

# Influence of chain extender on the rheological and thermal properties of polylactic acid (PLA)

*University of Groningen*

*Written by: Muhammad Saad Khan*

*Supervised by: Post Doc. Yifei Fan*

*Prof. Francesco Picchioni*

## Abstract

The aim of this research involves modification of polylactic acid (PLA) using twin screw brabender in order to improve its thermal stability and enhance its rheological properties. According to the results obtained, it is presented that neat polymers tends to degrade upon processing hence there is a decrease of molecular weight ( $M_w$ ) and viscosity. The modified PLA was blended with variable concentration of chain extension named 'Joncryl ADR', however, the emphasis of the study was on the 3% weightage. The incorporation of this chain extender bearing multifunctional epoxy groups showed an improvement in the polymer's melt stability. Thermal degradation of PLA has been reported by thermo-gravimetric (TGA) and gel permeation chromatography (GPC). GPC data of these modified PLA which were processed at different temperature (160, 180 and 200°C) showed an overall increase in molecular weight related to the formation of extended or branched chains. Furthermore, via differential scanning calorimetry (DSC), the thermal transitions occurring during the heating process for PLA, Joncryl and their respective blend were assessed. Rheological investigations for neat and modified PLA blends where carried out where modified PLA exhibited higher viscosity and dynamic moduli compared to the neat one.

## 1. Introduction

Plastic pollution and increasing oil prices have diverted the attention towards developing sustainable and environment friendly economy which includes biofuels and biopolymers that are generated from renewable resources. PLA has been one of the most prominent biopolymer that has come to limelight in recent years. In 2010, PLA had the second largest consumption of any bio plastic in the world [1]. It is a linear thermoplastic aliphatic polyester that is derived from readily available renewable resources like corn-starch, sugar cane or cassava roots etc. Unlike conventional plastics which are derived from non-renewable fossil resources and takes 10-1000 years to decompose, this polymer is ecofriendly and tends to degrade within 6-24 months [2]. PLA is synthesized via two process: condensation and polymerization. The most common polymerization technique is known as ring opening polymerization. In this process, metal catalyst (Tin octoate) is combined with lactide monomer to create larger molecules of PLA. The other method to generate PLA is condensation of lactic acid monomers which needs to be carried out below 200°C [2]. Due to the chiral nature of lactic acid, several distinct forms of PLA are available with variations in their physical characteristics via tuning the ratio of L and D lactides in the feeding monomers.

PLA has similar characteristics to polystyrene (PS), polyethylene (PE) or polypropylene (PP) [3]. PLA constricts under heat and is suitable as shrink wrap material. Similarly with the ease it melts, it is used in 3D printing where one of its interesting usage is as 'long PLA casting'. The other common uses of PLA include plastic bottles & cups, medical devices, tea bags etc. [2]. Despite all of its advantages, PLA has low toughness at room temperature, narrow processing window and poor thermal stability which limit its large scale processing applications (injection molding, blown filming and extrusion foaming). Extrusion is one of the commonly used industrial processing technique to produce blown films and foams. However, processing PLA is complicated as it is sensitive to heat and shear. Higher temperature, pressure and moisture can all result in the loss in molecular weight and mechanical properties.

In order to enlarge the processing windows of PLA and its application scope, PLA melt strength needs to be improved which has already been reported in numerous literature [4]. Copolymerization, addition of plasticizers and blending with other polymers are some of the main ways to achieve improvements in PLA properties [5]. It has been successfully blended with flexible polymers, such as poly (butylene-succinate-co-adipate) (PBSA) [6], poly (butylene succinate) (PBS) [7], poly (butyl acrylate) (PBA) [8] and poly (butylene-adipate-co-terephthalate) (PBAT) [9]. Recently, interest has been shown for chain extenders as it is proved that modification of polymer to get long and branched chain via chain extender is an efficient approach to control the degradation of PLA [10]. Degradation of PLA upon thermal processing mainly consists of random main chain scission and depolymerization reaction [15]. These random degradation

reactions involve hydrolysis, elimination, trans-esterification and oxidative degradation [11] where under thermal processing, any of these undesired reactions are dominant. Chain extenders therefore relinks polymer chain that have broken down due to any of these degradation reactions, and thus increase the molecular weight of polymer. Some of the extenders reported in literature are di and multi-functional epoxides [12], diisocyanate compound [12], dianhydride [13], bisoxazolines, tris (nonyl-phenyl) phosphate (TNPP) [14] and polycarbodiimide (PCDI) [14]. Multifunctional chain extender bearing epoxy groups have been extensively used in polyesters [15]. In this research, the chain extension reaction with PLA was carried out with 'Joncryl ADR' which is a styrene-acrylate copolymer bearing epoxy functionality. Unlike other chain extenders such as diisocyanate, Joncryl is nontoxic and reacts to improve  $M_w$  and melt viscosity of PLA. These epoxy functions in the chain extender can react with either hydroxyl (OH) or carboxyl (COOH) group in the polyester chain ends. It is offered as a flake or sugar size powder and can be used during the processing of PLA or during the polymerization process as well.

The current paper represents the approach to obtain a thermo-stable PLA via investigating the effect of chain extender reaction on rheological and thermal properties of modified PLA. Furthermore, in the coming sections of the report, the chain extender 'Joncryl ADR' and polymer 'polylactic acid' will be termed as Joncryl and PLA respectively.

## 2. Experimental Section

### 2.1 Materials and Method:

Polylactic acid was obtained from BASF in the form of white colored solid pellets whereas the branching agent 'Joncryl ADR', a solid oligomer chain bearing multiple epoxide functionalities was also obtained from the same company. Both of the materials were dried in an oven at 60°C for 3h and then left in a desiccator. The major characteristic of the materials used in this study are listed in Table 1 while the structures of these relative materials are shown in respective figures below.

Characteristics of PLA	Characteristics of Joncryl
<i>Chemical Formula: <math>(C_3H_4O_2)_n</math></i> <i>Melt Temperature: 170°C</i> <i>Glass Transition Temperature: 60°C</i> <i>Density: 1.25g/cc</i> <i>Supplier: BASF</i>	<i>Commercial Name: Joncryl ADR</i> <i>Glass Transition Temperature: 54°C</i> <i>Specific Gravity (25°C): 1.25</i> <i>Epoxy Equivalent Weight: 285g/mol</i> <i>Molecular Weight: 6800g/mol</i> <i>Functionality: f=9</i>

Table 1: Properties of materials used [16]

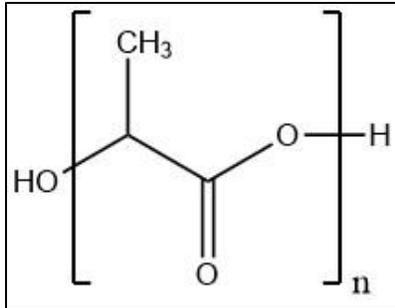


Fig. 2. Chemical structure of PLA

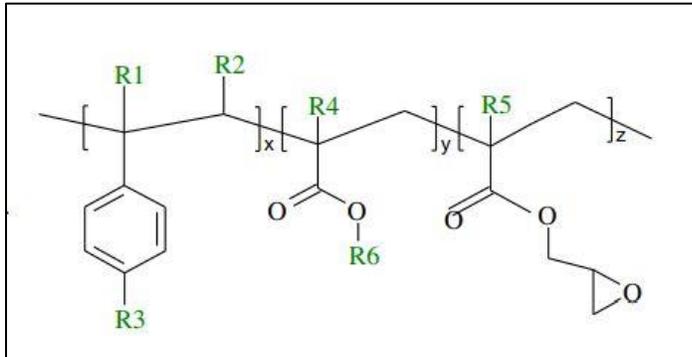


Fig. 3. Chemical structure of Joncryl [15]

## 2.2 Blend Processing:

The neat polymer was dried in an oven at 60°C for 3h before preparing blend composition in order to prevent hydrolytic degradation. Brabender equipped with twin counter-rotating screws was utilized to prepare the modified polymer blend. The blend was prepared in three different temperature (160°C, 180°C, 200°C) with Joncryl amount of (3wt.%) whereas for 200°C temperature condition, another batch with 1% ratio of Joncryl was prepared in contrast to previous one. 25.0g of PLA was weighed and added into the hopper section of machine with respective Joncryl amount (0 and 3wt.%) in weight respectively. The rotation of the screw speed was set at 20RPM. After 2min of mixing time, a small portion of the blend was taken out of the machine with the following time interval (0, 3, 5, 7, 10, 13, 15, 30, 60 min) and quenched in liquid nitrogen.

## 2.3 Characterization

### 2.3.1 Gel Permeation Chromatography (GPC):

The number and weight average molecular weight of neat and modified PLA at different processing temperature was measured with GPC. From the samples obtained through brabender at different time intervals, a single solution was prepared by dissolving 25mg of sample into 5ml of tetrahydrofuran (THF) along with two drops of toluene as the flow mark. The solution after being completely dissolved was later filtered through a 0.40 μm PTFE syringe filter into the sample vials. For certain samples, it was difficult to filter as they were cross-linked and could not pass through the filter. GPC analysis was performed in tetrahydrofuran (THF, as elution solvent with flow rate 1ml/min) at 40°C using a Hewlett Packard series 1100 system with a GBC LC 1240 refractive index detector and a series of three Polymer Laboratories PLGel columns (1 × 10 μm Mixed B and 3 × 3 μm Mixed E).

### 2.3.2 Thermo gravimetric Analysis (TGA):

Thermal degradation of respective materials (PLA and Joncryl) was measurement on a TGA-4000 thermo gravimetric analyzer from PerkinElmer. Samples of 10mg were heated from room temperature until 950°C at 10°C/min under nitrogen atmosphere.

### 2.3.3 Differential Scanning Calorimetry (DSC):

The thermal transitions (glass transition ' $T_g$ ', melting ' $T_m$ ' and crystallization ' $T_c$ ' peaks) of neat PLA, Joncryl and their blend were investigated with the 'Pyris Diamond DSC instrument' from PerkinElmer. Apart from above mentioned properties, DSC, was also employed, although unsuccessfully, to identify reaction temperature between PLA and Joncryl. Generally, two methods for sample preparation were used. For the first one, solid pellets of roughly 10 mg of (PLA, Joncryl, PLA/Joncryl) were taken and the respective analysis was studied on the DSC machine. Secondly in three tubes labelled as (PLA, Joncryl, PLA/Joncryl) roughly 1-2 g of the respective materials were prepared which were then dissolved in chloroform. These tubes were air-dried to remove most of the solvent and then put in a vacuum oven at 60 °C and left for overnight in order to evaporate all of the chloroform. For the modified PLA samples, the composition of Joncryl relative to PLA was 50wt%. From those dried tubes, 10 mg of sample was taken and analyzed on DSC. The temperature programming for above methods was as follows: the sample was heated from 5°C to 200°C at 10°C/min and then held for 2 minutes before cool down.

In addition to that, two other analysis method labelled as 6C and frozen were also used to figure out the lowest reaction temperature between PLA and Joncryl. In the 6C method, first the sample is heated from 20 to 130°C at 10°C/min. Then from 130-230°C, the heating rate is changed to 2°C/min. After that the sample is cooled back to 130°C at 10°C/min. This whole cycle is repeated for five more times.

In the frozen method, the sample is first heated from 20 to 160°C at 10°C/min. After that sample is rapidly cooled to 60°C at 50°C/min. From there it is again reheated to 120°C at 10°C/min. Afterwards the sample is heated in such a way that from 120-130-140.....-200°C, the heating rate is kept the same and for every interval, it is held for 4min.

### 2.3.4 Rheology Characterization:

The rheological properties in oscillatory mode for PLA, with and without chain extender was assessed using a 'HAAKE MARS' Advanced Rheometer. The samples were tested using a parallel plate geometry with a plate diameter of 25mm and gap of 1m. The chamber temperature was held at 190°C whereas the oscillatory frequency sweep test was performed at angular frequency of 0.1 to 100 rad/s. In order to assess the rheological properties of the polymer, round sample discs were prepared as following:

First via brabender machine, modified polymer blend was prepared with 25.0g of PLA and 0.75g (3wt.%) of Joncryl. The temperature condition and rotation speed for processing was set at 160°C and 20rpm respectively. After 5 min of reaction, the polymer blend was taken out and quenched in liquid nitrogen. Later the polymer blend was crushed into smaller pieces in order to make round discs for the later part of the rheological analysis. Another batch of neat PLA was also processed at same reaction conditions for comparison.

For compression molding, different conditions (temperature, time and pressure) were tested so that there were no bubbles in the round discs and also no extra over mark of sample around the disc. The best conditions for preparing round discs are listed in the table below:

Table3. Disc Preparation Conditions
Mass: 0.8g per disc
Temperature: 160°C
Pressure: 75KN
Time: 2min heat up + 5min processing

Under these conditions, 5 discs for each batch were obtained which were then later assessed in the rheology machine.

### 3. Results & Discussion

#### 3.1 Chain Extension Reaction:

Joncryl contains epoxide functional group which drives the chain extension reaction towards completion. Since there are multiple reactive end groups, several polymer chains can be chemically bounded with one Joncryl molecule which can either give a linear chain extended structure or branched/cross-linked structure in the polymer matrix. According to the literature, these epoxides group can theoretically react with either hydroxyl or carboxyl group of PLA (COOH/epoxide, OH/epoxide) [11, 12]. The branching occurs via a covalent bond formed between the hydroxyl group of PLA and the epoxide group which results in ring opening of epoxide, similarly there is an abstraction of hydrogen atom from hydroxyl group of PLA in order to facilitate the reaction. The predicted mechanism between Joncryl and PLA is shown in Fig. 3:

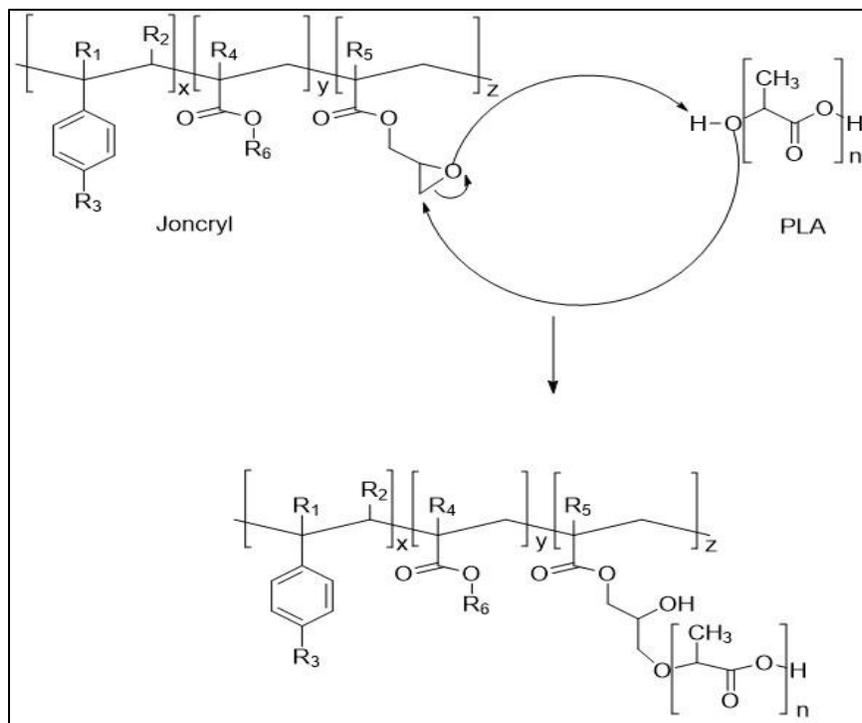


Fig. 3. Reaction mechanism between PLA and Joncryl

### 3.2 Thermal Analysis:

Thermo gravimetric instrument helped to elucidate the decomposition temperature profile of PLA and Joncryl before they were processed in brabender. In TGA, the mass of the relative sampling material is monitored as a function of temperature where the sample is subjected to heating in a controlled temperature program. Therefore, upon heating the sample, weight decreases and eventually reaches to zero thus marking the end of the analysis. The data obtained from the TGA instrument is shown in Fig. 4:

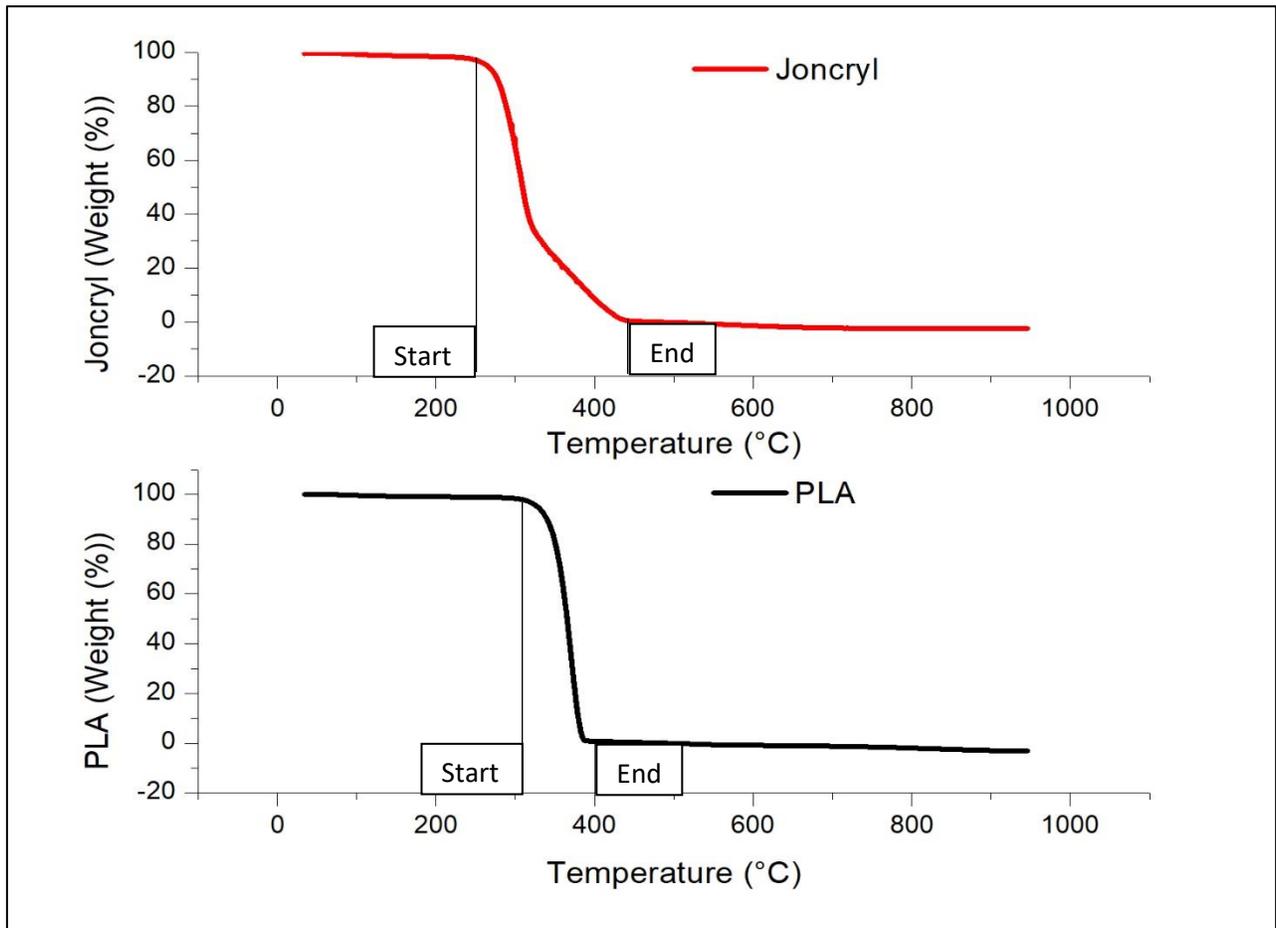


Fig. 4. Thermal degradation of PLA and Joncryl

As seen from the Fig. 4, PLA has a very narrow thermal degradation profile (305-390°C) whereas Joncryl has a broader profile (240-430°C). Even though Joncryl starts to degrade at lower temperature but can sustain higher processing temperature whereas PLA, completely degrades before reaching 400°C. This is due to the fact that Joncryl contains multifunctional styrene-acrylic-epoxide groups in its oligomer chain (shown in Fig. 3) whereas for PLA, it has mainly ester linkages. These ester linkages upon thermal processing are prone to undergo random main chain-scission or degradation reaction which also results in loss of molecular weight [17]. In chain scission, the polymer chain is broken down at a random point in the backbone under high thermal stress. Moreover, for PLA, the degradation reaction also involves hydrolysis, elimination or trans-esterification where any of these undesired reactions are favorable at temperature above 200°C [17]. As a result of this, an undesired molecular weight reduction and weight loss occurs at temperatures above 200°C.

### 3.3 DSC Analysis:

DSC thermographs are helpful to study the thermal transition profile of the polymer. The basic principle of DSC machine is to measure the difference in heat flow rate (mJ/sec) between a sample and inert reference pan as a function of time and temperature. A typical DSC thermograph for a semi-crystalline material is shown in Fig. 5:

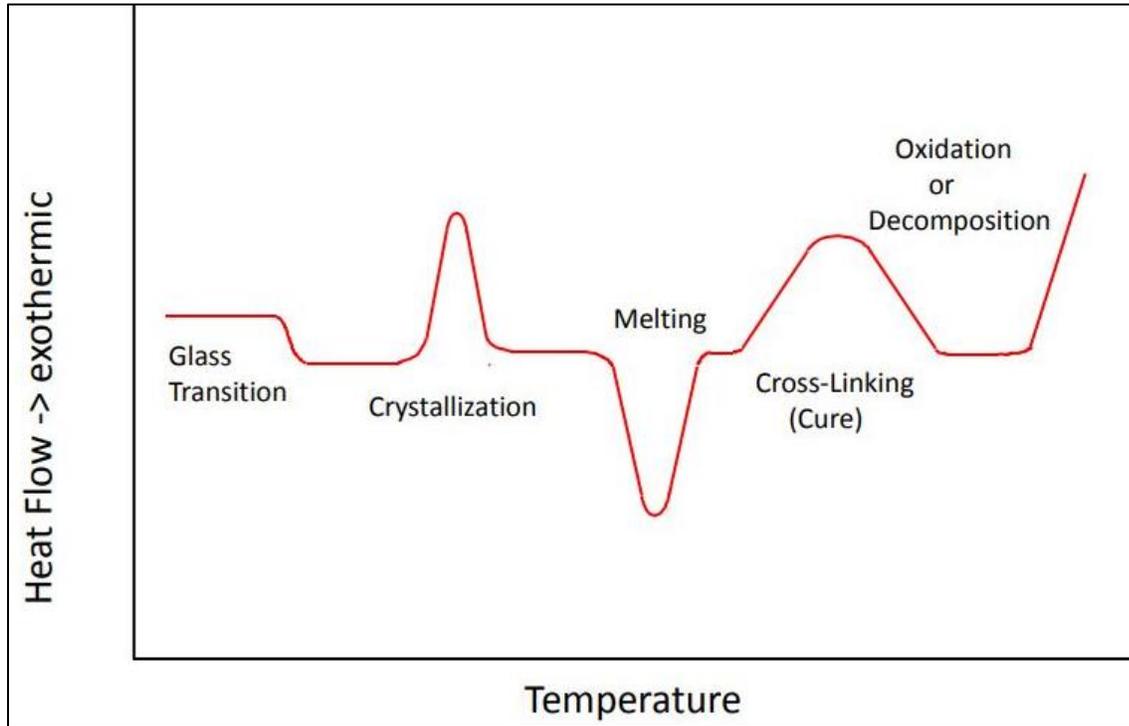


Fig. 5 Thermal transitions of interest in DSC output [18]

Glass transition ( $T_g$ ), crystallization ( $T_c$ ) and melting peaks ( $T_m$ ) plays an important role to elucidate the polymeric structure. These peaks represent portion of polymeric material which are randomly oriented in space (amorphous region) or are regularly arranged (crystalline phase). The amorphous material only shows ( $T_g$ ,  $T_m$ ) peaks whereas the crystalline material only shows ( $T_c$ ,  $T_m$ ) while the semi-crystalline material is the mix of two. Three different analysis methods were used not only to understand the structure of the polymer matrix but also to check if there is any reaction peak involved for the modified polymer blend. Not a substantial amount of data could be gathered as there was a very little deviation among data obtained for these different methods.  $T_g$  and  $T_m$  peaks determined via these methods showed a similar trend overall and no reaction peak was visible during the thermal transition of respective materials. Fig. 6 shows the DSC thermographs of unmodified PLA and Joncryl while the modified polymer blend heating cycle is presented in Fig. 7. For Fig. 6, the semi-crystalline PLA has a  $T_g$  and  $T_m$  of 60°C and 150°C respectively whereas Joncryl has a  $T_g$  and  $T_m$  of 62°C and 148°C. Both of these data values corroborated with the literature. Similarly, in Fig. 7, in the second heating cycle, there was a small dip close to melting peak. This peak is due to cold-crystallization phenomena that occurred upon rapid cooling of the polymer in the initial cycle. According to literature [15], PLA is an amorphous polymer with very low crystal content (3-5%). Therefore, the exothermic cold crystallization dip achieved during the subsequent DSC heating scan indicates a chain reorganization because the initial amorphous structure is crystallizing.

For the thermograph of frozen method in Fig. 8, no reaction peak was visible for modified polymer blend. This is because the melting peaks for both materials are quite similar and thus the reaction peak may have overlapped in between them. As a result of it, a distinct reaction peak could not be seen.

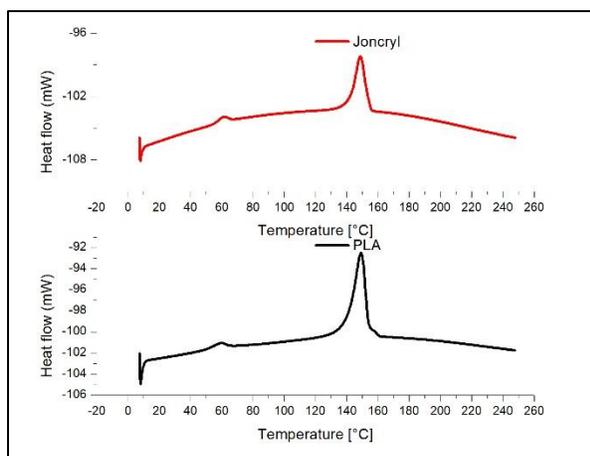


Fig. 6. Thermal transition for PLA and Joncryl (BA)

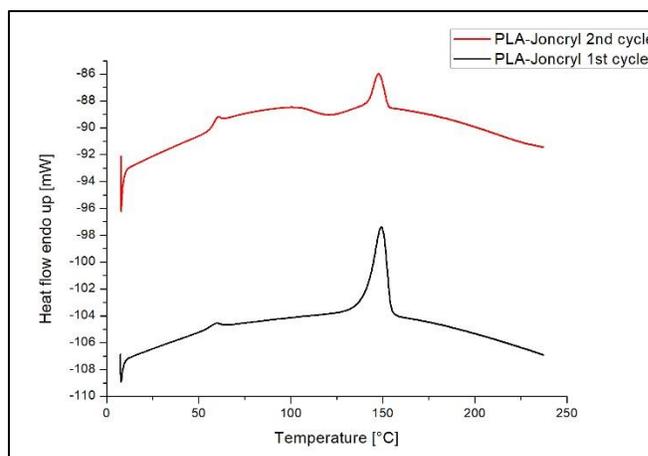


Fig. 7. Thermal transition for modified polymer blend

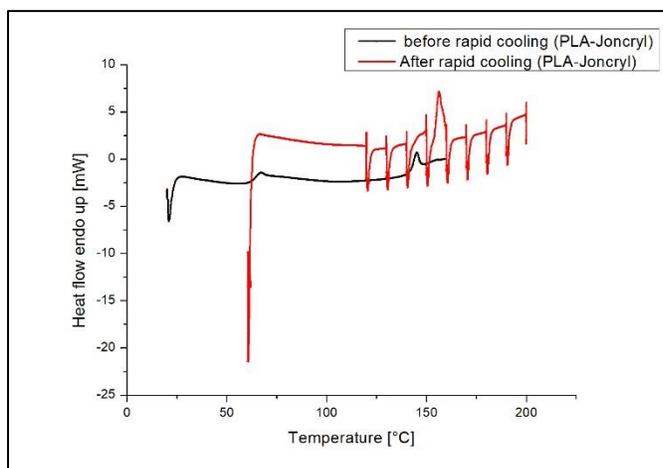


Fig. 8. Frozen method DSC heating graph

### 3.4 Molecular Weight Analysis:

To fully understand the effectiveness of chain extension/branching occurred during the reactive processing, the measurement of average molecular weight at different sampling time was carried out in Gel permeation chromatography (GPC). GPC technique characterizes the complete molecular weight distribution of a polymer where important parameters, such as number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), Z weight average molecular weight ( $M_z$ ) and the most fundamental characteristic of a polymer, its distribution curve can be determined [19]. These values are important since they affect many of the physical properties of a polymer which include tensile strength, melt viscosity, brittleness, toughness and tear strength etc. Separation of the molecules is based on the difference in their size. These variable sized molecules are pumped through a specialized column containing microporous beads. The smaller molecules can enter the pores easily and therefore spend more time in these pores, increasing their retention time. On the other hand, larger molecules spend little time in the pores and are eluted quickly. The columns packed with these tiny pores have a limited range of molecular weight

where separation can occur, therefore molecules above a certain size are totally excluded from the pores resulting in an inefficiency in the data. The incorporation of epoxy functions into PLA significantly increased the molecular weight. Fig. 9 presents the evolution of molecular weight depending on Joncryl concentration and the processing time at certain temperature. For neat polymer processed at 160°C and 180°C,  $M_w$  attains a steady profile for a longer period of processing time. On the other hand, for neat polymer at 200°C, the  $M_w$  start to gradually decrease as the time proceeds and a sharp decline is seen after 15min. It is a clear evidence that the polymer thermal stability is highly dependent on processing temperature. With the increase in temperature, the ester linkages are broken down and depolymerization start to take place. For the modified polymer blend with 3wt.% Joncryl, a significant dependence of the  $M_w$  on the amount of the multi-functionalized epoxy and reaction time can be observed. For example, after mixing for 10 minutes, it was observed that PLA formulation with 3wt.% Joncryl amount at (160, 180, 200°C) temperature showed an increase in  $M_w$  of 42%, 99.3% and 146% respectively, when compared with neat PLA  $M_w$  values. The drastic increase of  $M_w$  pointed out the presence of longer chains or even long chain branching in the polymer matrix. It has been reported [15] that under conditions where there is high thermal processing and Joncryl concentration (>1.5%), the polymer start to cross link. This can be seen in Fig. 9 below as after 15 minutes, there are no  $M_w$  values reported for modified polymer blend at following temperatures (180, 200°C). During the vials preparation under those temperature, the samples that were processed for longer time (>15min) were difficult to filter through micro-syringe due to formation of cross-linked structures into the polymer matrix. Fig. 10 depicts the dependency of  $M_w$  values with increasing amount of Joncryl at reaction conditions of 200°C and 10 min. It is shown that branching reactions occurs more efficiently and at a higher rate when Joncryl amount is increased.

The GPC analysis showed an improvement in the  $M_w$  of the polymer when it is blended with variable concentrations of epoxy functions. The molecular weight drastically increased and while the polymer was processed for a longer time, there was no thermal degradation even when the processing temperature was set at 200°C. A careful study of rheological behavior will provide more information on the melt strength and topology of the resulting polymeric structure in order to evaluate their processing behavior.

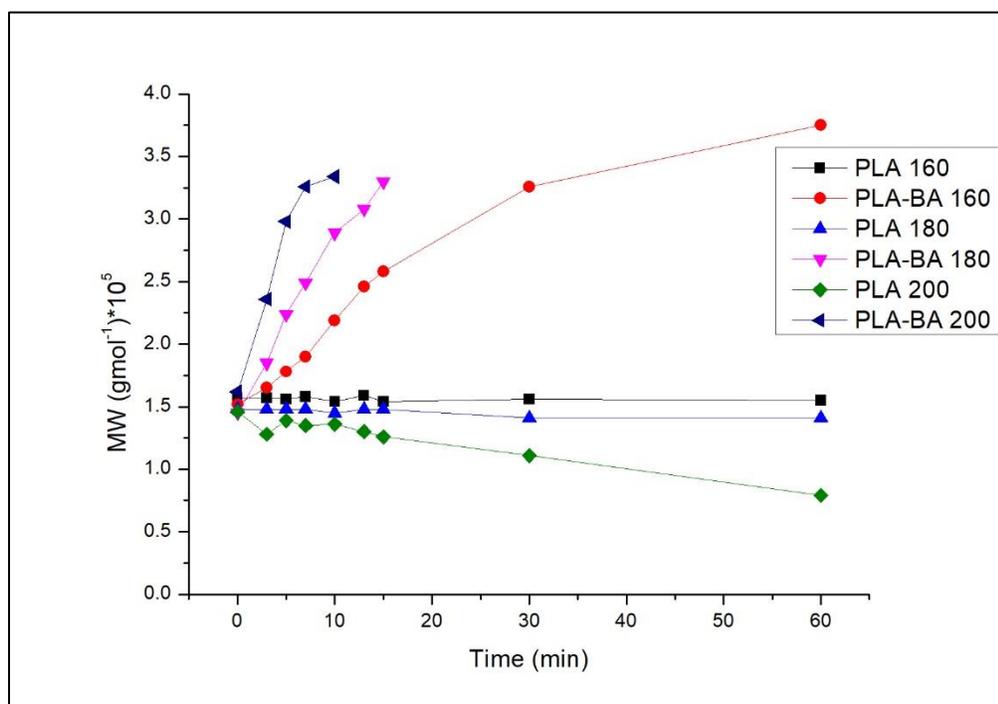


Fig. 9. Molecular Weight evolution versus time for neat and modified PLA at 160, 180, 200°C (BA\* [Joncryl])

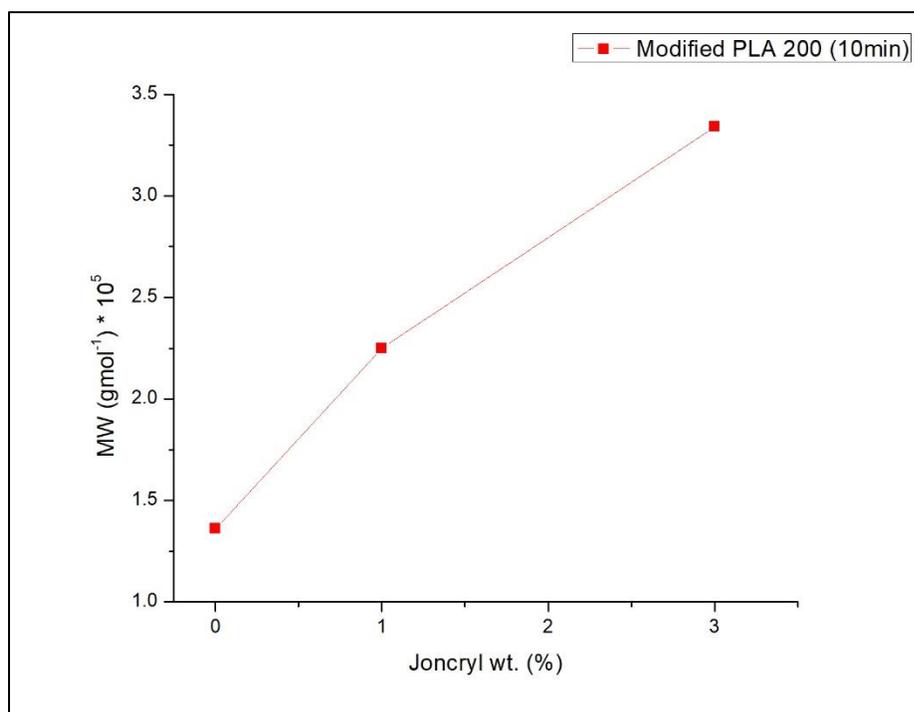


Fig. 10. Molecular weight dependency at variable concentration of Joncryl (0, 1, 3wt.%) at 10min processing time

### 3.5 Rheological Characterization:

Rheological test was carried out to evaluate the change in the melt strength of PLA, with and without chain extender. The melt strength is related to the viscosity as higher the viscosity, the better the tendency of polymer towards structural breakdown under high shear stress or strain. The experiment was carried out at 190°C and over a prolonged time. The complex viscosity plots for both neat and modified polymer blend were obtained in oscillatory mode and are shown in Fig. 11. The viscosity tends to decrease with an increase in angular frequency for both polymers. This is a typical shear thinning behavior and mostly occurs since molecular chains in PLA are broken down by the strong shearing action. Secondly, there is a significant increase in zero frequency viscosity when Joncryl is added into PLA. Since, Joncryl has multiple reactive end group (epoxides), it reacts with PLA and form chemical bridges between them. As a result of this, there is a possible creation of long chained branched structure. By taking the reference of 1rad/s,

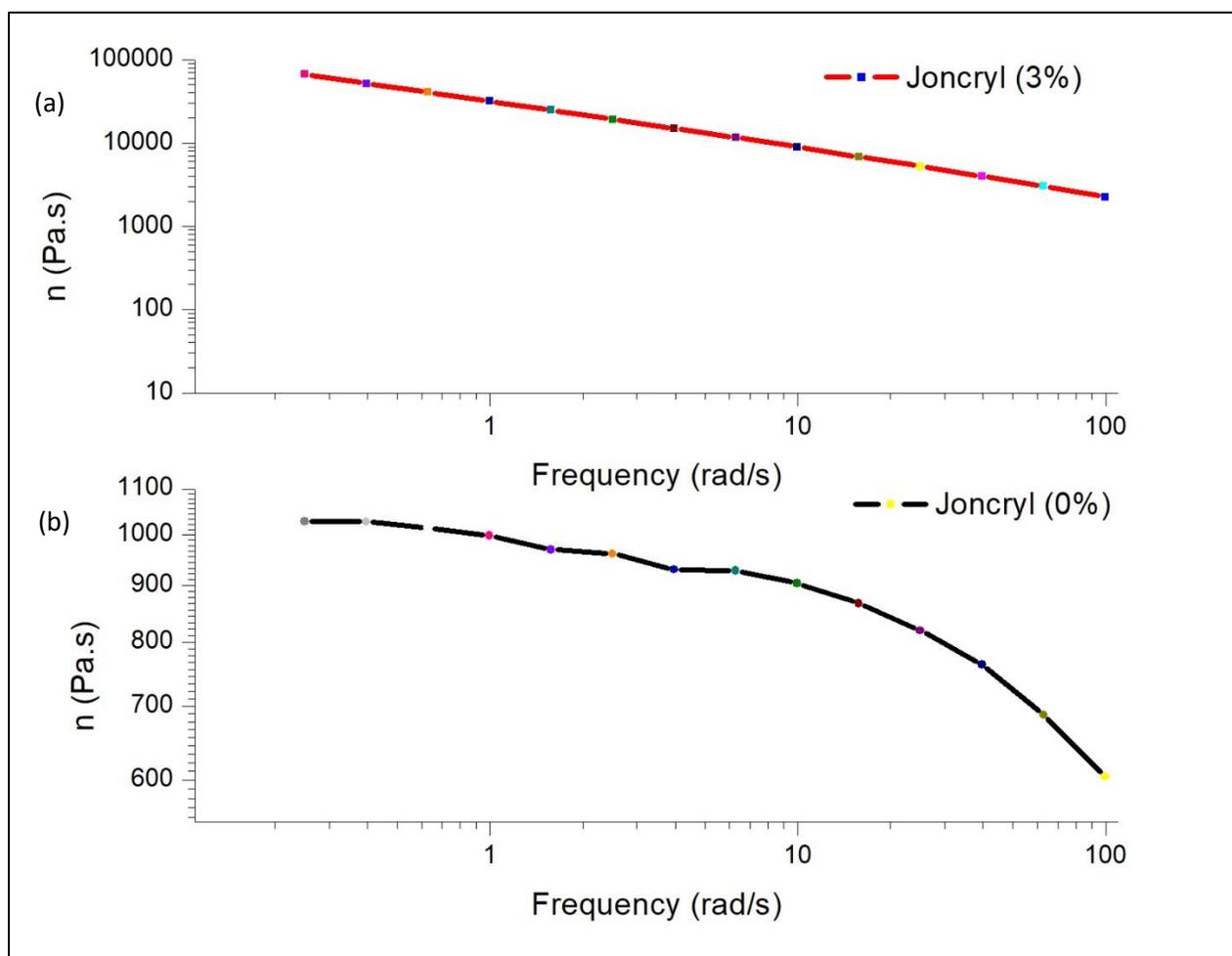


Fig. 11. Complex viscosity vs. angular frequency of modified PLA (a) and neat PLA (b)

PLA with 3wt.% Joncryl has a viscosity of '31797Pa' whereas for neat PLA, it has a viscosity of '998Pa'. This improvement in complex viscosity is related to the increase in the molecular weight of the polymers due to the reaction of the epoxy group with both chain-ends of the polymer.

From rheological analysis, a more detailed information about characterization of the molecular structure of modified polymer blend can be obtained. The viscoelastic properties of the polymer can provide a better analysis about the processing behavior of the polymer. The viscoelastic region comprises of dynamic moduli consisting of storage ( $G'$ ) and loss modulus ( $G''$ ). These factors are important to understand the response of the materials microstructure under variable stress and strain. When the applied force is smaller than the intermolecular forces of polymer matrix, then  $G'$  is larger than  $G''$ , the material has some capacity to store energy and should be able to return, to some extent, to its initial configuration before a mechanical force was applied. The material behaves as an elastic solid, although not an ideal one because some of the mechanical energy is dissipated as heat. However, when the applied force is higher, then the microstructure collapses and the mechanical energy given to the material is dissipated, meaning that the material flows where  $G''$  becomes larger than  $G'$  [15].

This change is depicted for both neat and modified PLA system in Fig. 12 mentioned below. The neat PLA shows a typical curve for the moduli of a viscoelastic melt with low elasticity. According to literature [19], upon examination of dynamic moduli of linear and branched polymer melts, the presence of long chained branching induces a relaxation mode at low frequency where factor  $G'$  crossovers the  $G''$ , which is not present in a linear material. This change of storage modulus at low frequency therefore can be used as an indication of long chained branching in the modified PLA blend. As seen from the Fig.12, the storage modulus for modified PLA crossovers at frequency of 4rad/s. By taking the inverse of this frequency, it gives the characteristic relaxation time for the polymer which was found to be 0.25sec.

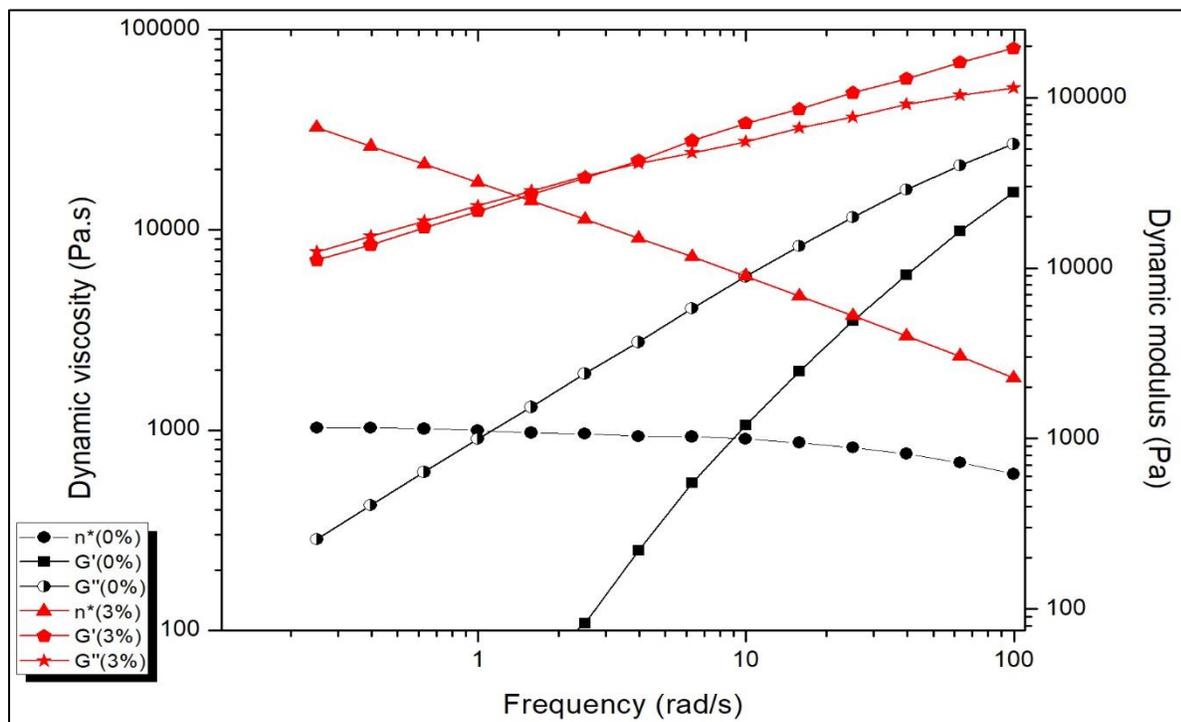


Fig. 12. Dynamic moduli of neat and modified PLA at 190°C

Lower relaxation time indicates higher elasticity and indirectly presence of greater extent of branching.

Fig 13 displays the curves of the storage modulus ( $G'$ ) as a function of the angular frequency for the neat and modified PLA system. With the addition of 3wt% Joncryl into PLA, the polymeric system shows higher values for  $G'$  and viscosity as compared to the neat one. There is a reduction in the slope of  $G'$  for modified PLA system hinting creation of chain extended-branched structure. The increase and shifting of Newtonian plateau upwards with a substantial increase in the zero-frequency dynamic viscosity overall confirms that the modification reaction induces long chained branching.

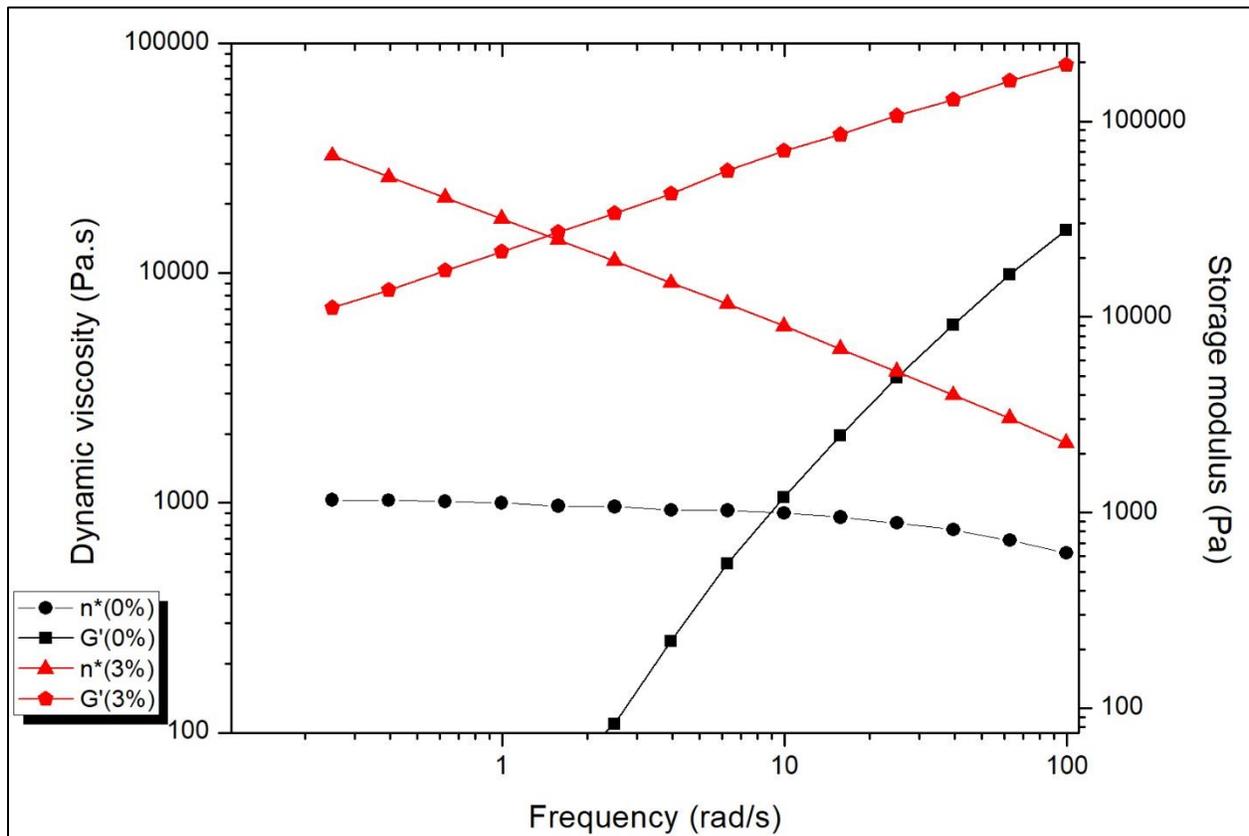


Fig. 13. Storage modulus and viscosity curves for neat and modified PLA at 190°C

Another way to analyze the presence of long chained branching in the polymer matrix is via investigating the loss angle ( $\delta$ ) which is equal to  $\arctan(G''/G')$ . The loss angle remains close to  $90^\circ$  at low frequencies and starts decreasing at higher frequencies. The plot is a semi-log graph and with the presence of branched structures, the curves introduces inflection points and the middle part of the curve sometimes leads to intermediate plateau [19]. All these characteristics can be related qualitatively to the increase of long chained branching in the polymeric system. The plot of the loss angle vs angular frequency is reported for both neat and modified PLA in Fig. 14. The neat PLA system overall shows a decreasing curve of loss angle. As the frequency approaches to ( $\omega \rightarrow 0$ ), the loss angel reaches close to  $90^\circ$  where the melt is a viscous liquid. At infinite frequencies, the material responds as an elastic solid and the loss angle goes to zero. On the other hand, the curve of modified PLA shows changes in both position and form. Firstly, there is much lower values for loss angle as compared to the neat PLA which indicates higher elasticity at the same frequencies. This in results shows improvement in polymers melt strength

and its processing behavior where elongational flow is important. The curve also shows deflection and an intermediate plateau around 10 rad/s. This behavior indicates presence of long chained branched structure in the modified PLA system.

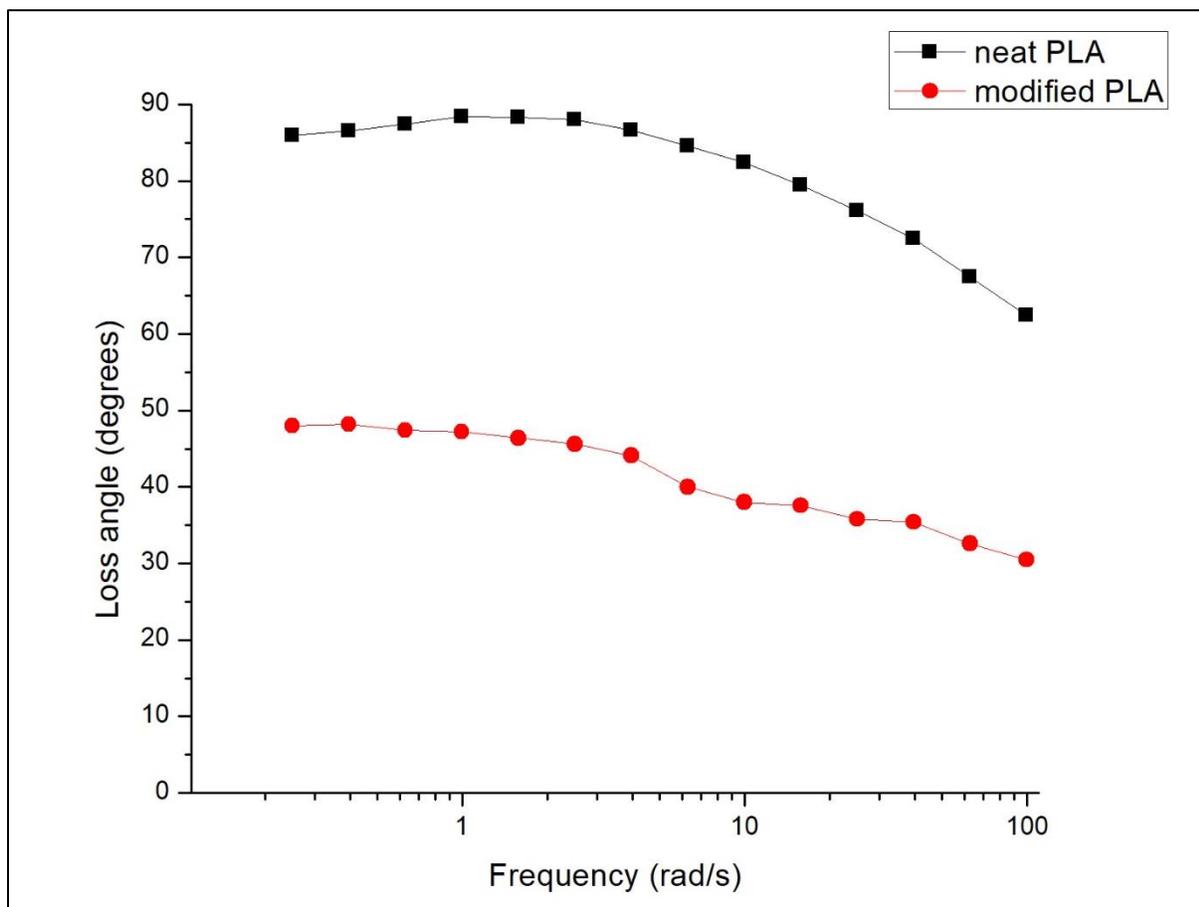


Fig. 14. Loss angle curve for neat and modified PLA

#### 4. Conclusion

The current study investigated the chain extension reaction effect on the thermal stability and rheological properties of modified polymer blend via incorporation of chain extender (Joncryl). PLA blend showed an improvement in thermal degradation phenomena and an increase in viscosity with the addition of chain extender. In this work, Joncryl ADR was used as a multifunctional epoxy chain extender. The reaction involves covalent bond formation between hydroxyl group of PLA and the epoxide group which results in ring opening of epoxide while simultaneously there is an abstraction of hydrogen atom from the hydroxyl group of OH, thus facilitating the completion of reaction. From the GPC analysis, it was shown that with the increase of Joncryl amount and reaction time, the molecular weight increased significantly. Similarly, in the GPC, for neat polymer system, thermal degradation was seen at different processing temperature. This phenomenon was eliminated upon addition of Joncryl which corroborates with the improvement in the thermal stability of PLA. Thermal analysis via TGA and DSC techniques helped to identify the thermal transitions for both PLA and Joncryl whereas the analysis for blend was investigated in the latter one (DSC). The viscoelastic region was determined via rheological characterization for both neat and modified PLA. This region exhibits a flow behavior that is a combination of irreversible viscous flow due to the chain

slippage of polymer as well as there is a reversible elastic deformation due to molecular entanglement. There was a substantial improvement in the rheological properties (viscosity, loss and storage modulus) of modified PLA when compared with neat PLA system.

## 5. Acknowledgements

Many thanks to the University of Groningen and Polymer chemistry department for all the support. The author also expresses his appreciation toward supervisor Yifei fan for all the support and help during the research.

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