, the trans-esterification reactions are avoided during the process by providing narrow molecular weight distribution. This approach entitles through the appropriate choice of the monomers to synthesize a variety of homopolymers and copolymers ([Tang and Chen, 2018](#); [Hori et al., 1995](#)).

The whole ROP process was carried out in two steps. First step , ring opening of lactide (L) or lactone such as Alpha Angelica Lactone (AAL) using different initiators such as Isosorbide (IS), 1,4 Butanediol (BD), Cis-2 butene-1,4 diol (C2BD); and a catalyst such as Tin (II)-ethylhexanoate and Methanesulfonic acid. Second, end functionalization of the obtained oligomers. The ROP was carried out with toluene and without toluene (i.e. solution and Bulk polymerisation).

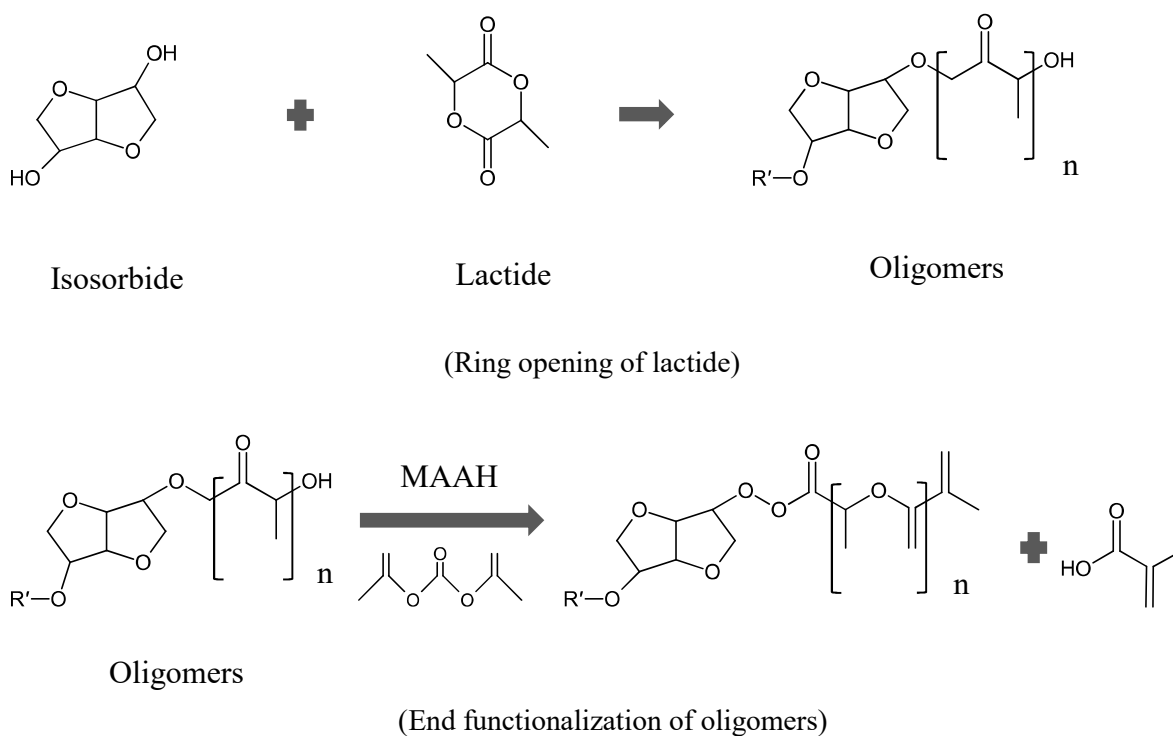
**Table 2.1** Ratio of Initiator to Monomer is as follow

Sr. No	Initiator : Monomer	Ratio
1	1,4 Butanediol : Lactide (BD:L)	1:4
2	Isosorbide : Lactide (IS:L)	1:4
3	Cis-2 butene-1,4-diol : Lactide (C2BD:L)	1:4
4	Isosorbide : Alpha Angelica Lactone : Lactide (IS:AAL:L)	1:1:3

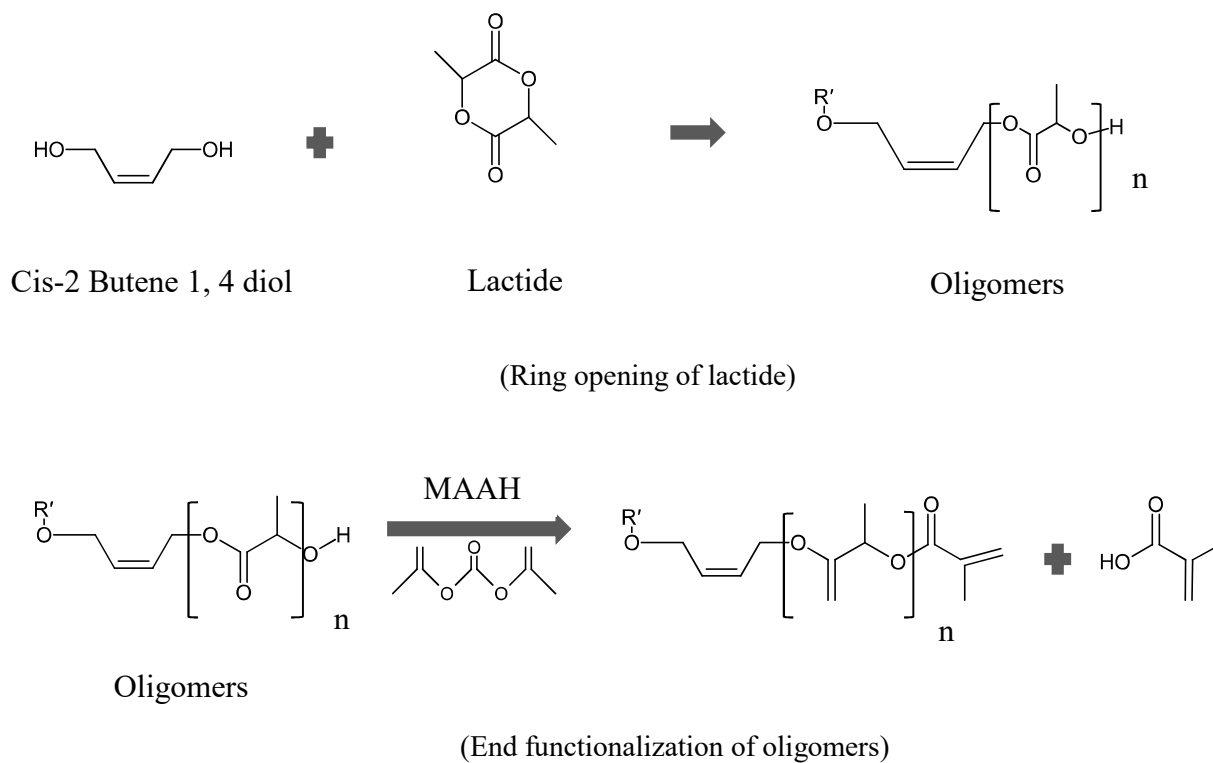
### Reaction Mechanism for different initiator and monomer



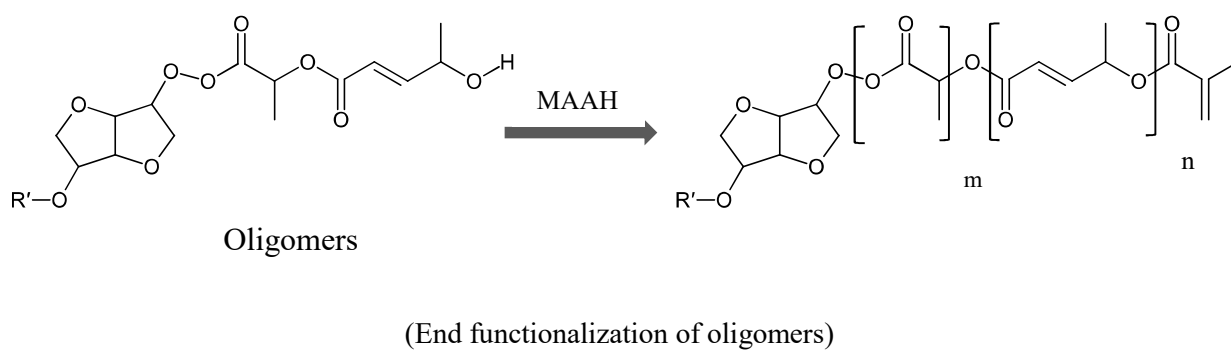
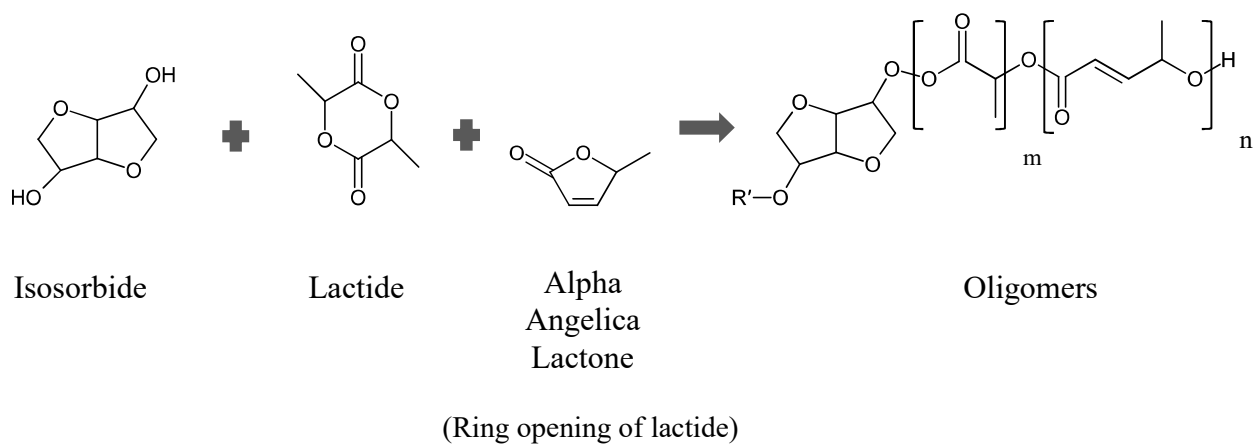
**Fig.2.1** Reaction scheme for 1,4 Butanediol-based resin



**Fig.2.2** Reaction scheme for isosorbide-based resin



**Fig. 2.3** Reaction scheme for Cis-2 Butene 1,4 diol-based resin



**Fig 2.4** Reaction scheme for Alpha Angelica lactone-based resin

### 2.3.1 Condensation Reaction (Step 1)

1,4 butanediol (0.044 mol or 4.04 g) and Lactide (0.112 mol or 16.16g) were added to 12.96 g of toluene in a three neck round bottom flask. 0.1 wt% Tin (II)-ethylhexanoate was added to the flask as catalyst. The flask was then immersed in oil bath. The flask was equipped with a glass condenser, nitrogen inlet and magnetic stirrer. The flask was heated under the constant stirring for 2 hrs. at 150°C. After 2 hr., the temperature was raised to 170°C for 1 hr. and then 190°C for 1 hr. The whole set up for the synthesis process is given in Fig.2.5. The other initiators and monomer ratios used are given in Table 2.1.

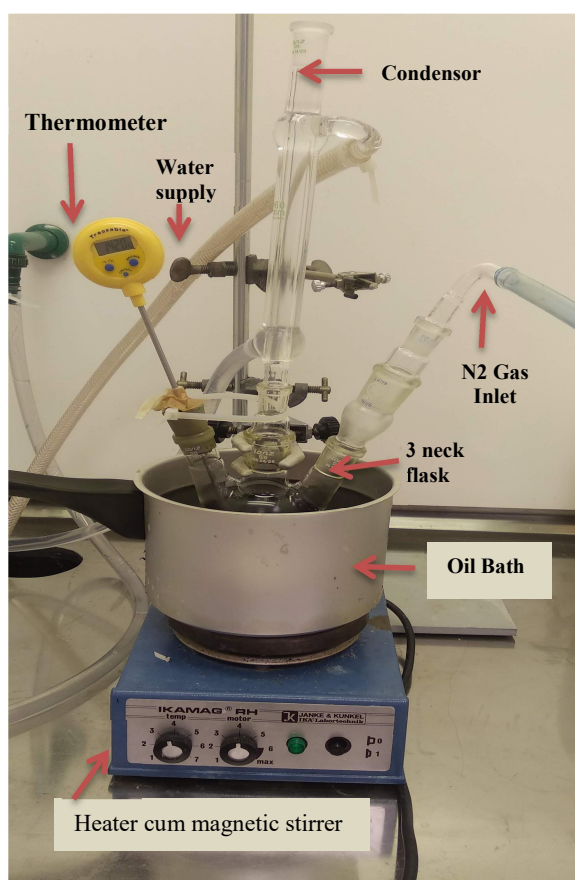


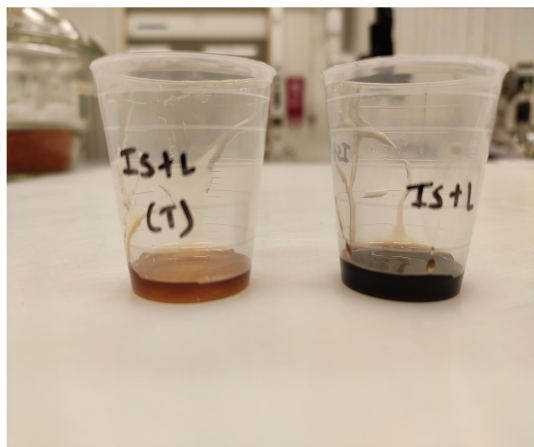
Fig. 2.5 Set up for the resin synthesis process

### 2.3.2 End-Functionalization (Step 2)

The obtained oligomer solution was further cooled to 105°C for further process. 0.3 wt. % hydroquinone was added to the solution as a stabilizer under continuous stirring. Stabilizer was used to prevent unwanted radical reaction and gel formation. During the first hour of the reaction, 0.0968 mol (15.875g) methacrylic anhydride was added in the flask using a dropwise funnel. Reaction was carried out at 105° C for 3 h under continuous stirring. After completion of the reaction, obtained resin was cooled and then residual toluene was



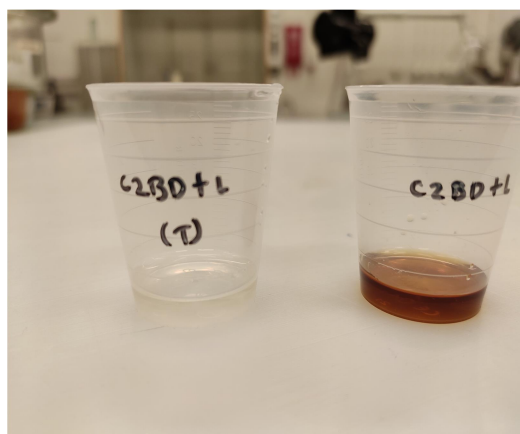
evaporated at 60-70° C using a rotary evaporator at 3-10 mbar vacuums. Resins synthesised through bulk and solution polymerisation methods are shown in Fig.2.6. (Note: The same process was carried out without toluene (i.e, Bulk polymerisation)).



(a)



(b)



(c)

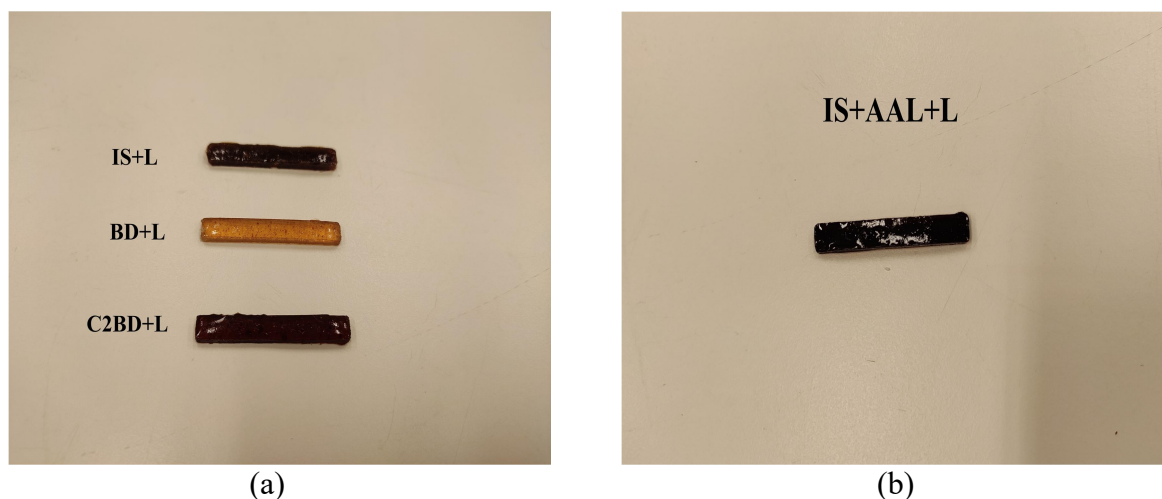
**Fig. 2.6** Different resins synthesised with toluene and without toluene. (a) Resins with IS initiator (b) Resins with BD initiator (c) Resins with C2BD initiator

### 2.3.3 Curing of the Resin

A free radical polymerisation method was used for curing of the obtained resin. 2 wt. % radical initiator (Benzoyl peroxide) and 2 wt. % curing accelerator (N, N-dimethyl aniline) was used. The sample mixture containing resin, initiator and accelerator was transferred into the mold to prepare samples for dynamic mechanical analysis (Fig.2.7). It was cured at room temperature (30°C) for 1 hr. and after it was placed in the oven at 150°C for 1 hr. The same sample mixture was also cured at room temperature (30°C) for 30 min. and then placed in the oven at 150°C for 30 min. The cured samples were then characterised using TGA, DSC, DMA and FTIR.

**Table 2.2** Details of curing methods

Curing Agent	Accelerator	Curing Method 1	Curing Method 2
2 wt.% Dibenzoyl Peroxide	2 wt.% N-N Dimethyl aniline	30°C – 1 hr. 150°C – 1 hr.	30°C – 30 min. 150°C – 30 min



**Fig. 2.7** Cured resins (a) (from top to bottom) resin with IS, resin with BD, resin with C2BD (b) Resin with AAL.

Several approaches were tried to synthesise different resins. All approaches are given in Table 2.3.

**Table 2.3** Different approaches for synthesis of resins

No.		Solution Polymerisation (With Toluene)	Bulk Polymerisation (Without Toluene)	Result
1	Synthesis Steps	Step 1: 4 h	Step 1: 4 h	<p>➤ A Lot of unreacted groups of MAH, LA, MA found during solution poly.</p> <p>➤ The curing of the AAL-based resin was not successful.</p>
		Step 2: 3 h (105°C)	Step 2: 3 h (105°C)	
	Initiators-Monomers	BD, IS,C2BD,L,AAL	IS, AAL,L	
	Catalyst	Tin (II)-ethylhexanoate		
2	Synthesis Steps	-	Step 1: 8 h	Produced resin could not cure properly
			Step 2: 3 h (105°C)	
	Initiators-Monomer		IS, BD,C2BD,L	
	Catalyst		Tin (II)-ethylhexanoate	
3	Synthesis Steps	-	Step 1: 8 h	Produced resins were cured properly
			Step 2: 4 h (120°C)	
	Initiators		IS, BD,C2BD,L	
	Catalyst		Tin (II)-ethylhexanoate	

## **Chapter 3: Characterisation**

### **3.1 Nuclear Magnetic Resonance Spectroscopy (NMR)**

Nuclear magnetic resonance technique gives information about the number of C and H atoms in a molecule as well as which atom is attached to which. So, the composition of the produced polymer, its length and end capping can be determined by using it. The resin synthesised from stage two is examined using  $^{13}\text{C}$  NMR at 850 MHz.

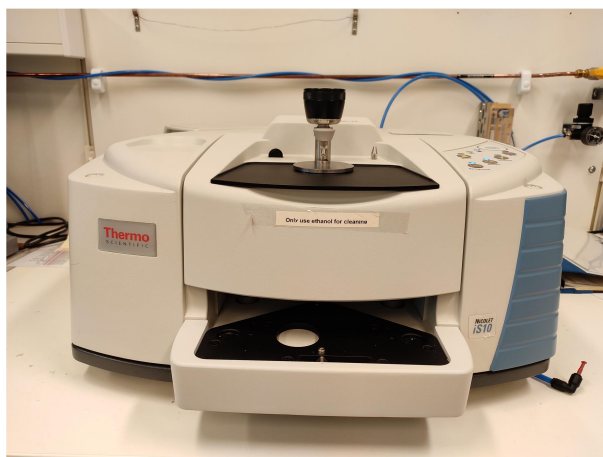
(*Note:* The resin samples were sent to Finland for the NMR test. The test was performed by Mr. Andrew Root, Magsol, Finland)

### **3.2 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform infrared spectroscopy technique is used to identify the components and their chemical groups. This technique gives a spectrum of emission, absorption and photoconductivity of solid, liquid and gas. It is widely used in biological, chemistry and geological research.

The resin synthesised during first step, second step and cured are analysed using Nicolet iS10 spectrometer (Thermo Fisher Scientific, MA).

For the FTIR test, first it is important to take background on the FTIR software. After collecting background resins synthesised during each step have been tested.

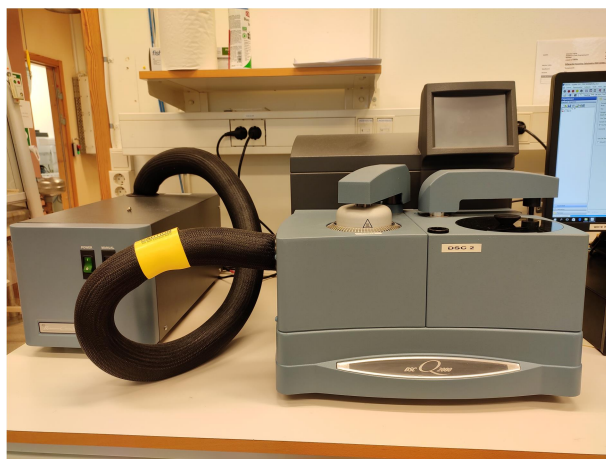


**Fig. 3.1** FTIR Nicolet iS10 spectrometer (Thermo Fisher Scientific, MA)

### 3.3 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter is used to measure how the physical properties of a sample change with temperature against time. In this method, the contrast in the amount of heat requires to increase the temperature of a sample and reference is measured as a function of temperature.

In the beginning of the test the samples were sealed in a small aluminium pan. It was equilibrated at 0°C and then run using three cycles. In the first cycle, samples were heated at a heating rate of 10°C min<sup>-1</sup> from 0°C up to 200°C. In the second cycle, the samples were cooled at a cooling rate of 10°C min<sup>-1</sup> from 200°C to 0°C and in the third cycle the samples were again heated from 0°C up to 200°C using same heating rate as first cycle. Each heating/cooling step was carried out following isothermal hold of 1 min.



**Fig. 3.2** DSC (DSC Q2000)

### 3.4 Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis is a thermal analysis method. TGA measures the mass of the sample over time while the temperature changes. It gives information about absorption, adsorption, desorption, phase transitions, chemisorption, thermal decomposition, thermal stability etc.

In this test, cured resin samples were heated at a heating rate of 10°C min<sup>-1</sup> from ambient to 700°C in the nitrogen atmosphere.

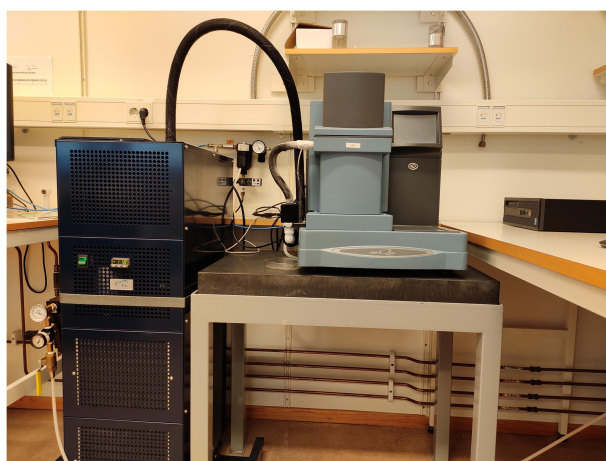


**Fig. 3.3** TGA (TGA Q500)

### 3.5 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis technique is used to study the viscoelastic behaviour of the polymers. A Sinusoidal stress is applied on the material and the strain generated in the same material is measured to learn the complex modulus. The temperature, frequency and amplitude can be varied. This technique is also used to verify the glass transition temperature.

For the DMA test, the first sample has been equilibrated at  $-20^{\circ}\text{C}$  and then heated at a heating rate of  $3^{\circ}\text{C min}^{-1}$  up to  $150^{\circ}\text{C}$  under the frequency of 1 Hz and amplitude of 10  $\mu\text{m}$ .

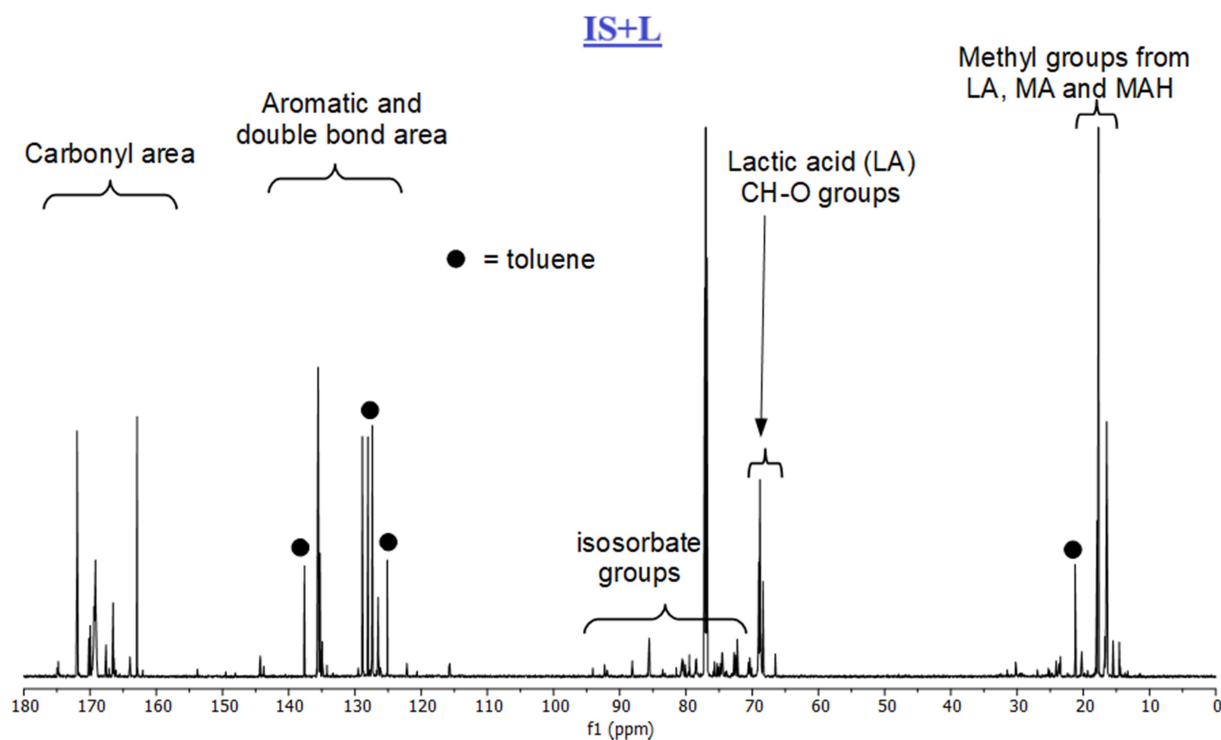


**Fig. 3.4** DMA (DMA Q800)

## Chapter 4: Result and Discussion

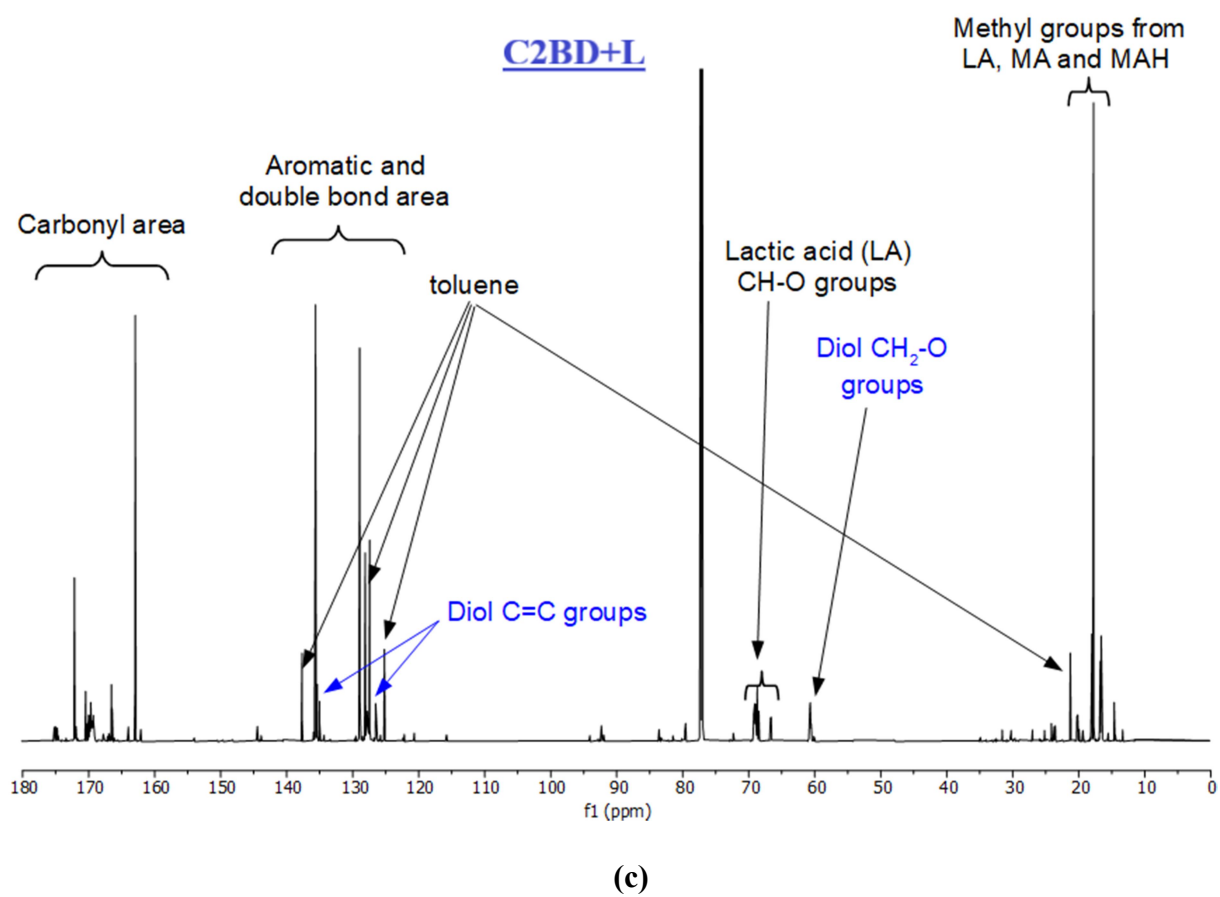
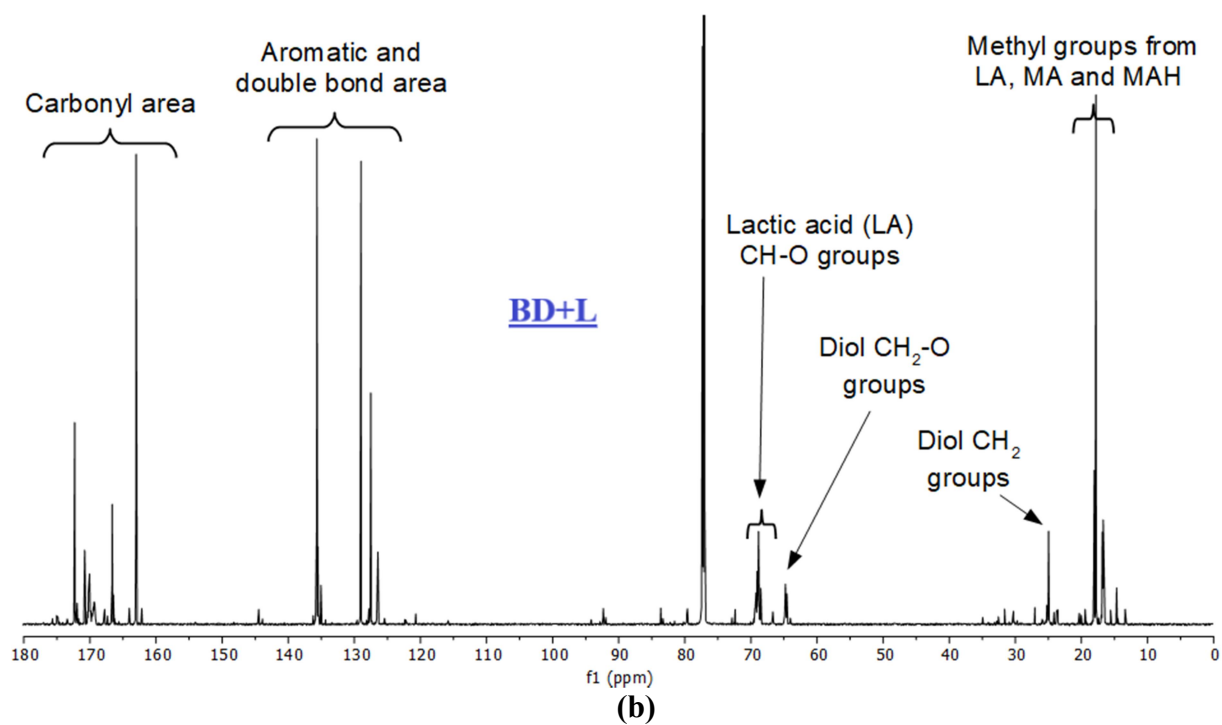
### 4.1 NMR Analysis

NMR test was performed to determine the composition of the synthesised polymers. These assignments are based on earlier analysis data of similar types of resin prepared using lactic acid and glycerol (F.O. Bakare et al., 2014). Fig. 4.1 is a full  $^{13}\text{C}$  NMR spectrum of resin with IS, BD, C2BD and IS+AAL, respectively. The carbonyl area is the most important area in the whole spectrum where all components present in the resin will give signal. The spectrum of resins with IS, BD and C2BD shows that initiators and Methacrylic anhydride (MAH) had reacted with lactide. While the resin with IS+AAL shows a different spectrum from the other resins. The spectrum shows ketone groups around 207 ppm.

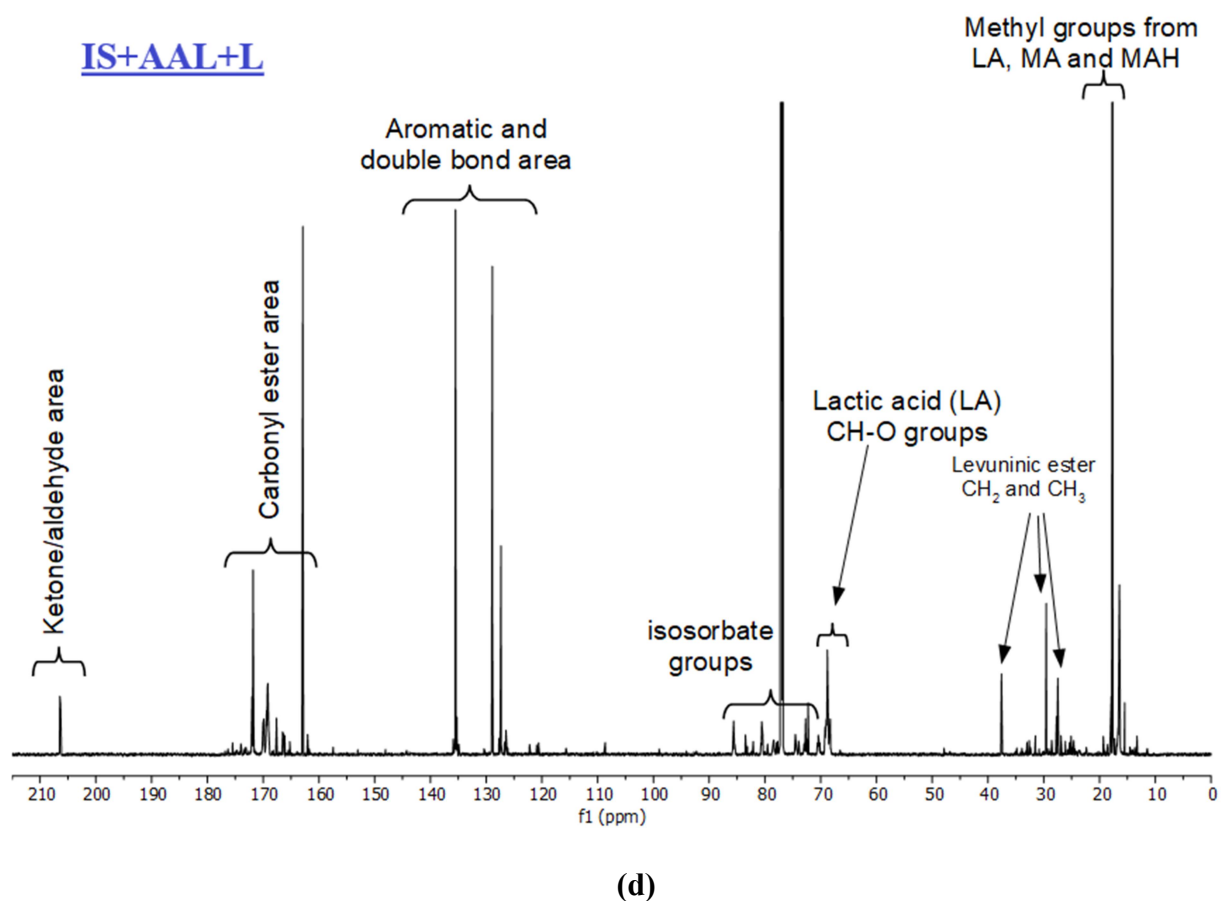


(a)

Though the spectrum shows some reaction between initiators, monomer and anhydride, but there are so many free Methacrylic anhydrides (MAAH) and maleic acid (MA) found in the resins (See, Table 4.1) which remained unreacted.







**Fig. 4.1**  $^{13}\text{C}$  NMR spectrum of resin with different initiators; (a) IS, (b) BD, (c) C2BD and (d) IS+AAL

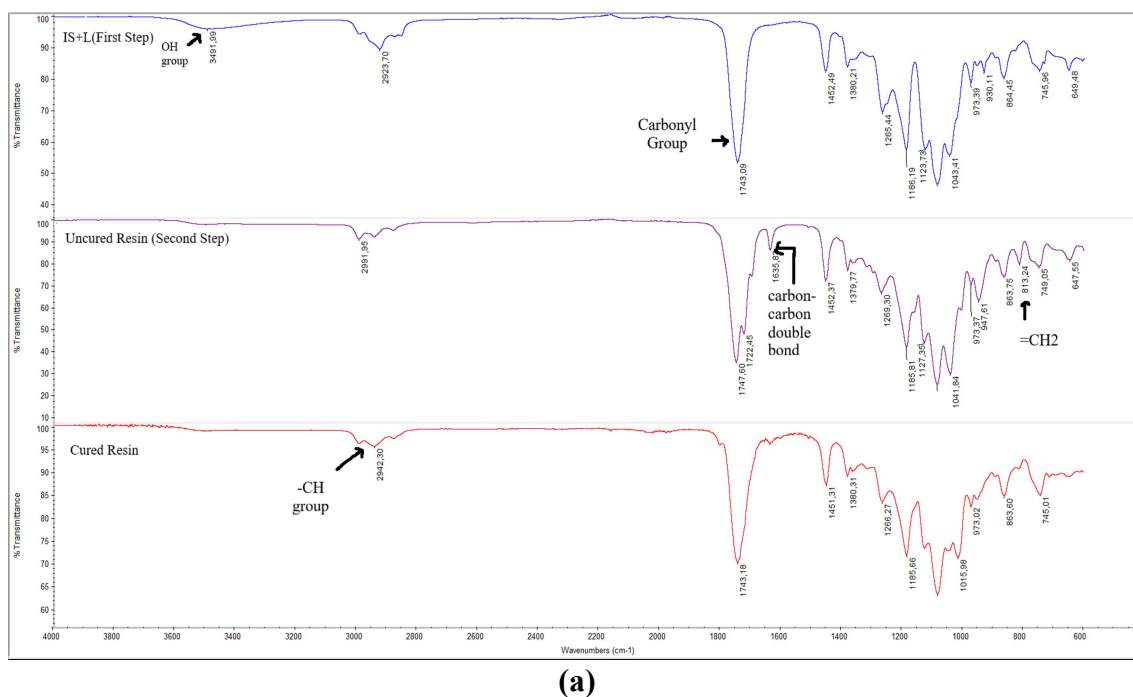
**Table 4.1** Distribution of MA in different resins

	IS+L	BD+L	C2BD+L	IS+AAL+L
	(mole %)			
<b>Bound MA</b>	28.5	25.4	21.6	18.0
<b>Bound MA to diol</b>	7.0	5.9	6.6	0
<b>Free MA</b>	37.2	25.9	27.9	31.9
<b>Free MAH*</b>	27.2	42.8	44.0	50.1

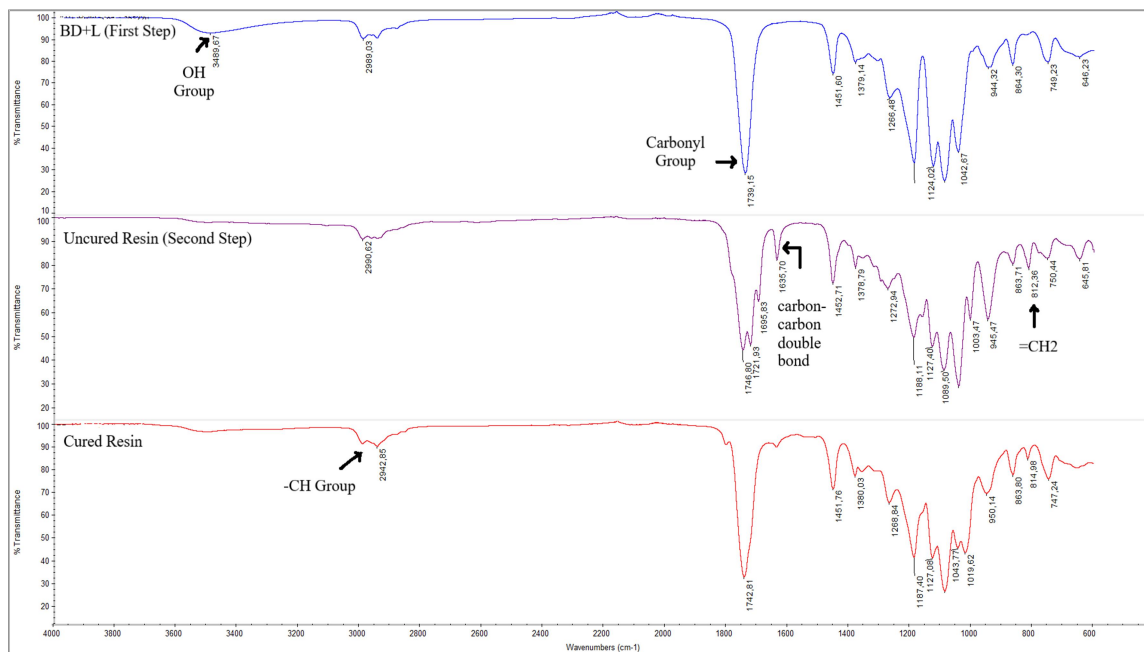
\* given in terms of moles of MA (MAH has 2 moles)

## 4.2 FTIR Analysis

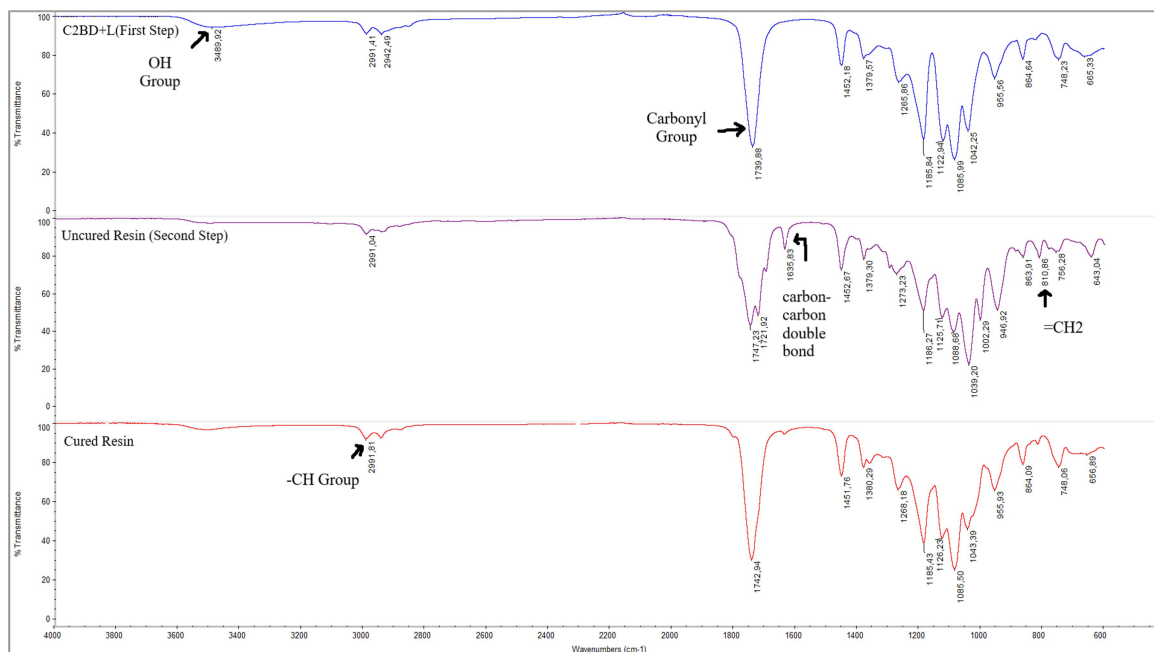
The FTIR test was carried out to verify the functionalization of resin with the methacrylic anhydride in the second step of synthesis. The spectrum of the second step has been compared with the spectrum of the first step. The cured resin sample was also tested to verify curing reaction. In Fig.4.2(a), the spectrum of uncured resin (second step) shows stretching of carbon-carbon double bond at about  $1635\text{ cm}^{-1}$  and bending at about  $813\text{ cm}^{-1}$  ( $=\text{CH}_2$ ) (Ahmad et al., 2017). The same bond was not present in the first spectrum (first step) of the resin. This indicates that end functionalization has taken place. In the cured resin spectrum, the carbon-carbon double bond peak disappeared and at about  $2942\text{ cm}^{-1}$  there is increase in the band  $-\text{CH}$ . This shows that crosslinking reaction has occurred in the resin and disappearance of the carbon-carbon double bond indicates that all the double bonds have reacted during crosslinking (Öztürk and Küsefoğlu, 2010). Moreover, the disappearance of the peak at about  $3491\text{ cm}^{-1}$  after end functionalization (second step) indicates that nearly all the hydroxyl groups have reacted.



The same results were obtained with another two resins; resin with BD and Resin with C2BD (See Fig. 4.2 (b)-(c)).



(b)



(c)

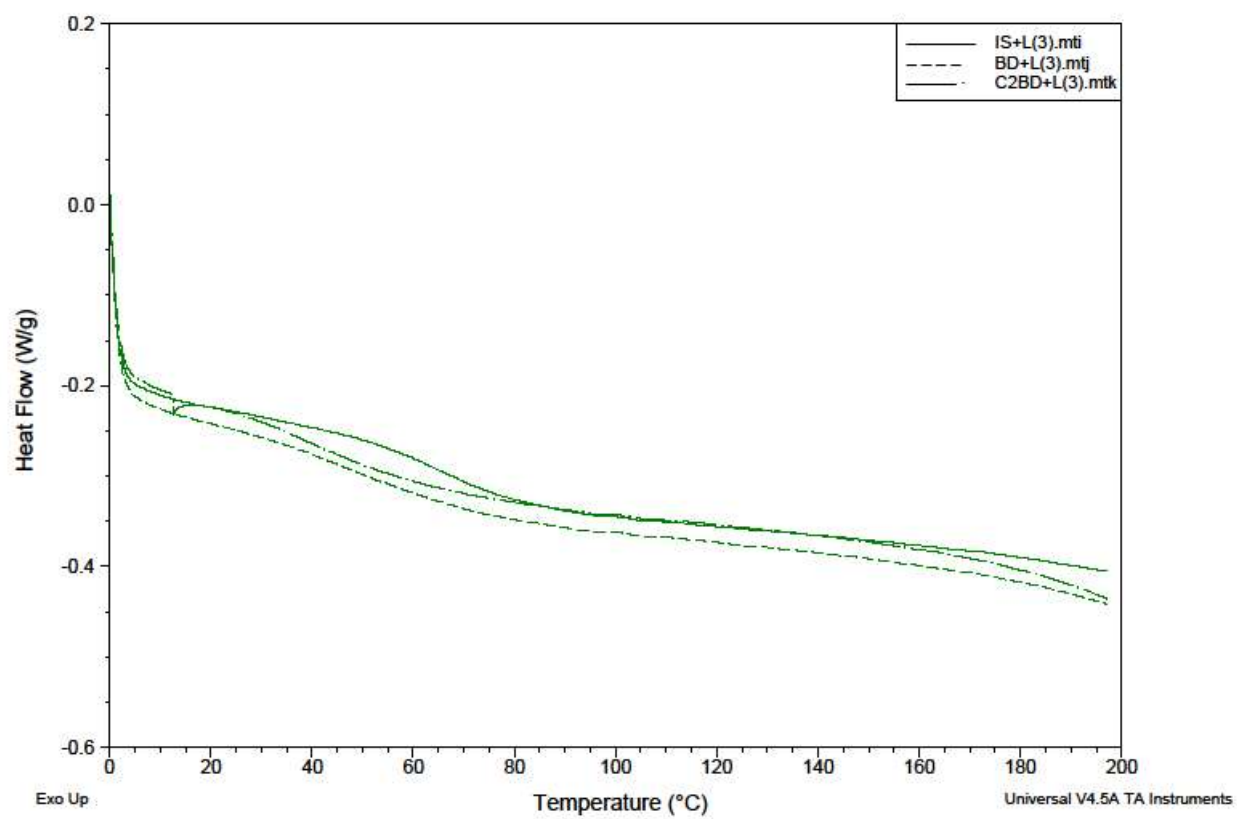
**Fig. 4.2** FTIR spectra of different resins (a) Resins with IS (b) Resins with BD (c) Resins with C2BD

### 4.3 DSC Analysis

DSC was used to investigate the glass transition temperature ( $T_g$ ) of the cured resin. Three samples of each resin were tested. Fig.4.3 shows DSC curve of different cured resins. Resin synthesised with IS initiator shows notable difference in  $T_g$  values while resin with BD and C2BD shows almost similar values (See, Table 4.2). Absence of residual exotherms in DSC curve indicates that all resins were cured properly (Esmaeili et al., 2017). Resin with IS, BD, C2BD had  $T_g$  about 63°C, 46°C and 41°C respectively. Comparing these  $T_g$  values with commercial unsaturated polyesters, it is lower for these bio-based resins. One reason for higher  $T_g$  value of commercial UPs is that it comes pre-blended with styrene. Styrene acts as a reactive diluent and its aromatic ring structure in UPs usually increases the  $T_g$  value. Therefore, it is not good to compare  $T_g$  values of bio-based UPs with commercial UPs.

**Table 4.2**  $T_g$  values of different resins cured with two different curing methods

Sr. No	Sample Name	Curing Method 1	Curing Method 2
		$T_g$ (°C)	$T_g$ (°C)
1	IS+L	30	63
	STDEV	7	6
2	BD+L	46	46
	STDEV	8	4
3	C2BD+L	41	41
	STDEV	3	2



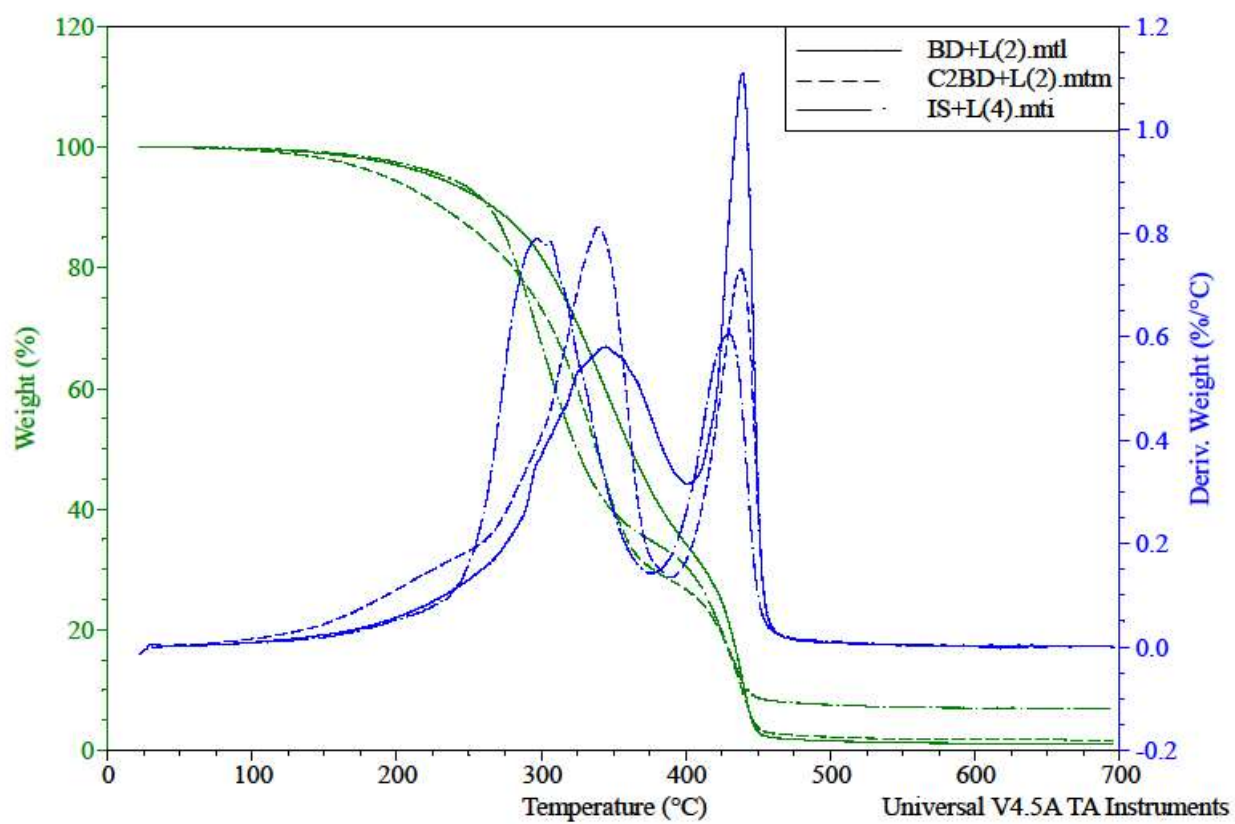
**Fig. 4.3** DSC curves of resins with IS, BD & C2BD

## 4.4 TGA Analysis

TGA test was carried out to investigate the thermal stability of the resin by measuring the percentage weight loss of the cured resin sample on application of heat. The thermogravimetric curves in Fig 4.4 shows two stage weight loss. The resin with IS was stable up to 235°C. At about 261°C it had lost 10% weight, at about 320°C it had lost 50 % and at about 437°C it had almost lost 90% weight. At about 427°C, the derivative weight curve had a second peak. Resin with BD was stable up to 223°C. At about 263°C it had lost 10% weight, at about 361°C it had lost 50% and at about 445°C it had lost 90% weight. The curve for derivative weight had a second peak at about 441° C. The resin with C2BD was relatively stable up to 195°C. It had lost 10%, 50% and 90 % weight at about 233°C, 339°C and 443°C respectively (See, Table 4.3). The curve for derivative weight had a second peak at about 440°C. Here, resin with isosorbide showed better stability, but it degraded gradually at lower temperature compared to the other two resins. Degradation in the resin occurred due to the decomposition of the crosslinked polymer network ([Adekunle et al., 2009](#)). All three resins showed better thermal stability when compared to Bakare research (2014).

**Table 4.3:** Degradation characteristics of different resins

Sr. No	Sample Name	Stability (°C)	Degradation of weight			Second Derivative Peak (°C)
			10%	50%	90%	
1	IS+L	235	261	320	437	427
	STDEV	4	3	4	6	3
2	BD+L	223	263	361	445	441
	STDEV	11	9	3	4	3
3	C2BD+L	195	233	339	443	440
	STDEV	9	10	1	4	2



**Fig 4.4** TGA curve for the resins with IS, BD and C2BD

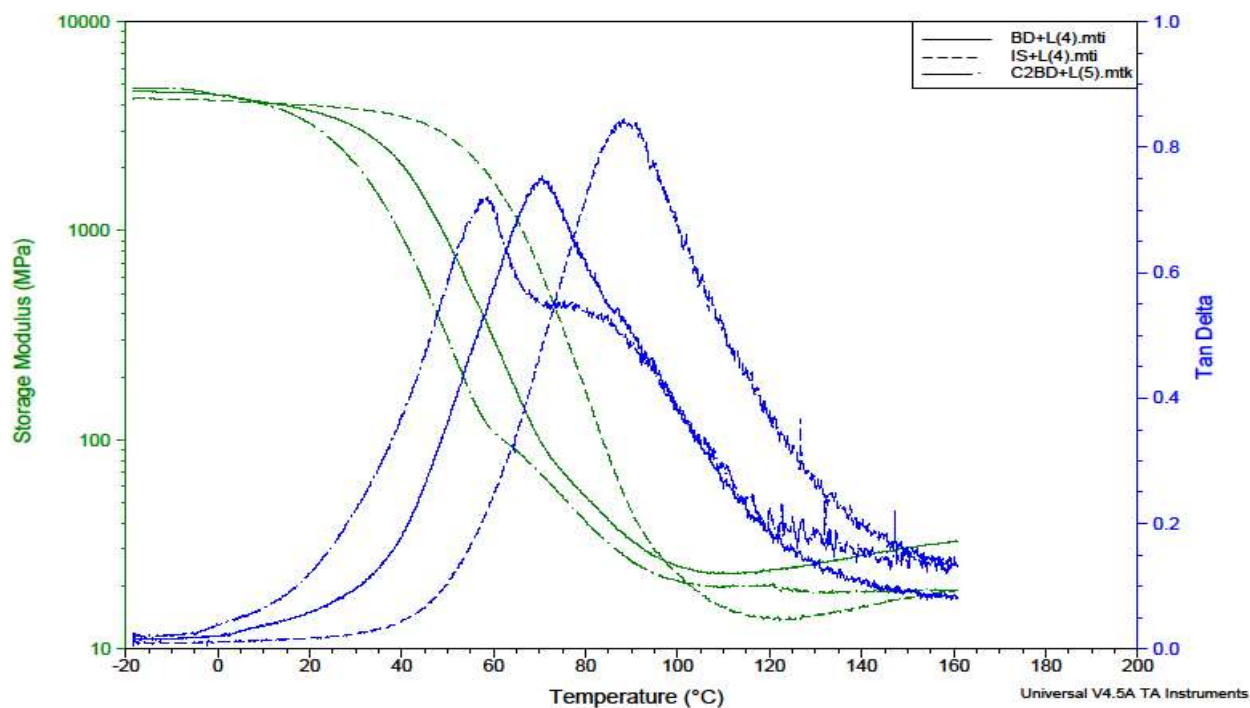
## 4.5 DMA Analysis

DMA analysis was carried out to determine viscoelastic properties of the cured resins. Fig.4.5 (a) shows the storage modulus  $E'$  at 25°C.  $E'$  for the resin with IS, BD and C2BD was approximately 3841, 3430 and 2765 MPa, respectively. Fig. 4.5(a) also shows  $\tan \delta$  peaks for the resins with IS, BD and C2BD where it is recorded as 81, 69 and 59° C, respectively. Resin with C2BD shows two  $\tan \delta$  peaks and this is perhaps due to immiscible system or improper molecular weight distribution. Fig.4.5(b) shows loss modulus  $E''$  at 25° C.  $E''$  was 74, 304 and 446 MPa for the resin with IS, BD and C2BD, respectively. It increased with the increase in the temperature (See, Table 4.4). Comparing the obtained results with Bakare research (2014) the values of  $E'$ ,  $E''$  and  $\tan \delta$  is lower while compared to Åkesson research (2009) all three values are high.

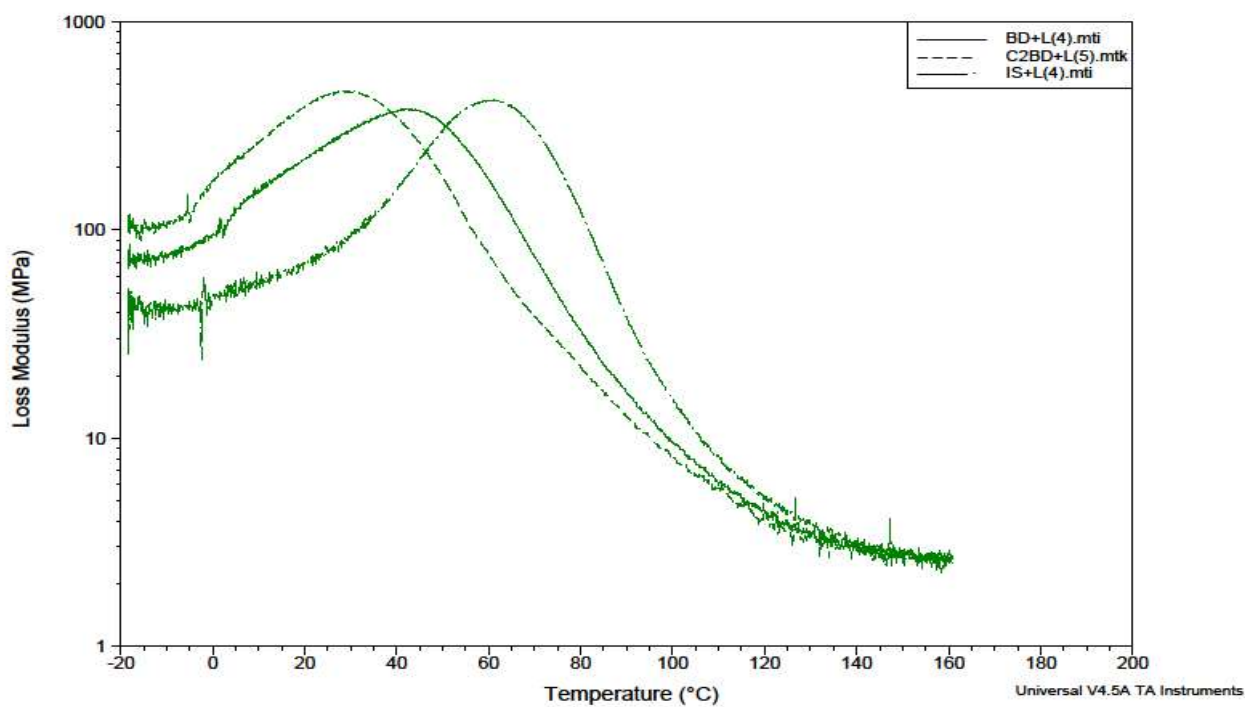
**Table 4.4** Storage modulus  $E'$ , Loss modulus  $E''$  and  $\tan \delta$  for different resins

Sr. No.	Sample Name	Storage Modulus $E'$ at 25° C (Mpa)	Loss Modulus $E''$ at 25° C (Mpa)	Loss Modulus $E''$ at high peak (Mpa)	Tan delta $\delta$ (°C)
1	IS+L	3841	74	409	81
	STDEV	255	9	16	7
2	BD+L	3430	304	397	69
	STDEV	358	46	16	2
3	C2BD+L	2765	446	463	59
	STDEV	273	35	16	6





(a)



(b)

**Fig. 4.5** (a) DMA curves (storage modulus & Tan  $\delta$ ) for different cured resins (b) DMA curves for different cured resins (loss modulus)

## ❖ Summary of findings

**Table 4.5** Summary of thermal analysis

Resin	<u>DSC</u>	<u>TGA</u>		<u>DMA</u>		
	Tg (°C)	Stability (°C)	Second derivative peak (°C)	Storage Modulus E' at 25°C (MPa)	Loss Modulus E'' at 25°C (MPa)	Tan δ (°C)
IS+L	63 ± 6	235 ± 4	427 ± 3	3841 ± 255	74 ± 9	81 ± 7
BD+L	46 ± 4	223 ± 11	441 ± 3	3430 ± 358	304 ± 46	69 ± 2
C2BD+L	41 ± 2	195 ± 9	440 ± 2	2765 ± 273	446 ± 35	59 ± 6

## **Chapter 5: Conclusion**

Bio-based unsaturated polyester resins were tried to develop using different initiators such as diols with monomers such as lactide and lactone. The resins were synthesised in two steps. In the first step, oligomers of lactide monomer were prepared by using diols as initiators through a condensation reaction. In the second step, the produced oligomers were further reacted with methacrylic anhydride to produce unsaturated polyester resin. The study shows that resin can be cured by using peroxide as initiator and N-N dimethyl aniline as accelerator within 1 hr. NMR result shows that lot of MAAH and MA found unreacted in the obtained resins synthesised via solution polymerisation. The highest amount of unreacted MAAH and MA has been found in the alpha angelica lactone-based resin. The curing of the AAL-based resin was also not successful. Therefore, it is correct that the development of lactone based-resin is thermodynamically difficult due to its low strain energy.

The crosslinked resin with isosorbide has glass transition temperature ( $T_g$ ) of  $63^{\circ}\text{C}$  which is better than other obtained bio-based resins. Stability of IS-based resin is up to  $235^{\circ}\text{C}$ . Second derivative peak for IS-based resin is at about  $427^{\circ}\text{C}$ . Storage Modulus  $E'$ , loss modulus  $E''$  and  $\tan \delta$  for IS-based resin is 3841 MPa,  $74^{\circ}\text{C}$  and  $81^{\circ}\text{C}$ , respectively which is good compare to resin with BD and C2BD. IS-based resin showed superior thermomechanical properties and it may be due to its aromatic structure.

The results indicate that synthesis of bio-based unsaturated polyester resins using renewable resource (i.e. initiators such as diols and monomer such as lactide) is possible. This will minimize the hazardous waste occurring problem during production of UPs. Moreover, the results obtained are good enough for the future publication.

## **Chapter 6: Recommendation for Future Work**

The synthesis of UPR with lactone monomer seems thermodynamically difficult, but it can be synthesised using drastic reaction conditions such as changing pressure or lowering the reaction temperature to minus degrees.

Bio-based unsaturated resin produced using isosorbide initiator is highly viscous and difficult to process it. Therefore, it is recommendable to pursue research on lowering the viscosity of this kind of resin.

In addition, thermal properties such as the glass transition temperature and storage modulus of obtained resins are acceptable, but more work can be done to enhance it. These resins further can be used as matrix in natural fiber reinforced composites. The mechanical properties of the composites can be investigated.

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