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## **ABSTRACT**

### **THE COMPLEX BEHAVIOR OF POLY(DTE)CARBONATE AND ITS BLEND PROPERTIES**

**by  
Christopher George Elvin**

Over the years a number of different polymers have been studied for bone applications. Polyesters such as the poly lactic acids (PLA), poly glycolic acids (PGA), and their copolymers have been studied intensely for bone regeneration purposes. Poly(DTE)carbonate has been found useful for bone regenerative purposes and is under review by the U.S. Food and Drug Administration.

The purpose of this study was to investigate the properties of poly(DTE)carbonate when PLLA, PLGA, and P(LcoDL)LA was blended with it. The desired outcome was to produce miscible polymer blends or significant phase shift in the blended materials which will make them at least partially miscible to each other.

Differential scanning calorimetry (DSC) and thermally stimulated current (TSC) analysis of the material identified temperature regions where complex thermal events were occurring. From the experiments it was determined that at certain temperatures poly(DTE) carbonate dipoles spontaneously rearranges while an electric field is across the polymer. Multiple thermal regions were identified and in some cases there are plasticizing and anti-plasticizing events occurring for the blends.n

**THE COMPLEX BEHAVIOR OF POLY(DTE) CARBONATE  
AND ITS BLEND PROPERTIES**

**by  
Christopher George Elvin**

**A Thesis  
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**APPROVAL PAGE**

**THE COMPLEX BEHAVIOR OF POLY(DTE) CARBONATE  
AND ITS BLEND PROPERTIES**

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*First,*

*I would like to thank the **Lord** for blessing me with the wisdom, fortitude, and passion to make my life better through the abundance of knowledge I've acquired over the years.*

*This thesis is dedicated to my parents, **Patricia Brady and Clinton Elvin** for without their struggle I would not have made it out of the poverty stricken environment in Jamaica.*

**Thanks for believing in me.**

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# CHAPTER 1

## INTRODUCTION

### 1.1 Objectives

As the medical field becomes more advance with breakthrough medicine, technologies and health awareness, the lifespan of humans have increased with the practice of new preventative medicine. The longer people live, the more they are prone to problems associated with their mobility. It is up to collaborators such as orthopedics and biomedical engineers to come up with novel devices that can facilitate uses as biomedical devices for the body. For example, the older generation usually suffers bone density loss, making them more susceptible to fractures. They also suffer from osteoporosis which leads to severe pain in the inflamed body joints. In the older population bone regeneration is slower resulting in longer trauma time. To increase bone generation at a fractured site, biomaterials that can serve as fillers and induce bone generation are commonly used. For the more severe case where a body part such as hip or knee has to be replaced, prosthetics are needed. The ideal case is for the prosthetics to last the lifespan of the patient. Hence better prosthetic's design and biocompatible materials are desired.

Over the years a number of different polymers have been studied for bone applications. Polyesters such as the PLA and PGA and their copolymers have been studied intensely for bone regeneration purposes. A new polymer which has been under review by the FDA for biomedical applications is poly (desaminotyrosyl-tyrosine ethyl) carbonate [poly(DTE) carbonate]. This polyester compound has been found to be useful for bone regeneration purposes.

The purpose of this study is to investigate the physical and mechanical characteristics of three different polyesters blends; PLLA, PLGA, and P(LcoDL)LA blended with poly(DTE) carbonate. The desired outcome is to produce miscible or partially miscible polymer blends. The cost of poly(DTE) carbonate is high so blending the polymer with a cheaper polymer that has the similar properties is economical. The new material will be investigated to see if the blends have similar mechanical and behavioral properties as that of poly(DTE) carbonate.

## **1.2 Background**

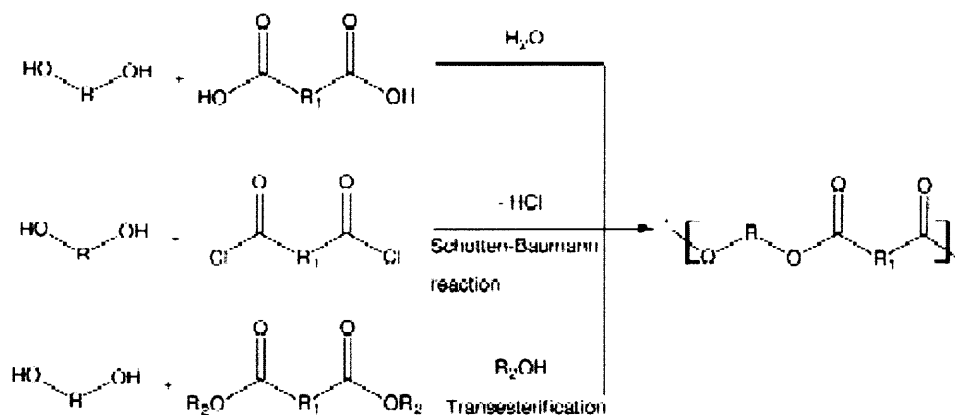
A history of blends, particularly polyester-polyester and polyester-polycarbonate blends will be summarized to have an idea as to how poly(DTE) carbonate could behave since it is comprised of a polyester component and a carbonate component. A summary of their miscibility and tendency to be miscible is investigated.

### **1.2.1 Polyesters**

There is a wide variety of polyester polymers and applications for these polymers. Polyesters are a class of polymers that is comprised of the ester functional group in the main chain. The reaction of an acid with an alcohol is the basic mechanism use to form polyesters. These polymers form a broad range of materials that have distinct characteristics such as being liquid crystals, fibers, biomedical matrices, and temperature resistant performance material as a result of the chemistry and structural units connecting the ester groups [5].

### 1.2.2 How They Are Made

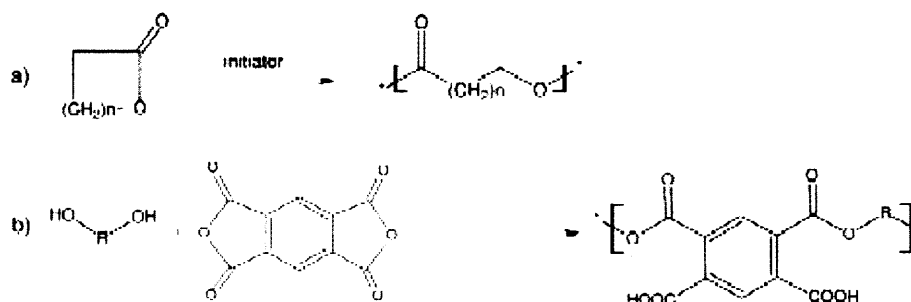
Polyesters are usually synthesized by stepwise polymerization of the bifunctional monomers through a process known as polycondensation. Polyesters are formed from the reactions of diacids and diols, diacid chlorides and diols, or ester interchange of diesters and diols, with the elimination of byproduct such as water [5, Figure 1.1].



**Figure 1.1** Preparation of polyesters by stepwise polycondensation (U. Edlund, 2003).

There are some disadvantages to this process. Continuous removal of the byproduct, long reaction times, and high temperatures are needed for the reaction to yield long polymer chains.

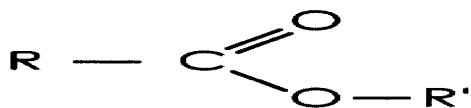
A more convenient method to achieving long ester linkage is by ring opening polymerization (ROP). Milder conditions and shorter reaction time is needed to produce aliphatic homo and copolyester. For example in the presence of a catalyst, polyesters can be produce from the ring opening of cyclic polyanhydrides [5, Figure 1.2].



**Figure 1.2** Preparation of polyesters by ring opening polymerization using (a) lactones, and (b) cyclic anhydrides (U. Edlund, 2003).

For polyesters that are derived from bacterial origins such as polylactic acids, enzymatic polyesterification is the novel technique. Enzymes such as lipase can be used as a catalyst in the esterification of various diacids and their derivatives as monomers. This process offers more control and specificity over the reaction in milder test condition compared to condensation reaction.

More recently, the condensation reaction leading to polyester formation has been evolving with the incorporation of a new technique in which macromer or oligomer is used. These molecules have several functional groups that can be linked together to form complex polyesters by using different techniques such as radical, ionic, coordination, condensation or ROP polymerization. Figure 1.3 is a representation of the ester group that makes up polyester.



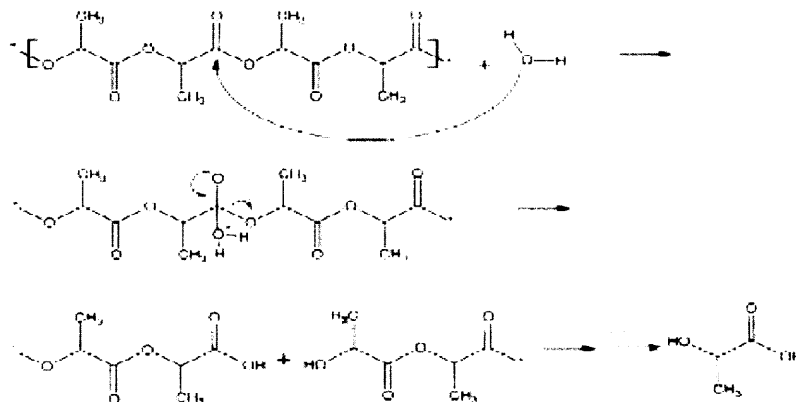
**Figure 1.3** The general formula for an ester.

### 1.2.3 Polyester Characteristics

All polyesters are characterized by the general formula in Figure 1.3. R and R' is either an alkyl or aryl group. The ester components participate in hydrogen bonding by accepting hydrogen ions, but are incapable of donating any hydrogen ions.

All polyesters are degradable. However, their rate of degradation depends on the length of the main chain (the shorter ester chain will degrade faster over a reasonable time scale). There are a number of ways to degrade polyester segments. Two such processes are hydrolysis and microbial degradation. Hydrolysis is the breaking of the ester linkages by water molecules with either an acid or base being the catalyst. When polyester is hydrolyzed in the presence of a base the reaction is called saponification. The result of the hydrolysis is the formation of alcohol and the carboxylate salt or carboxylic acid. Microbial degradation is a result of enzymes excreted from the microorganism.

An example of the steps involved in the degradation of a polyester molecule can be represented by Figure 1.4.



**Figure 1.4** The degradation of polyester (polylactide) by hydrolytic scission of the main chain ester bonds. (U. Edlund, 2003)

The most abundantly used polyester is poly (ethylene terephthalate) (PET), which is used commercially for packaging, stretch-blown bottles and for the production of fibers for textiles products. Another polyester product which is similar to PET is poly(butylenes terephthalate) (PBT), except that it has longer more flexible butylenes side chain linkage, making it more susceptible to rapid crystallization rate. It is used for electrical and electronic components due to its high temperature resistance and good electrical properties. Being the most popular of the family of polyesters used in industry, PET finds itself in other applications; with the addition of minerals, glass and other materials, PET composites are able to meet different processing demands. Additions can make PET a valuable commodity for replacing metals such as zinc in motor or pump housing and structural steel in furniture, as well as replacing die-cast aluminum [18].

#### 1.2.4 Polyester Blends

Use of polyesters in some applications can be limited by processing difficulties. For example, the tensile properties on poly (ethylene 2,6-naphthalate) (PEN) depends on its molecular weight (MW). The higher the MW of PEN, the higher the tensile properties.



It is difficult, however, to process high MW PEN due to its high shear viscosity [13]. To reduce the viscosity a low molecular weight polymer such as a low MW PEN could be used as a plasticizer.

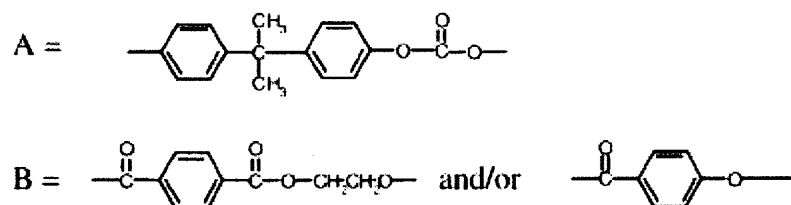
Polyester like all polymers can be blended together by two processes; blending by mixing the polymers in a solvent, or by using a melt blending technique. The literature on blends suggests that the final product achieved depends on the method of preparation. For example when low MW and high MW PEN is mixed in solution the blend formed is immiscible, but when annealed above the glass transition temperature ( $T_g$ ) of the high MW PEN, a miscible blend is formed [13]. Before comparing the differences within the blends, information about the component polyesters have to be determined. The intrinsic viscosity (IV) measurements and differential scanning calorimetry (DSC) experiments are necessary to estimate the MW and  $T_g$ , respectively, of the high MW and the low MW PEN.

The two polyesters are then blended with a solvent or a melt blending technique. The DSC results show that for the solution blend two  $T_g$  is present, but for the melt blend one  $T_g$  is present. For the melt blend the  $T_g$  found is similar to that of the low MW PEN. This could be a result of what is observed that ester interchange reaction (transesterification) and molecular degradation often takes place in melt blending for polyester-polyester blends [19].

It is not only polyester-polyester blends formed from the same type of polyester that are immiscible using a solvent to form the blend, other combinations show similar characteristics. Guo et al. reported that blends such as PET/PEN shows phase separation when mixed in a solvent.

A way to improve on the properties of phase separated polymer blends is with copolymers that can act as interfacial modifiers. A copolymer that consists of two monomers that make up the homopolymers, could be used as a modifier to form a bridge between the homopolymers. The two homopolymers are intended to participate in transesterification at elevated temperature. The initial reaction forms a diblock copolymer arrangement between the two homopolymer. On further transesterification, the diblock copolymer will continue to rearrange until it forms a more random microstructure. This reaction occurs at the interface of two phases in the phase separated system. This random microstructure of the copolymer will now be able to act as an interfacial modifier to strengthen the blend at the interfaces where needed [17, Figure 1.5].

RADMARD AND DADMUN

1<sup>st</sup> reaction

AAAAAAAAAAAAAABBBBB

2<sup>nd</sup> reaction

BBBAAAAAAAAAAAAABBBBB

3<sup>rd</sup> reaction

AAAAAABBBBBAAAAAABBBBB

.....

Many reactions

BABBAABBABAABABABBAABAABABA

**Figure 1.5** The steps involve in transesterification (Radmard, 2000).

### 1.2.5 PET/PC BLENDS

Two of the more well known polymers are poly (ethylene terephthalate) (PET) and bisphenol A-2,2'-bis(4-hydroxyphenyl)propane carbonate (PC). PET is produced in the billions of pounds globally and accounts for about 45% of all fiber application. PET is synthesized in two ways from the substances dimethyl terephthalate (DMT) and terephthalic acid (TA). The first process is a two step process to include:

1. Solution polymerization in order to create ester interchange between TA and ethylene glycol and thus forming the monomer bis-hydroxyethyl terephthalate and short oligomer chains.
2. The second step is polycondensation reaction. In this step transesterification is taking place in the melt phase. The by-product ethylene glycol is removed at elevated temperature under vacuum.

The second technique involves the production of PET from DMT and ethylene glycol. Transesterification of DMT with ethylene glycol also produces the monomer bis-hydroxyethyl terephthalate and the by-product methanol [18].

PET forms a crystal that melts at 270 °C. The stiff polymer chain gives it its good mechanical strength, toughness, and fatigue resistance up to a temperature of about 150-175 °C. The stiff polymer chain also contributes to the polymer chemical, hydrolytic and solvent resistance. It has great advantages for fiber applications because it has great crease resistance, good abrasion resistance when cross-linked with resins, and when blended with cotton and other fibers, the physical features (feel, moisture permeation) changes in the material.

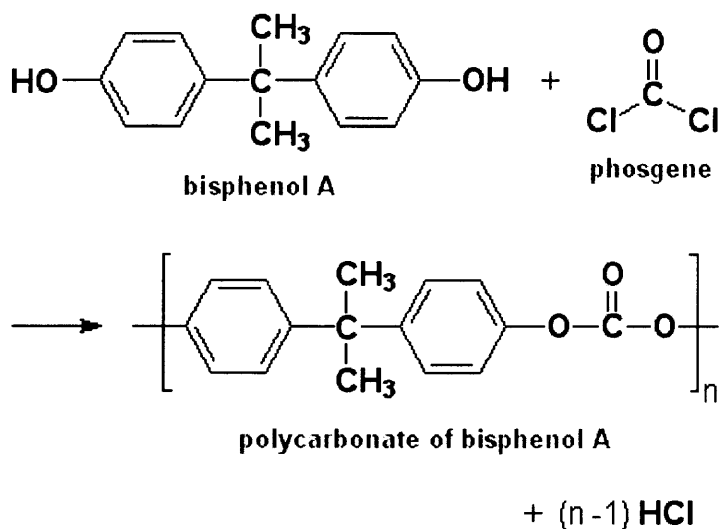
PC is derived from the polymerization of carbonic acid and Bisphenol A. Polycarbonate is synthesized using two different techniques; from dihydric phenol with phosgene or by the ester interchange with diphenyl carbonate. The phosgene method is preferred commercially because the MW can be controlled [Figure 1.6]. The steps involve are as follow:

- 1) Dissolve bisphenol A in an aqueous alkali to produce phenolate salt.
- 2) Add the salt to an organic solvent such as THF, chlorobenzene, 1,2 dichloroethane followed by phosgene.

The organic solvent has two roles; one is to prevent the loss of phosgene by hydrolysis and two is to prevent precipitation of the forming polymer before it reaches the desired MW.

The most common form of PC is the amorphous state with a glass temperature of 150 °C, but, it can be manufactured to be crystalline with a melting temperature of 27 °C. The two benzene rings in the main chain of the monomer results in the stiffness of the polymer. The material's mechanical properties make it an ideal candidate for application where resistance to acid and oxidants and resistance to aliphatic and aromatic solvent are needed. It is less resistant to polar organic solvent. Mechanically the material also exhibits good impact resistance (toughness) and good dimension and creep resistance.

Some common application for PC includes: materials for compact disks, glazing (windows and sunglasses), medical components for dialysis, blood collection, and surgical devices, material for power tools and appliance housing, refrigerator interiors and safety helmets.



**Figure 1.6** Polymerization of bisphenol A with phosgene to form polycarbonate. (www.chemheritage.org)

Debates about the miscibility of PET blended with PC are inconclusive. Some authors suggest that the blends form are miscible with higher percent of PET, other suggest that the blends are immiscible at all ratios [15].

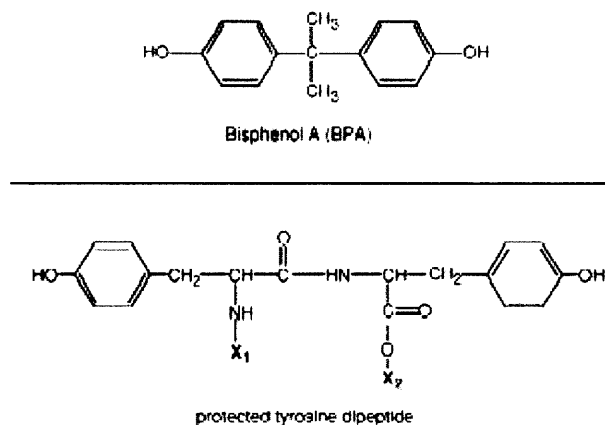
Y. Kong believes that the final outcome of these blends is based on the experimental procedures used and other factors such as ester exchange reaction, difference in molecular weight, and data analysis technique use to identify compatibility. From experiments done he reports that blends prepared without catalysts are immiscible. The blends in the absence of a catalyst form a clear two phase structure; this is confirmed by the two T<sub>g</sub> present when a DSC experiment is run for the blends. Blends in the presence of a catalyst are partially miscible due to the much smaller phase domains that are present.

The PET/PC combination forms an amorphous structure that is ductile. Under stress strain experiment, necking usually occur followed by strain hardening and then failure. For blends formed in the presence of a catalyst the elastic modulus increase with an increase in PC content and decrease for blends without catalyst [15].

#### **1.2.6 Comparison of PC to Poly(DTR) carbonate**

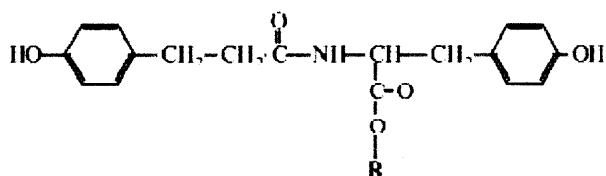
Polycarbonate is an ideal material for medical applications based on its mechanical properties. The aromatic rings in the backbone make the material very rigid and strong, an ideal property for some medical application such as in the design of orthopedic devices. The disadvantage of PC is that it is a cytotoxic material that will have severe effects if implanted in vivo.

The only material that is similar in structure to PC (having the aromatic rings) and the only natural nutrient with aromatic hydroxyl group is tyrosine [1]. Tyrosine has been used to synthesize the library of polymers commonly classified as poly(DTR) carbonate. R refers to an alkyl group that makes up the side chain or pendant chain [Figure 1.7].



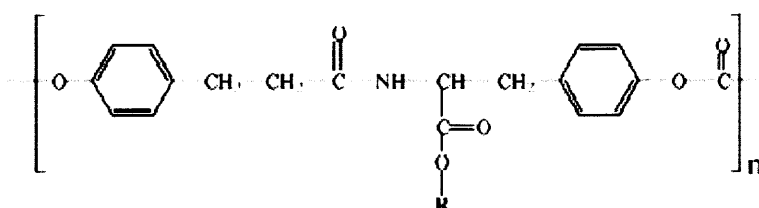
**Figure 1.7** Comparing the chemical structure of bisphenol A to tyrosine dipeptide. (S. Bourke, 2003)

Early poly(DTR) carbonate polymer was composed of only diphenol tyrosine in the backbone chain. The material form was not favorable for implant application because it was difficult to obtain a material that is readily processed. The problem was too many inter-chain hydrogen bonding sites present per monomer unit. To change the material characteristics, one of the tyrosine molecules is replaced by desaminotyrosine [3-(4'-hydroxyphenyl)propionic acid] to form what is known as desaminotyrosyl-tyrosine alkyl ester [1, Figure 1.8].



**Figure 1.8** Chemical structure of desaminotyrosyl-tyrosine alkyl ester. (S. Bourke, 2003)

The desaminotyrosyl-tyrosine alkyl ester is then polymerized with either phosgene or bis(chloromethyl) carbonate triphosgene to give poly(DTR)carbonate [Figure 1.9].



**Figure 1.9** Chemical structure of tyrosine derived polycarbonate. (S. Bourke, 2003)

There are three types of bonds present in the DTR carbonate monomer, an amide bond, an ester bond, and a carbonate bond. The carbonate and ester bonds are more suitable for hydrolysis than the amine bonds in aqueous media (37 °C, pH 7.4) that do not contain enzymes. The rate of hydrolysis is determined by length of pendant chain and the pH of the media. It is observed that longer pendant chain has the ability of decreasing the rate of ester and carbon chain cleavage by possibly increasing the hydrophobicity of the molecule [21]. The other factor that affects the hydrolysis of DTR molecule is the pH of the media. A neutral or slightly acidic pH will enable the carbon bond to hydrolyze faster than the ester bond. The reverse is true for highly acidic media.



Tangpasuthadol et al. noted from experiments done that the pendant chain has considerable effect on the properties of the polymer; properties such as the T<sub>g</sub>, surface free energy, and mechanical properties is determined by varying the length of the alkyl ester chain [20]. This amorphous, hydrophobic materials range in T<sub>g</sub> from 52 to 93 °C (longer pendant chain has lower T<sub>g</sub>) and has a decomposition temperature of 290 °C. Thin solvent cast films are made and the tensile properties was determined. The polymers have mechanical strengths between 50 to 70 MPa and stiffness 1 to 2 GPa [1].

Poly(DTE) carbonate (E-ethyl) is one of the polymers that make up the library of poly(DTR) polymers. It is under review by the FDA for medical device application. Results show that the polymer has osteoconductive properties and may be able to be used in bone fixation devices. The present cost for the material makes it use impractical. In order to lower the cost, poly(DTE) carbonate will be blended with other polymers that have been studied and proved to be an osteoconductive material.

### **1.2.7 Lactides and Glycolides**

The polyesters such as the lactic acids and glycolic acids and their copolymers are widely used for tissue and bone applications. In the field of orthopedics the polylactides (PLAs) and polyglycolides (PGAs) are being used for fracture fixation devices and scaffolds for tissue growth. Studies have shown that these polymers are capable of being used as devices for implants to accelerate bone healing without the toxic effect or any inflammatory response. These polymers are hydrolytic and bioerodeable and the rate of degradation are dependent on the size and shape of the polymer, the isomer ratio, and the temperature.

For instance, PLLA undergoes degradation by a number of mechanisms: thermally at about 200 °C and above, by hydrolysis, oxidative main chain scission, and by inter and intramolecular transesterification reactions [9]. PLLA has a T<sub>g</sub> of about 55 °C and a T<sub>m</sub> of about 170 to 180 °C. These temperatures make the polymer processing window to be very narrow. Temperature above T<sub>m</sub> will cause chain scission reaction and a loss in molecular weight and thermal degradation. To modify the thermal properties of PLLA, portions of an enantiomeric polymer can be added to the polymer. Over time these polymers breakdown in the body to form nontoxic materials which the body is able to remove through the Krebs cycle primarily as carbon dioxide and water.

## CHAPTER 2

### POLYMER BLEND FUNDAMENTALS

To determine if two polymers are miscible together has been the concern for scientists for many years. A number of theories have been derived by people such as Hildebrand, Van Krevelen, Flory, Huggins and others. Basically these treatments involve the development of a formulation that is used to describe the solubility of polymers based on defined parameters.

The process of mixing is based on the equation free energy:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad 2.1$$

$\Delta G_m$  is the change in free energy,  $\Delta H_m$  is the heat of mixing, and  $\Delta S_m$  is the entropy of mixing. It is theorized that mixing occurs when the free energy is negative.

Hildebrand derived an equation for determining  $\Delta H_m$ . According to him

$$\Delta H_m = \Phi_1\Phi_2(\delta_1 - \delta_2)^2 \quad 2.2$$

$\Phi_i$  is the volume fraction of component 1 and 2 and  $\delta_i$  is the solubility parameter for component 1 and 2.

$$\delta = (\Delta E_{\text{vap}}/V)^{1/2} \quad 2.3$$

If  $\delta$ s are nearly equal then the substances will be miscible.

In deriving the equation for the solubility parameter, Hildebrand assumed that no specific forces are active: Strong polar groups such as hydrogen are not playing any role

in the miscibility study. The solubility of polymers cannot be determined directly because polymers cannot be vaporize without decomposition, therefore the solubility parameter is determined by the solvent into which the polymer will completely mix without volume change, and without any reaction.

Van Krevelen has developed a method also to estimate solubility parameters of polymers. His method is based on the idea that different structure components of a polymer, when added together can determine the solubility parameter. His theory strictly applies to molecules that do not have strong polar groups. His work is based on two rules to describe that describe the solubility of polymers: First of all, the chemical and structural similarities favor solubility. It is believed that solvent solute affinity is greatest when the polymer and solvent have similar polarities. Secondly, fractioning the polymer into its structure components and determining the solubility is easier for longer polymer chain molecules since the solubility decrease with an increase in molecular weight [22].

Van Krevelen group additive relationship in determining polymer properties is given as,

$$F = \sum n_i F_i \quad 2.4$$

Where  $F_i$  defines the identity and contribution of a functional group  $i$  and  $n_i$  corresponds to the number of times the functional group is repeated in the molecule. When the Van Krevelen constant is known it can be used to determine the solubility parameter for a polymer from this equation

$$F = \delta M / \rho \quad 2.5$$

Just as Hildebrand determined that the polymer should not have strong polar groups, so too is Van Krevelen theory limited to compounds that do not have strong hydrogen bond unless the functional group constitute a small part of the molecule [22]. The table below list the Van Krevelen constant for some functional groups within a polymer chain.

**Table 2.1** Group Components Value Used in Equation Derived by Van Krevelen

Atom or Group	$F_i (\text{cal.cm}^3)^{0.5}/\text{mol}$
C	0
H	68.5
O	
ether	125
ester	125
ketonic	335
alcoholic (primary)	360
alcoholic (secondary)	300
phenolic	250
S	
thioether	225
thiol	250
F	80
Cl	230
Br	300
I	420
Double bond (non-aromatic)	80
Double bond (aromatic)	133
Triple	215
N	
aliphatic primary amine	100
aliphatic secondary amine	140
aromatic primary amine	65
heterocyclic	115
nitril	480
N + O in	
nitro aliphatic	460
nitro aromatic	325
acid amide	600
	400
non-aromatic ring	60
ramification in chain	-20
conjugation of double bonds	25
2 OH on adjacent C atom	-190

Source: D.M. Van Krevelen & Hoftyzer, "Properties of Polymers: correlation with chemical structure." (Amsterdam, New York: Elsevier Pub. Co., 1972).

Flory and Huggins also contributed to the quest of defining the solubility of polymers. Both contributed to the parameters used to determine solubility of polymer solution based on their work in the 40's. Huggins derived an equation to determine the activities of solvent and solute based on their mole fraction in solution [12]. Part of Flory's contribution is based on his work on how a polymer solution is capable of becoming miscible depending on their entropy of mixing [7]. Based on classical formula,

$$\Delta S_{\text{mixing}} = -R(n_1 \ln X_1 + n_2 \ln X_2) \quad 2.6$$

which is in turn based on ideal solution theory that there is no interaction between the polymer molecules. An alternate formula that takes into account interaction of the polymer molecules based on its configurations in solution was developed.

$$\Delta S_{\text{mixing}} = -k[ n \ln(n/n+xN) + N \ln(N/n+xN)] + k(x-1)N[\ln(\gamma-1)-1] - kN \ln 2 \quad 2.7$$

$N$  = the number of polymer molecules, each composed of  $x$  segments.

$\gamma$  = a coordination number for the lattice (the number of "first neighbor" cells in the lattice available to the next consecutive segment of the polymer chain).

$n$  = the number of pure solvent.

The assumptions used to derive the above expression are; One, the mixture and solvent conforms to a quasi-rigid lattice in the liquid, interchangeability of segments of the polymer chain with solvent molecules, and independence of lattice constant on composition. Two, all the polymer molecules are the same size. Three, the average concentration of polymer segments in cells adjacent to cells unoccupied by the polymeric solute is taken to be the overall average concentration. Four, the expected number of

available positions for each successive segment can be determined (takes into account the impossible ways the polymer chains might fit on the lattice). The equation for  $\Delta S_{\text{mixing}}$  is used to describe the process of mixing  $n$  pure solvent and  $N$  perfectly arranged (or oriented) polymer molecules [8].

If the mixture of polymer and solvent are not perfectly arranged that is they are randomly oriented, then

$$\Delta S_{\text{mixing}} = -k [ n \ln(n/n+xN^2) + N \ln(xN/n+xN) ]$$

Or

2.8

$$\Delta S_{\text{mixing}} = -k ( n \ln v_1 + N \ln v_2 )$$

where  $v_1$  and  $v_2$  are volume fraction of solvent and polymer.

$$v_1 = N_1 / (N_1 + xN_2)$$

and

2.9

$$v_2 = xN_2 / (N_1 + xN_2)$$

For a polymer-polymer solution

$$v_1 = x_1 N_1 / (x_1 N_1 + x_2 N_2)$$

and

2.10

$$v_2 = x_2 N_2 / (x_1 N_1 + x_2 N_2)$$

Based on the assumption that a polymer molecule has a number of segments, each occupying one lattice site, the Flory-Huggins derived expression is for the approximation of the conformation of the polymer. (The problem was how to calculate the number of



ways of placing the polymer chains on the lattice). An expression for the free energy of mixing was obtained by combining entropy of mixing with the enthalpic term for mixing, which is denoted by the interaction parameter

$$\chi = \Delta H_m / kTN_1v_2 \quad 2.11$$

$k$  is the Boltzmann constant

$N_1$  is a count of the number of polymer molecules in the solution

$v_2$  is the volume fraction of solvent

The chi parameter and the entropic term is put together to give Gibbs free energy of mixing,

$$\Delta G_{mix} = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \quad 2.12$$

While the above theories can explain the miscibility of homopolymer solution to a great extent, it has little bearing on explaining the behavior of homopolymer/copolymer blends or copolymer/copolymer blends. Copolymers are polymer compounds derived from combining two or more polymers together. To explain copolymer-copolymer blends or a mixture of homopolymer-copolymer blends new theories had to be derived. Using the principles already known and assumptions that are already made, the Flory-Huggins theory can be expanded to include these complexes.

For a mixture of two random copolymers an expression for the free energy of mixing can be determined.

$$\Delta G/RT = (\Phi_1/N_1) \ln \Phi_1 + (\Phi_2/N_2) \ln \Phi_2 + \Phi_1 \Phi_2 [xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD}] \quad 2.13$$

$x$  and  $y$  denote copolymer composition (volume fractions of the two copolymers  $(A_xB_{1-x})_n$  and  $(C_yD_{1-y})_n$  of volume fractions  $\Phi_1$  and  $\Phi_2$ )

A and B makes copolymer 1, and C and D makes copolymer 2,

$N_1$  and  $N_2$  are the degree of polymerization [2]

The two cases where the equation is applicable are as follow:

Case 1: For a mixture of homopolymer and copolymer.  $A(x = 1)$  and copolymer

$$(C_yD_{1-y})_n \dots \chi_{\text{blend}} = y\chi_{AC} + (1-y)\chi_{AD} - y(1-y)\chi_{CD} \quad 2.14$$

Case 2: For a mixture of two copolymers that differ only in copolymer composition

$$(A=C, B=D) \dots \chi_{\text{blend}} = (x-y)^2\chi_{CD} \quad 2.15$$

It is found that there is a pair-wise interaction between the segments of blends which gives the chi parameter for the blend ( $\chi_{\text{blend}}$ ). In this type of model it is assumed that the copolymers consist of a number of individual segments which make up the overall mixture. Vukovic et al. determined that “the  $\chi_{\text{blend}}$  parameter can be expressed as a linear combination of the segmental interaction parameters  $\chi_{ij}$ :

$$\chi_{\text{blend}} = xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad 2.16$$

$x$  and  $y$  are the volume fraction in the copolymers.

The terms in the equation are used to represent the nature of how the segment in the mixture interacts i.e. additive intermolecular interactions between the non-bonded component monomers and the intramolecular interactions between two different

monomers comprising each of the copolymers. Miscibility for such a mean-field model is determined when the  $\chi_{\text{blend}}$  is less than the critical value  $\chi_{\text{crit blend}}$  [14].

$$\chi_{\text{crit blend}} = 0.5(N_1^{-0.5} + N_2^{-0.5})^2 \quad 2.17$$

## **CHAPTER 3**

### **MATERIALS AND EXPERIMENTAL PROCEDURE**

#### **3.1 Polyester Blends**

Blends of poly(DTE) carbonate with three polyesters materials: PLLA, PLGA and P(LcoDL)LA copolymer were made.

##### **3.1.1 Poly(DTE) Carbonate**

Poly(DTE) Carbonate is supplied by Rutgers University, New Brunswick, NJ. From GPC experiments done on the polymer, an average molecular weight (Mw) 90781 is determined. The polymer is mixed in dichloromethane (DCM) solvent at room temperature to make a 5 wt % polymer solution.

##### **3.1.2 PLA/PGA Polymers and Copolymers**

Two kinds of PLA were used; P(LcoDL)LA supplied by Osteotech Inc., and PLLA (Resomer L 20 b) supplied by Boehringer Ingelheim, Ingelheim am Rhein Germany. PLGA is supplied by Alkermes, Inc. Wilmington OH. It is a copolymer of lactide/glycolide 75/25 (Medisorb, grade 7525 DL, low IV). These polyesters are also mixed in DCM to make a 5 wt% polymer solution.

### 3.2 Thin Films from Blends

5% w/v solutions of each component polymer were made. After the solutions were made poly(DTE) carbonate was blended with the other component to make up a 10 gram blend solution. The measured blend solution is then mixed for about fifteen minutes. The different blend percentage of poly(DTE) carbonate to the other polyesters are 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100, respectively. After the blend ratios are allowed to mix, 5 grams of each was then pipetted in small aluminum dishes and allowed to dry overnight for vaporization of solvent at room temperature. The blends are then placed in a vacuum at room temperature for about three days for additional removal of any solvent and moisture from the blends. The films formed are less than 1mm thick and are carefully removed from the bottom of the aluminum dish in order to obtain the film with high mechanical integrity.

A second batch of the blends comprising of the same blends ratio of poly(DTE) carbonate to the other polyesters was made for reproducibility studies. The same blending technique followed by similar drying time was used.

### 3.3 Characterization

Thermal and mechanical characteristics of the material is important to see if blending Poly(DTE) carbonate with the known polyesters that have been used over the years for biomedical applications will change the properties of the component polymer. To determine the resulting properties of blending, thermal analysis as well as mechanical analysis is done by differential scanning calorimetry (DSC) (TA instruments Q 100),

thermogravimetric analysis (TGA) (TA instruments Q50), thermally stimulated current analysis (TSC), and using an Instron machine for mechanical analysis.

### **3.3.1 Differential Scanning Calorimetry (DSC)**

Differential scanning calorimetry (DSC) measures the changes in specific heat of a material as a function of temperature, and time. The samples were analyzed under three cycles; heating, cooling, and reheating.

The films with 100% Poly(DTE) carbonate and 100% of P(LcoDL)LA, PLGA, and PLLA respectively are first analyzed to see the thermal properties present with these solvent cast films. Once the baseline behavior for component material is determined, the thermal properties of the blends in different proportion are then determined.

The parameters used for the DSC experiment is as follows: A heat cool heat cycle with the starting temperature at -20 °C and the maximum temperature at 140 °C. The heating rate is 5 °C/min and the cooling rate is 10 °C/min. The third cycle is used in determining the glass transition temperature ( $T_g$ ) and or melting temperature ( $T_m$ ). Only the third cycle is analyze in the experiments in order to determine the behavior after the removal of any imposed process history. The first heating can drive the residual solvents away. Usually, there is a remnant of the solvent use in casting these films or in some cases the polymers used might be hydroscopic, hence absorbing moisture in the films.

### **3.3.2 Thermally Stimulated Current (TSC)**

Thermally stimulating current (TSC) method can be use to determine the current generated when a material is placed within an electric field and heated. Current is

generated from the material as a result of displacement of charges [4]. The two methods use to determine the current generated are the thermally stimulated polarization (TSPC) method and a modified thermally stimulated depolarization (TSDC) method.

For the TSPC method, the material is heated from  $-20\text{ }^{\circ}\text{C}$  at  $7\text{ }^{\circ}\text{C}/\text{min}$  to  $140\text{ }^{\circ}\text{C}$  within an electric field. For the modified TSDC method, the material is heated to  $112\text{ }^{\circ}\text{C}$  and held for two minutes. An electric field of 100 volts was applied across the film to align the polar groups. The material is cooled at  $7\text{ }^{\circ}\text{C}/\text{min}$  to  $-20\text{ }^{\circ}\text{C}$  and held at this temperature for a minute. The current generated during the cooling cycle with the field on was determined. The electric field is turned off and the material is then heated from  $-20\text{ }^{\circ}\text{C}$  at a rate of  $7\text{ }^{\circ}\text{C}/\text{min}$  to the final temperature of  $140\text{ }^{\circ}\text{C}$ . Again current is generated by the material as the polar groups begin to regain mobility by relaxing to a more stable unaligned configuration. The material was run multiple times to see if the results are reproducible.

The TSPC analysis with the field on was first done for a piece of Teflon material. The Teflon was placed between the electrodes inside the TSC cell and the temperature where activity was observed for the piece of Teflon film was recorded. This temperature will be used as a reference point that is not associated with the events of the films to be tested. The Teflon will serve as an insulating material between the bottom electrode and the polymer films to be tested. Any charge that might have been induced on the polymer film is prevented from interfering with the TSC results obtained.

TSPC experiments were run for the polymer films with and without an electric field. After the TSPC analysis, TSDC experiments were run and current was measured for the cooling and heating phase of the films tested.

### **3.3.3 Thermogravimetric Analysis (TGA)**

TGA experiments are done to see at what temperature these polymer blends degrade. The experiment can also be used in determining the amount of residual solvent and/or moisture that is contained in the blends. TGA, measures the change of weight of a material as a function of temperature or time. The method use is the ramping technique. The material is ramped up at 5 °C/min from room temperature to 300 °C. The results indicated that in some cases significant amount of moisture and/or solvent is absorbed within the films.

### **3.3.4 Instron Mechanical Analysis**

An Instron machine is used to measure the mechanical properties of the materials. Small rectangular films that are 2-2.5 mm in width and approximately 2 cm in length are stretched and the mechanical properties are determined. Two rectangular films from the same blend ratios are tested and the averaged results are compared with what is noted in literature for Poly(DTE) carbonate.



## CHAPTER 4

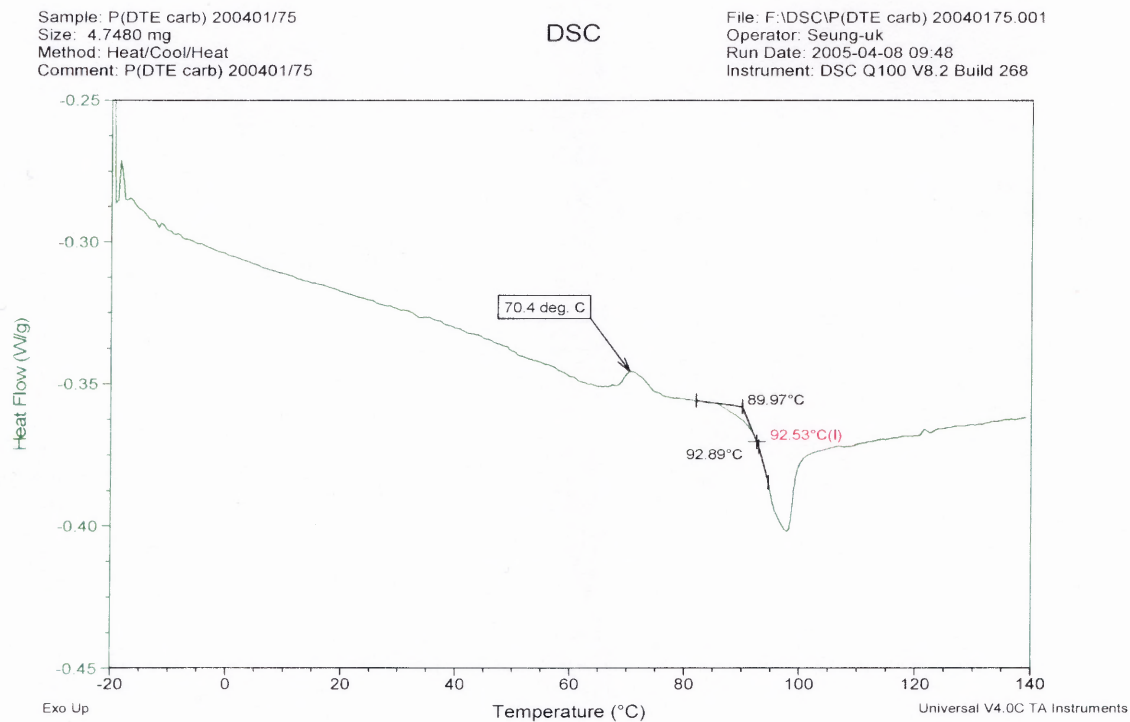
### RESULTS

#### 4.1 Thermal Analysis

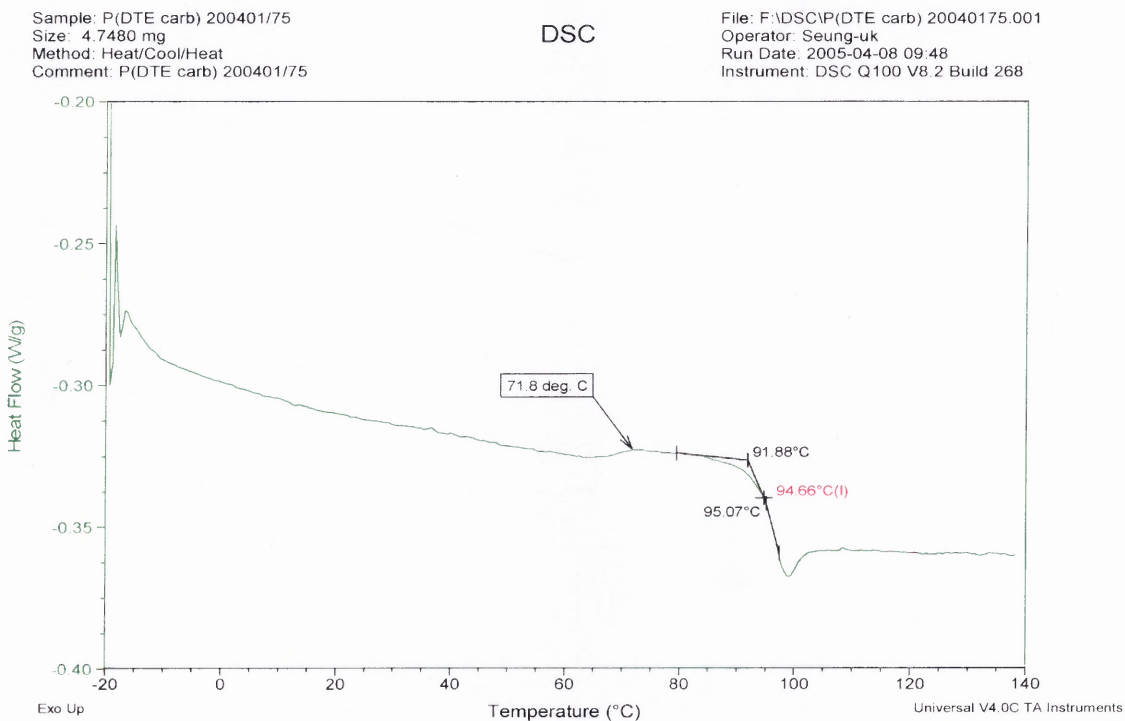
The thermal analysis data for the blends of DTE with P(LcoDL)LA, PLGA, and PLLA are analyzed. From the results it is evident that reproducibility is an issue with the blends formed. From the two batches of films that were cast, the DSC data shows that the blends made of PLLA are more consistent in results obtained. TGA results show significant weight loss at 150 °C point for the blends with P(LcoDL)LA. The thermally stimulated current results for poly(DTE) carbonate and P(LcoDL)LA show that the two components have complex behavior when heated.

##### 4.1.1 Pure Polymer Films DSC Results

Poly(DTE) carbonate is an amorphous polymer that has a glass transition of about 95 °C [20]. Before poly(DTE) carbonate is solvent cast, the powder form is analyzed by DSC. In Figure 4.1 of the first heating, a thermal event similar to a small exothermic peak around 70 °C is observed followed by a glass transition around 92 °C. In the second heating, the thermal event at the 70 °C temperature was not as pronounced and the T<sub>g</sub> determined is 94.6 °C [Figure 4.2].

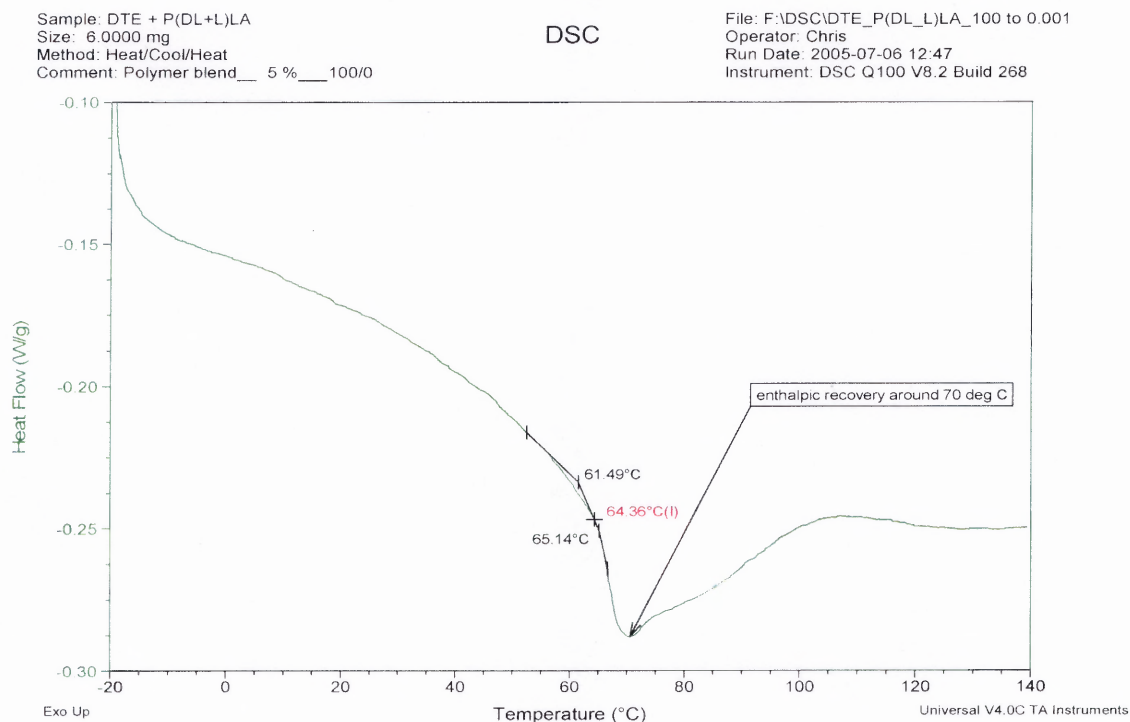


**Figure 4.1** Plot of the first heating of 100 % Poly(DTE) carbonate powder.



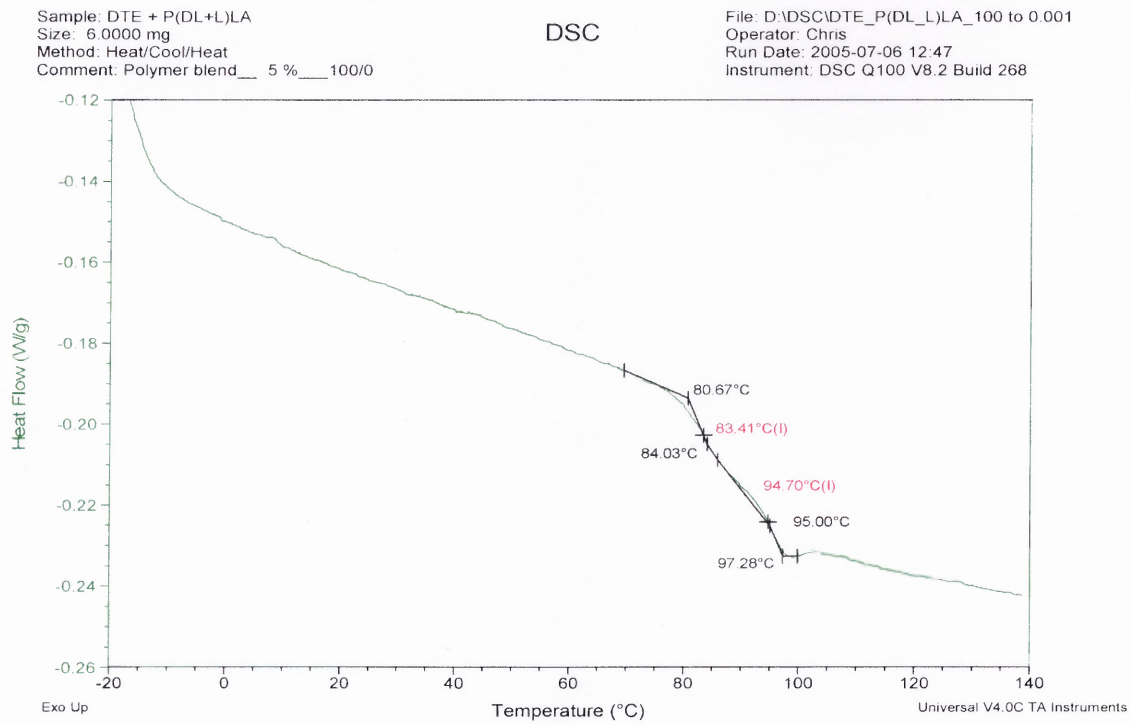
**Figure 4.2** Plot of the second heating of 100 % Poly(DTE) carbonate powder.

For figure 4.3 the first heating cycle for the solvent cast film was analyze using the DSC and an event resembling an enthalpic recovery process is observed at the 70 °C temperature position. The position where the T<sub>g</sub> occur is lower than what is observed for the powder form.



**Figure 4.3** Plot of first heating for the 100% poly(DTE) carbonate film showing the T<sub>g</sub> around 64 °C and an enthalpic recovery process around 70 °C.

In figure 4.4 of the second heating of the 100% solvent cast Poly(DTE) carbonate film the thermal event at 70 °C temperature is not present. However, there seem to be two thermal events, around 84.3 °C and 94.7 °C at the temperature location where the glass transition is determined.



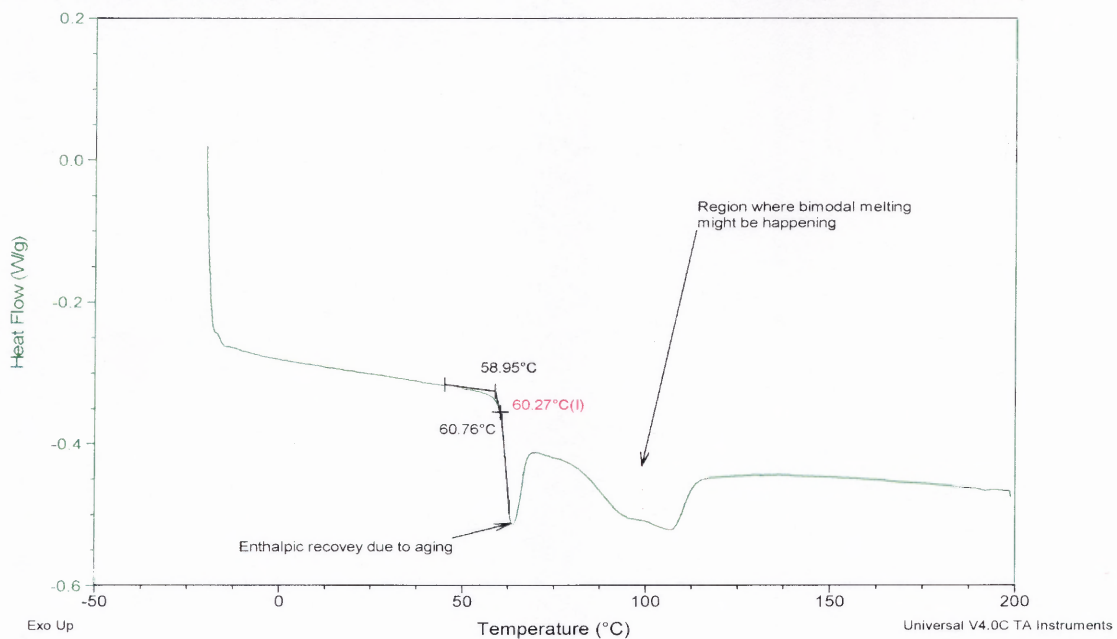
**Figure 4.4** Plot of the second heating for the 100 % Poly(DTE) carbonate film with the two thermal events.

In figure 4.5 for the first heating for P(LcoDL)LA pellets show complexities in the thermal events happening. There is a glass transition temperature followed by an enthalpic recovery as a result of aging. The polymer also shows a region where there seems to be some form of bimodal melting occurring.

Sample: P(L-lac-co-D,L-lac) osteotech  
Size: 9.8370 mg  
Method: Heat/Cool/Heat  
Comment: P(L-lac-co-D,L-lac) osteotech H,C 10C/min from -20 to 200

DSC

File: F:\DSC\IP(L-lac-co-D,L-lac) osteotech.001  
Operator: Seung-uk  
Run Date: 2005-06-02 14:05  
Instrument: DSC Q100 V8.2 Build 268



**Figure 4.5** The first heating cycle for P(LcoDL)LA pellets using DSC analysis.

Figure 4.6 shows the  $T_g$  determined from the second heating cycle for the P(LcoDL)LA pellets before it is solvent cast. The  $T_g$  determined is about 57 °C and the complex region was erased.

File: F:\DSC\IP(L-lac-co-D,L-lac) osteotech.001  
Operator: Seung-uk  
Run Date: 2005-06-02 14:05  
Instrument: DSC Q100 V8.2 Build 268

Sample: P(L-lac-co-D,L-lac) osteotech  
Size: 9.8370 mg  
Method: Heat/Cool/Heat  
Comment: P(L-lac-co-D,L-lac) osteotech H.C. 10C/min from -20 to 200

DSC

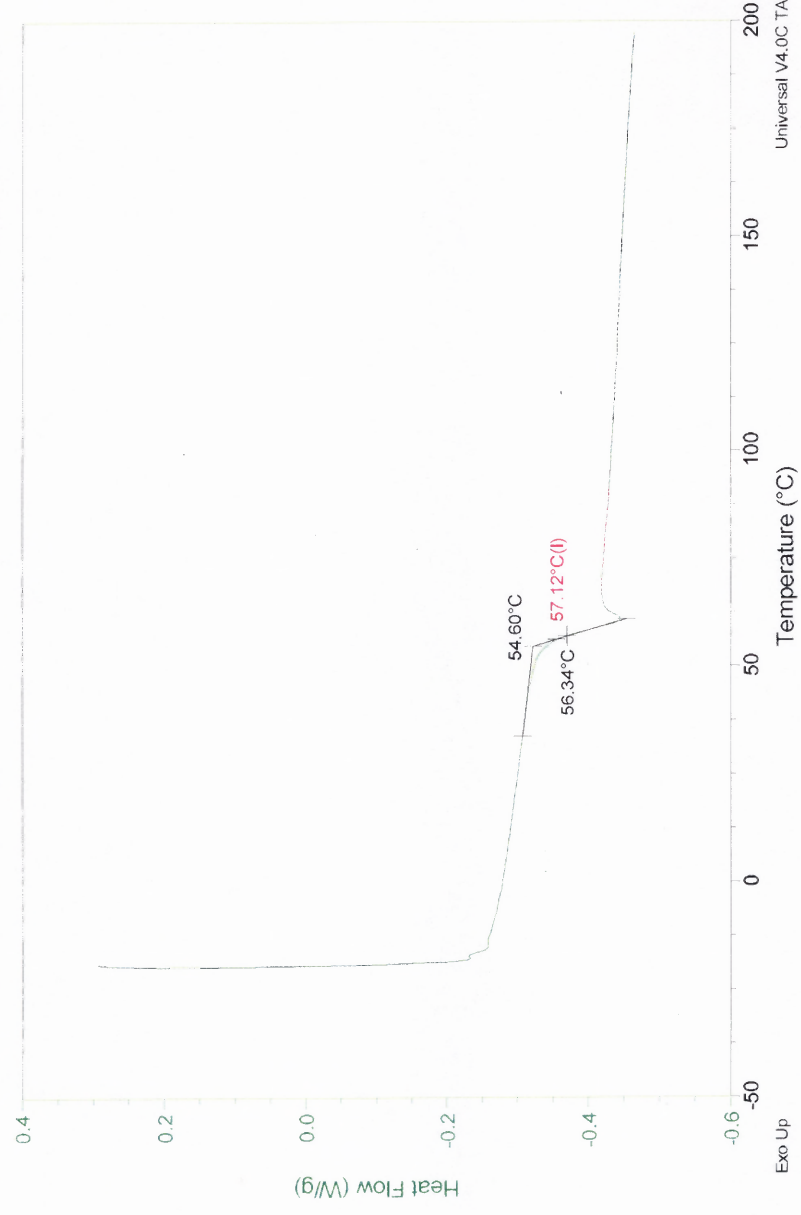
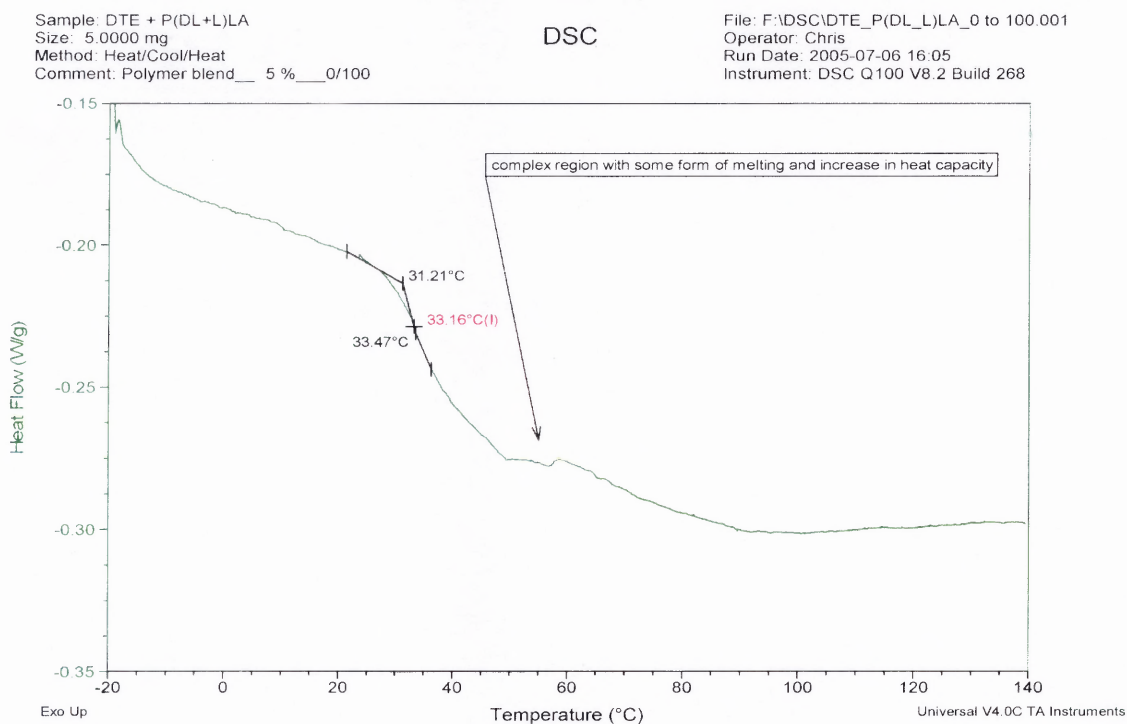


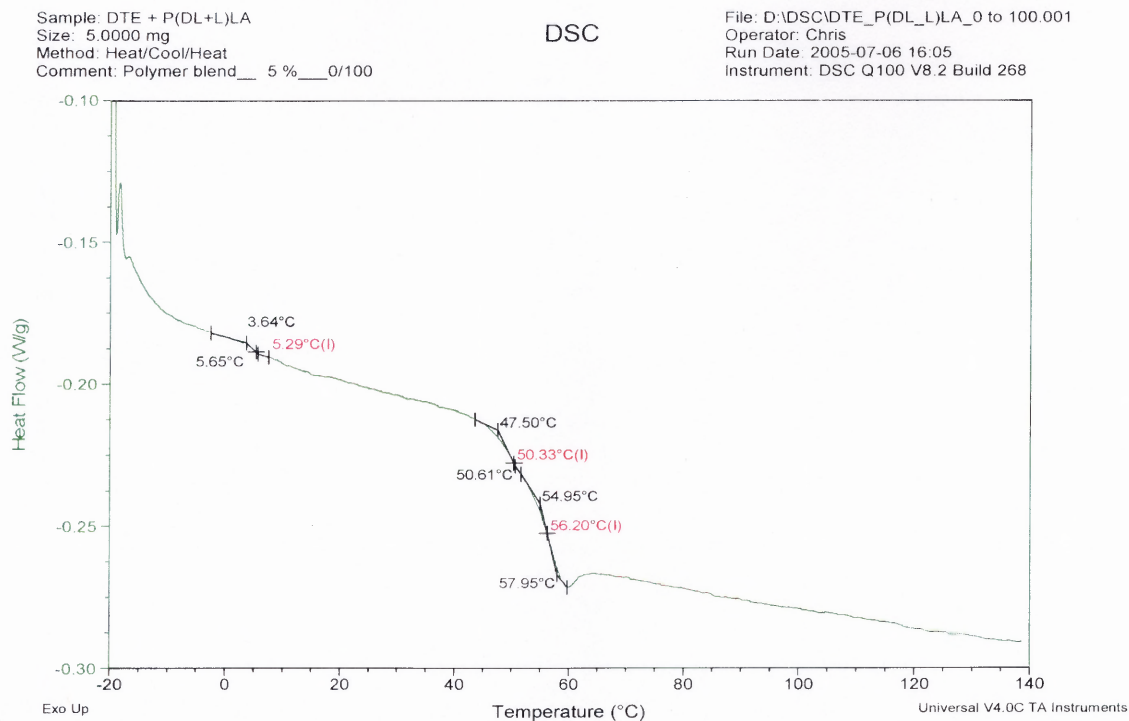
Figure 4.6 Plot of Tg for the second heating of 100% P(LcoDL)LA pellets.

When the pellets were solvent cast film and analyzed using the DSC method a number of events are determined. A representation of the processes are shown in Figure 4.7 for the first heating of the P(LcoDL)LA film. A glass transition occurred around 33 °C followed by a complex region where there seem to be some form of melting of the material, followed by an increase in heat capacity within the material.



**Figure 4.7** DSC analysis of the first heating of the P(LcoDL)LA film.

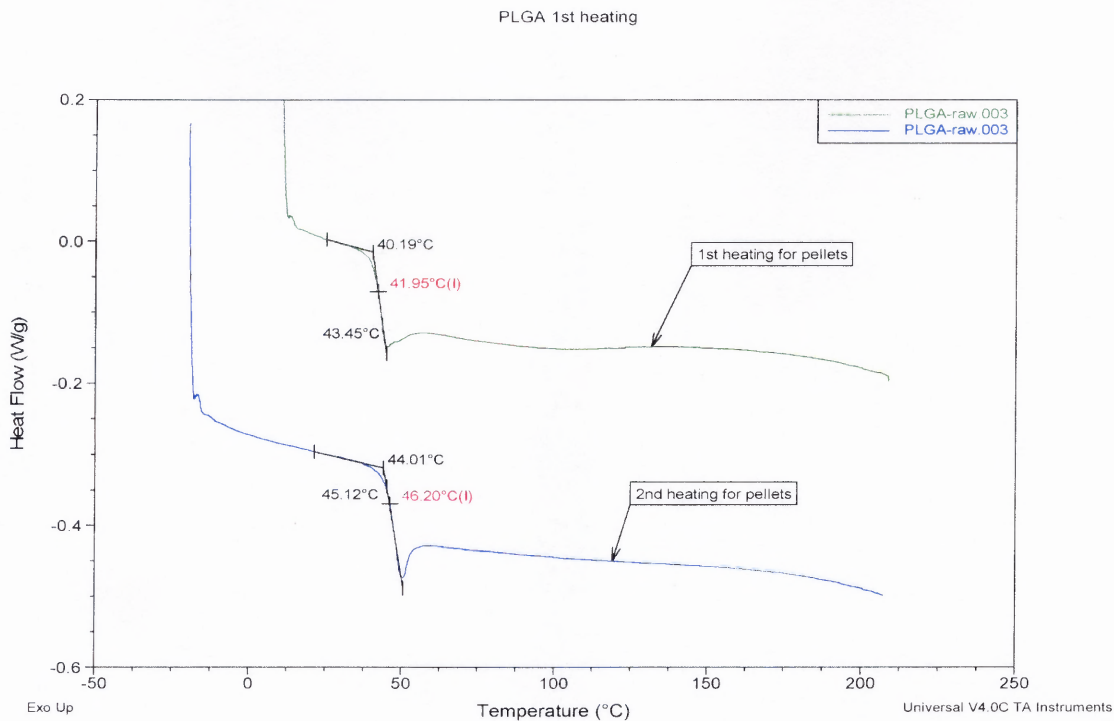
The second heating for the P(LcoDL)LA solvent cast film showed two events at 50 and 56 °C and also at 5 °C thermal activity was detected [Figure 4.8].



**Figure 4.8** Plot of T<sub>g</sub> of 100 % P(LcoDL)LA film, second heating of film.

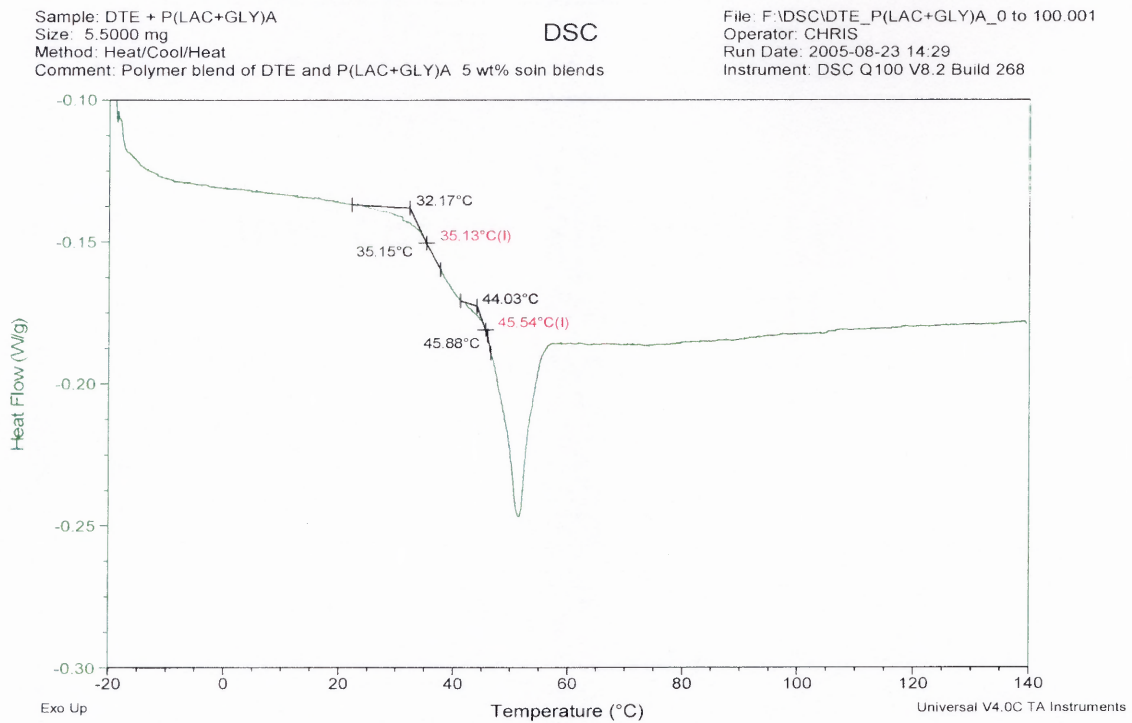
Figure 4.9 is a typical representation the first and second heating for the PLGA pellets. The difference between the T<sub>g</sub> for the two runs is minimal. No significant differences is observed for both runs.





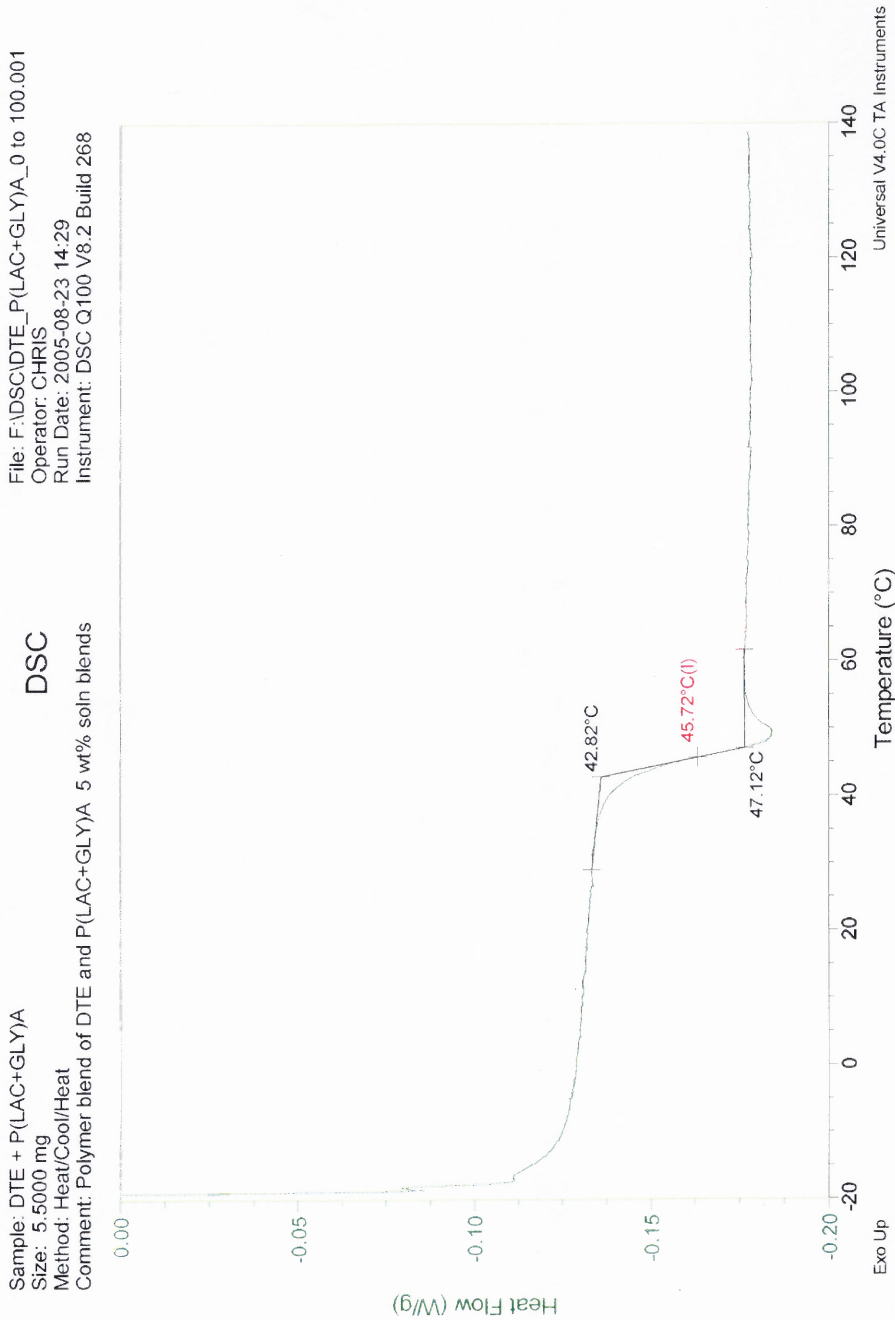
**Figure 4.9** DSC thermograph for the first and second heating of the PLGA pellets. Courtesy of Shobana Shanmugasunderam Ph.D Candidate, MDCL Medical Laboratory, New Jersey Institute of Technology.

Figure 4.10 and 4.11 represent the thermographs of the first and second heating of 100% PLGA film. For Figure 4.10, the first heating two thermal events occurred around 35 and 45°C, respectively. The pellet form of the polymer is composed of 75% lactide and 25% glycolide. The two events observed in the first heating of the solvent cast film could be a result of the polymer phase into its component polymers. An enthalpic recovery peak is also observed around 50 °C.



**Figure 4.10** DSC analysis for the first heating of PLGA solvent cast film.

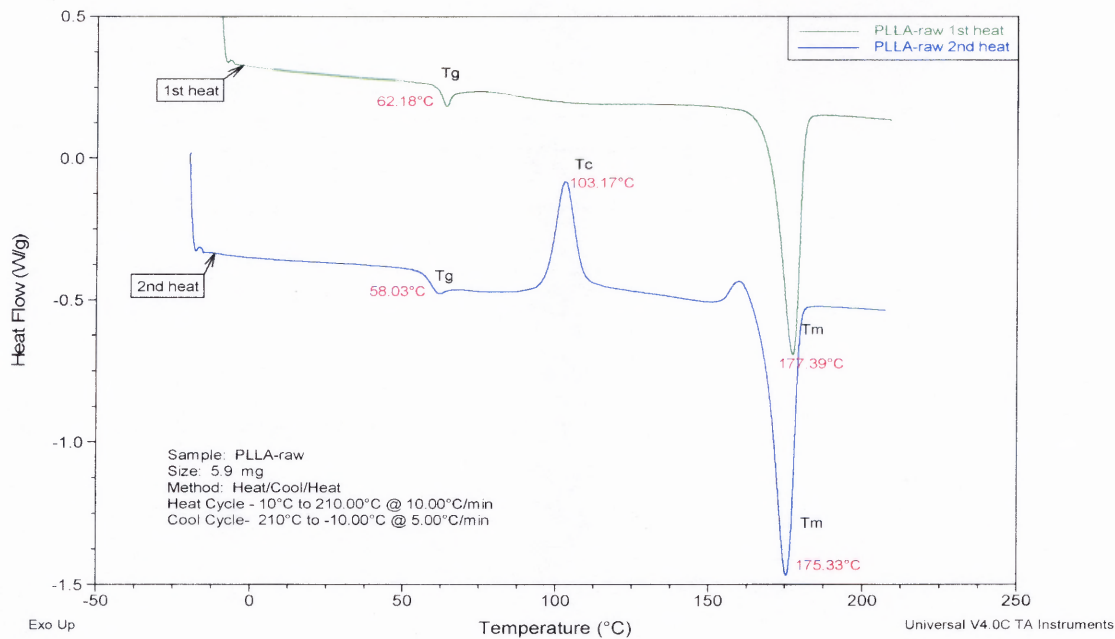
The second heating had a smooth curve with only one T<sub>g</sub> present at 45.7 °C and a decrease in the heat capacity observed at the enthalpic recovery point.



**Figure 4.11** Plot of the T<sub>g</sub> of the 100 % PLGA film, second heating.

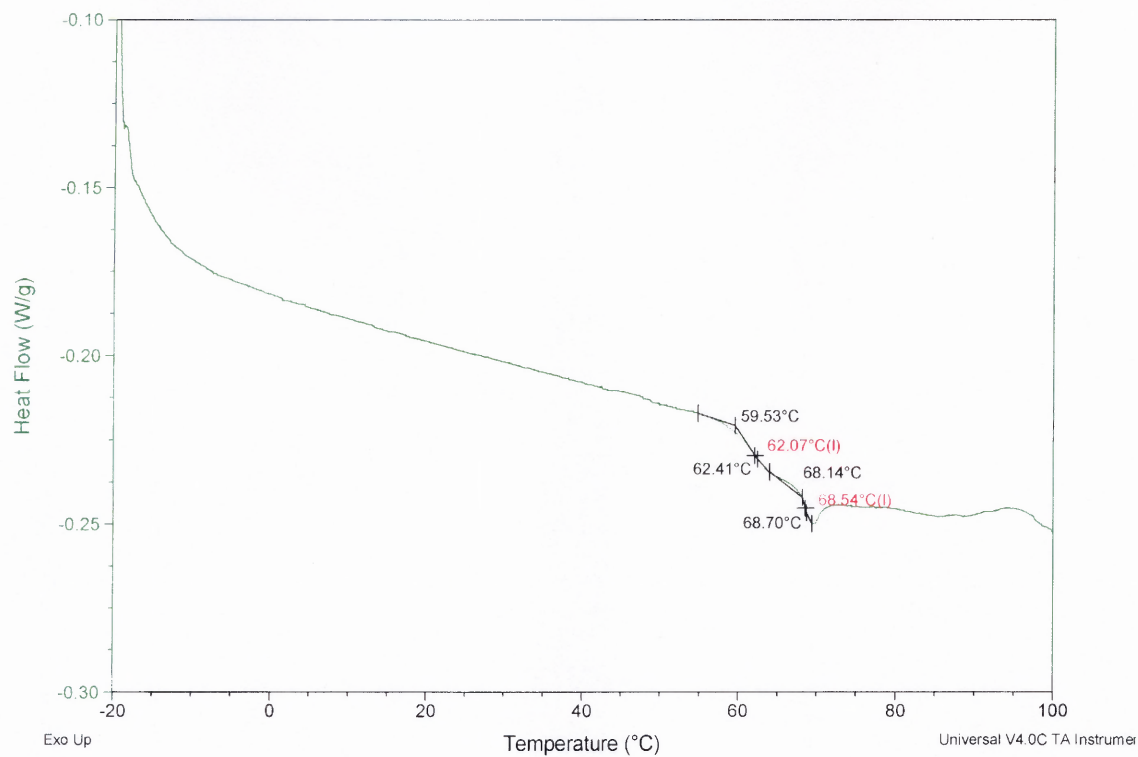
A typical plot of the PLLA pellets is shown in figure 4.12 below. For the first heating the T<sub>g</sub> is around 62 °C and the melting temperature is around 177 °C. A similar

curve is observed for the second heating except, an increase in heat capacity is observed around 103 °C signifying the material has gone through an cold crystallization process.



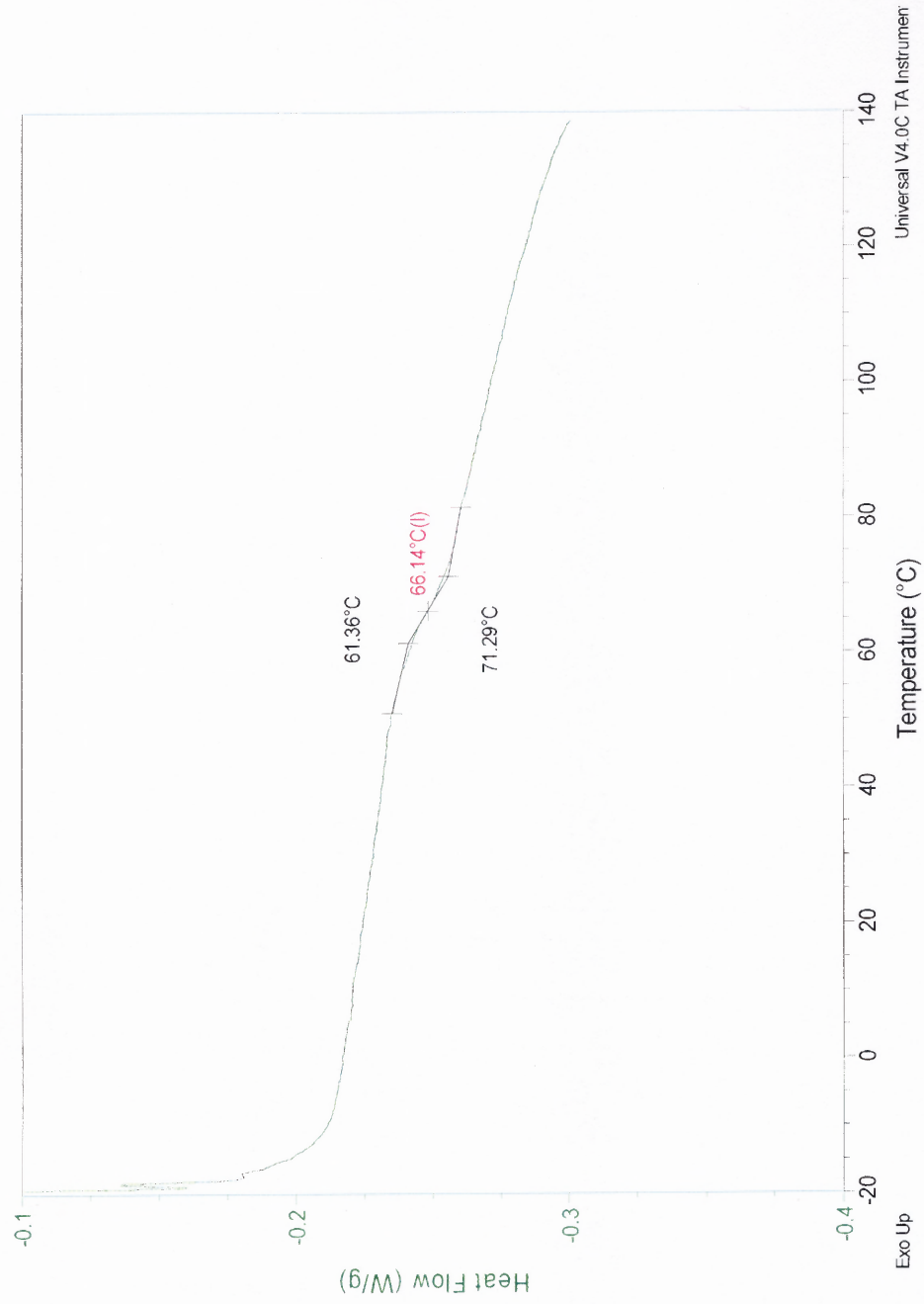
**Figure 4.12** DSC thermograph for the first and second heating of the PLLA pellets. Courtesy of Shobana Shanmukasunderam, Ph.D Candidate, MDCL Medical Laboratory, New Jersey Institute of Technology.

For Figure 4.13, the first cycle for the PLLA films showed evidence of phase separation with two events at 62 °C and 68 °C. An enthalpic recovery process is observed after 68 °C.



**Figure 4.13** DSC thermograph of the first heating of PLLA solvent cast film.

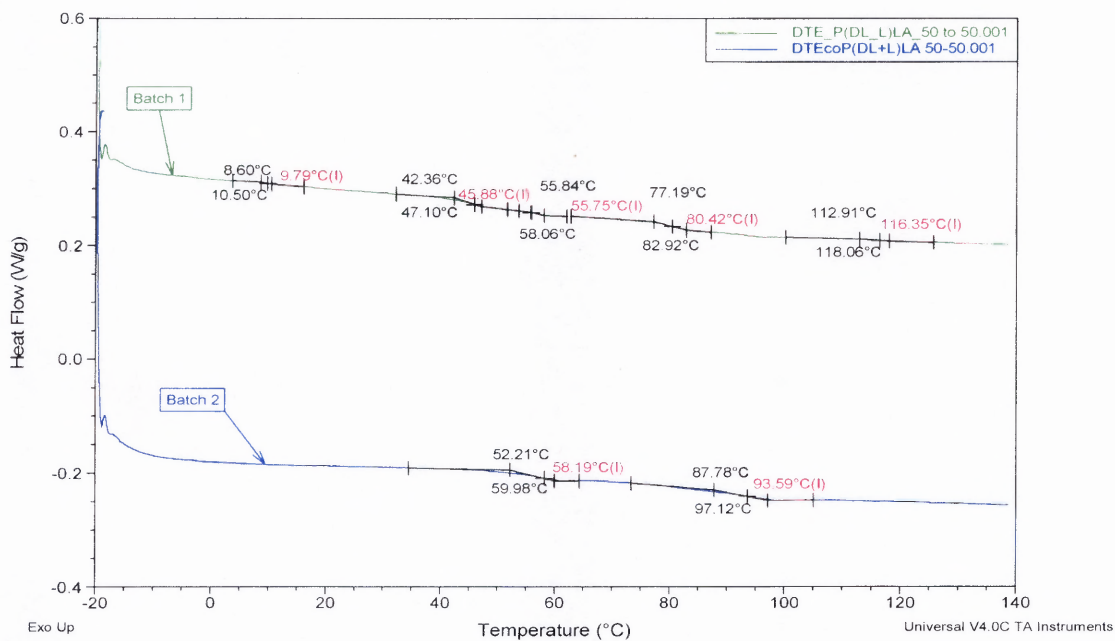
When the second heating of the PLLA solvent cast film, represented in Figure 4.14 is analyzed, only one event is observed at 65 °C and the enthalpic peak is not present.



**Figure 4.14** Plot of Tg of 100 % PLLA film second heating

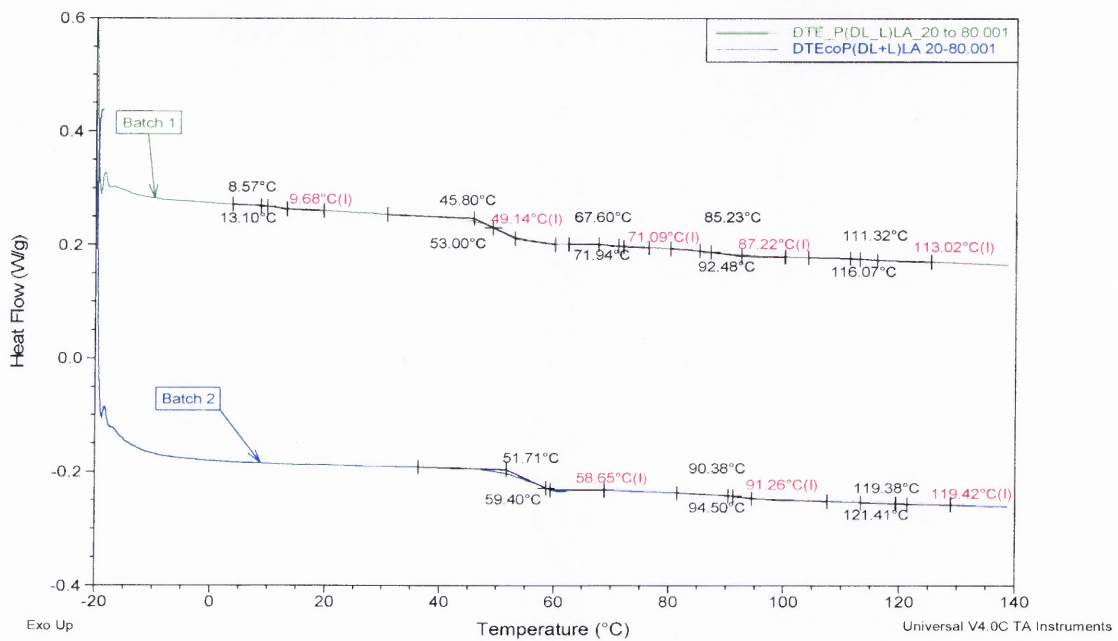
#### 4.1.2 DSC Results for Polymer Blends

From visibly inspecting the films of the blends formed, it is obvious that there is phase separation within the films. The films show opaque and more transparent regions. The DSC results are consistent with thermal events as shown in figure 4.15 for batch 1 of a 50-50 blend of poly(DTE) carbonate blended with P(LcoDL)LA.



**Figure 4.15** Graph depicting the multiple thermal events identifiable for batch 1 of the Poly(DTE) carbonate and P(LcoDL)LA blend.

To assess the reproducibility of the thermal events observed a second batch was made for each polymer combination with Poly(DTE) carbonate and the DSC results are compared. An example of that comparison is also shown in figure 4.16 for batch 1 and batch 2 of 20-80 blends of poly(DTE) carbonate and P(LcoDL)LA.



**Figure 4.16** DSC results comparing the thermal events of batch 1 and batch 2 of poly(DTE) carbonate blended with P(LcoDL)LA.

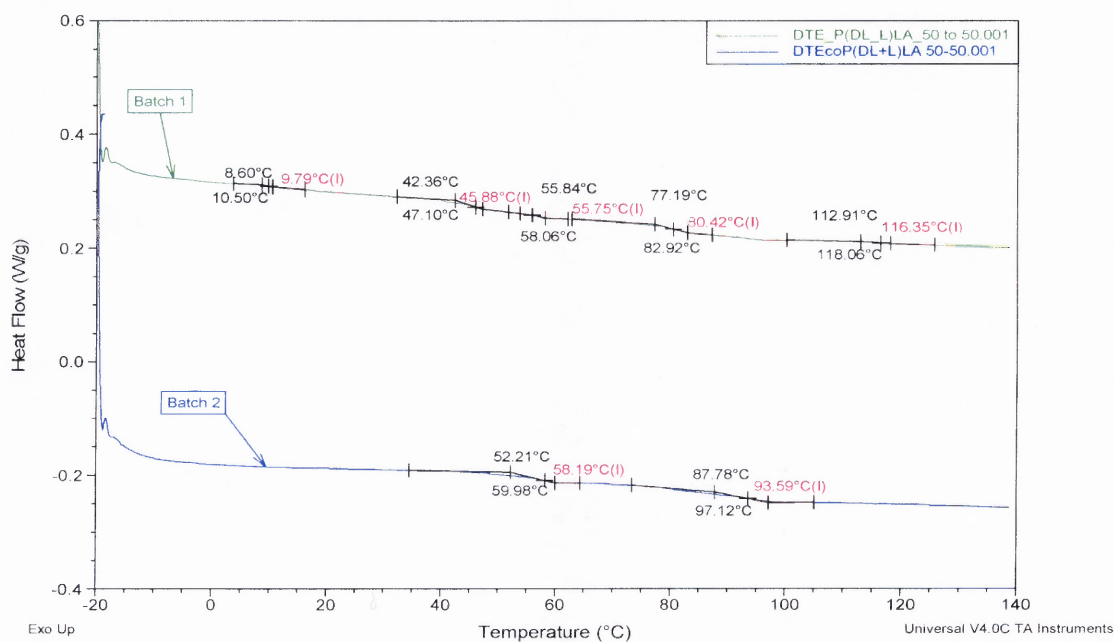
The DSC results indicate that it is difficult to achieve reproducibility in most of the DSC results for these blends. Similar experiments are run on other blend composition and the DSC results are summarized in table 4.1.



**Table 4.1** Compared DSC Results for Different Blend Components

	RATIO	BATCH 1					BATCH 2					
		Apparent "Tg's" °C					Apparent "Tg's" °C					
<b>DTE</b> + <b>P(LcoDL)LA</b>	100:0	83.4			94.7		NA					
	80:20	9.4		57.7		94.8		56.9	95.5	119.5		
	60:40	58.6			92.5			56	93	109.2		
	50:50	9.8	45.9		55.8	80.4	116.4		58.2	93.6		
	40:60	10.6		42.4		79.3		107.8		23.5	58.6	92.8
	20:80	9.7	49.1		71.1	87.2	113		58.7	91.3	119.4	
	0:100	5.3		50.3		56.2		NA				
<b>DTE</b> + <b>PLGA</b>	80:20	20.9	50.1	93.9	112.6		46.5	78.8	119			
	60:40	49.7		91.2		115.3		45.2		79.1		
	50:50	48.9			91.2			45.9	77.1	108.2		
	40:60	48.3		60.9		90		47.4		83.6		
	20:80	48.9			88.7			40		78.9		
	0:100	45.8					NA					
<b>DTE</b> + <b>PLLA</b>	80:20	48.9		92.4		119.9		46.8	93.7	115.6		
	60:40	38.2		67.8		95.1		69.8	94.2	112.7		
	50:50	19.7	62.8	92.7	114		25.5	64.1	90.2	127.2		
	40:60	20.8	71.4	94.5		114		24	65.1	94.5	120	
	20:80	29	67.9	95.5	114.7		26	70.7	96.0	122		
	0:100	65.7					NA					

The results presented in the table show that the P(LcoDL)LA and PLGA blends, prepared by solvent mixing are not as reproducible as those prepared with PLLA. For some of the blends it is hard to determine consistent thermal properties of the material. That is, in some cases when films of the same blend ratios are compared using the DSC result; the number of thermal events present varies. For example in figure 4.17 poly(DTE) carbonate blended with P(LcoDL)LA (50:50) shows that for the films of the two batches, the number of thermal events is not the same: For batch 1 five thermal events within the experiment is determined and for batch 2 only two are identifiable.



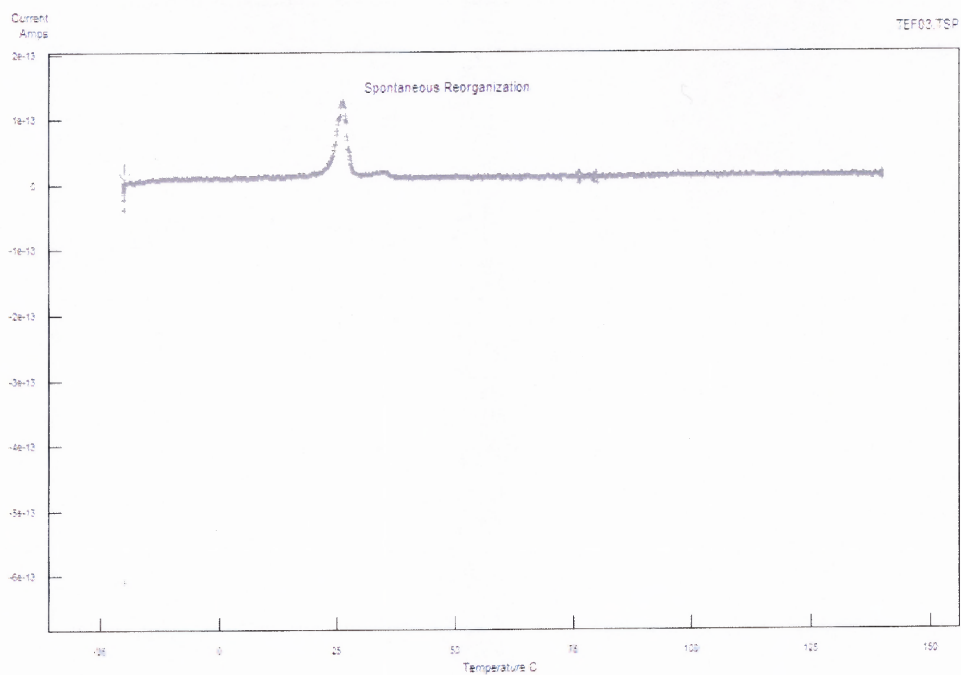
**Figure 4.17** Graph depicting the difference in number of thermal events identifiable for same blend ratio two different samples of Poly(DTE) carbonate and P(LcoDL)LA.

For poly(DTE) carbonate blended with PLGA it is also possible from visual inspection that the films formed from these two components are not miscible with each other. Circular agglomerates are evident. For some of the blends made of poly(DTE) carbonate and the PLGA, the apparent inter phase adhesion is so weak that portions of the films break off when they are being removed from the aluminum pan and no coherent film could be attained.

The DSC results for the separate batches of Poly(DTE) carbonate with P(LcoDL)LA and PLGA polymers are not consistent. The numbers of events taking place within the films are not the same when the two batches are compared. In addition, the temperature positions of the events are in most cases not similar. For example the "Tgs" for Poly(DTE) carbonate blended with PLGA (80:20) films are 20.9 °C, 50.1 °C, 93.9 °C, and 112.6 °C, respectively for batch 1 and for the second batch with the same ratio they are 46.5 °C and 78.8 °C, and 119 °C, respectively [Table 1].

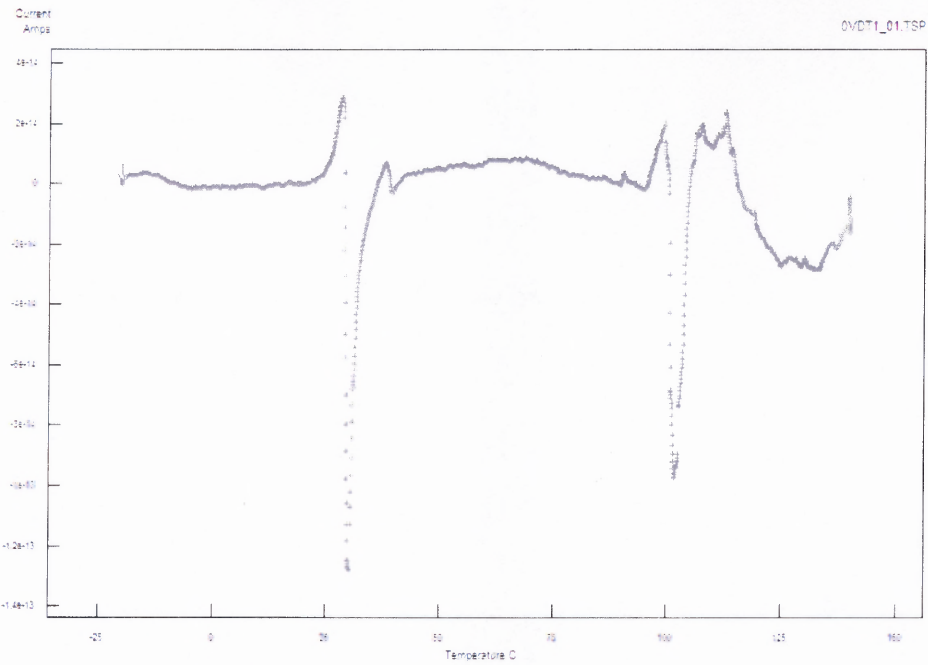
#### **4.1.3 TSC Results for Blend Components**

The results for poly(DTE) carbonate and P(LcoDL)LA were determined using both TSPC and TSDC methods. The experiment was run using the TSPC method in the absence of the electric field to see the activity of the material. Before any test was done on the two blend components, the behavior of the Teflon film was determined. Figure 4.18 represents the temperature position where activity is observed for the Teflon film when the TSPC method was employed.

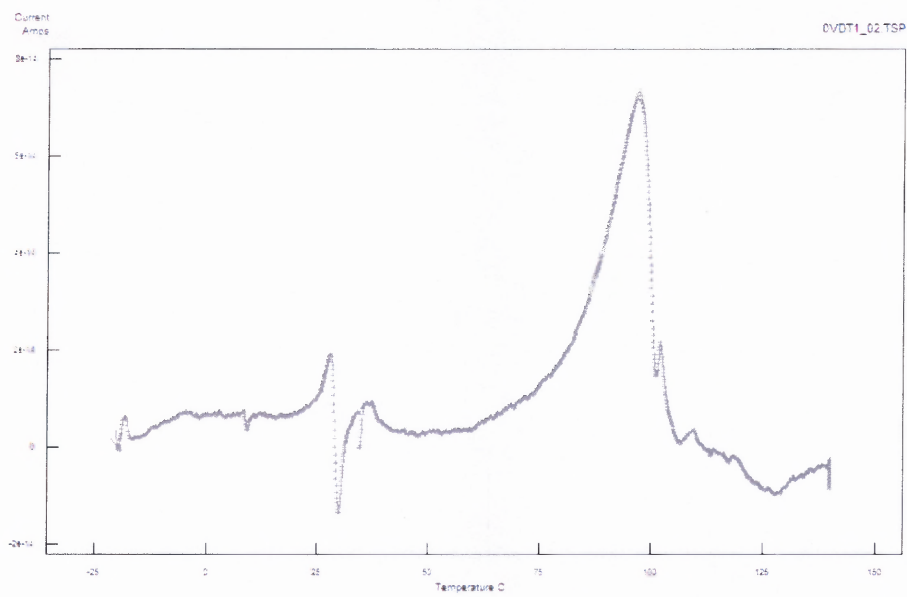


**Figure 4.18** TSPC analysis of the Teflon film.

Figures 4.19 and 4.20 represent the events occurring with poly(DTE) carbonate as the material is heated from  $-20$  °C to  $140$  °C. As the same film was reheated, a difference in the pattern of thermal events was observed.

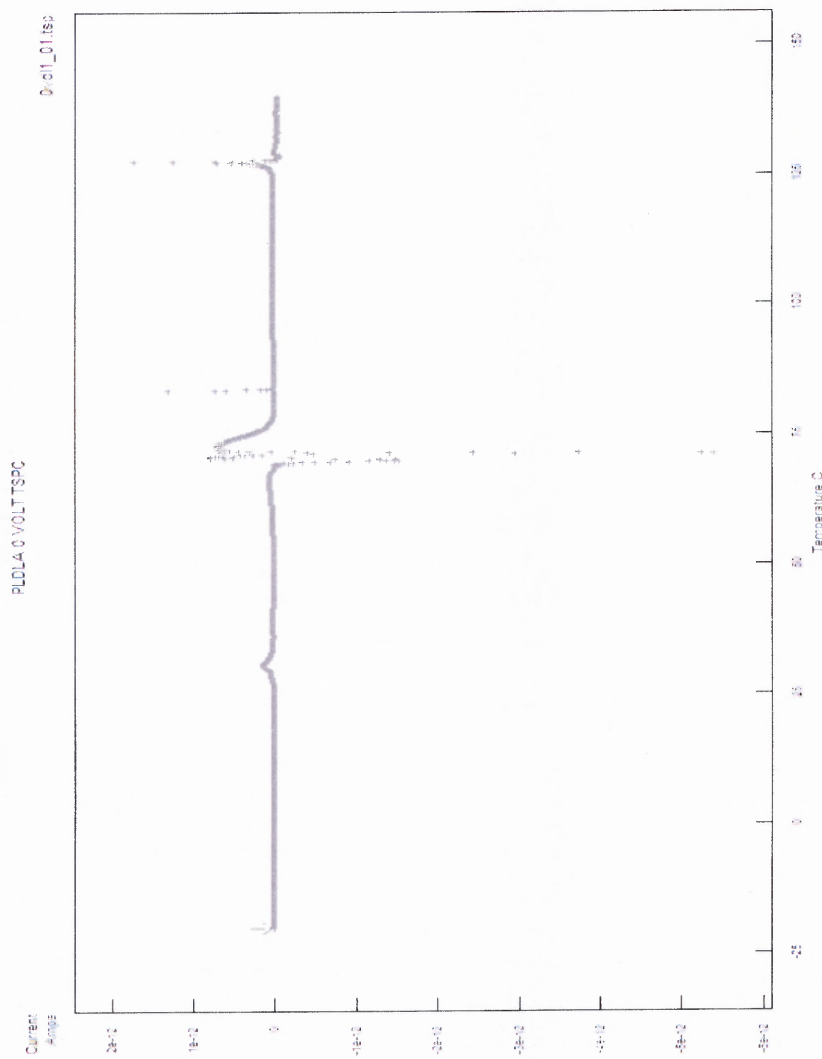


**Figure 4.19** TSPC analysis of the first heating of poly(DTE) carbonate with no electric field



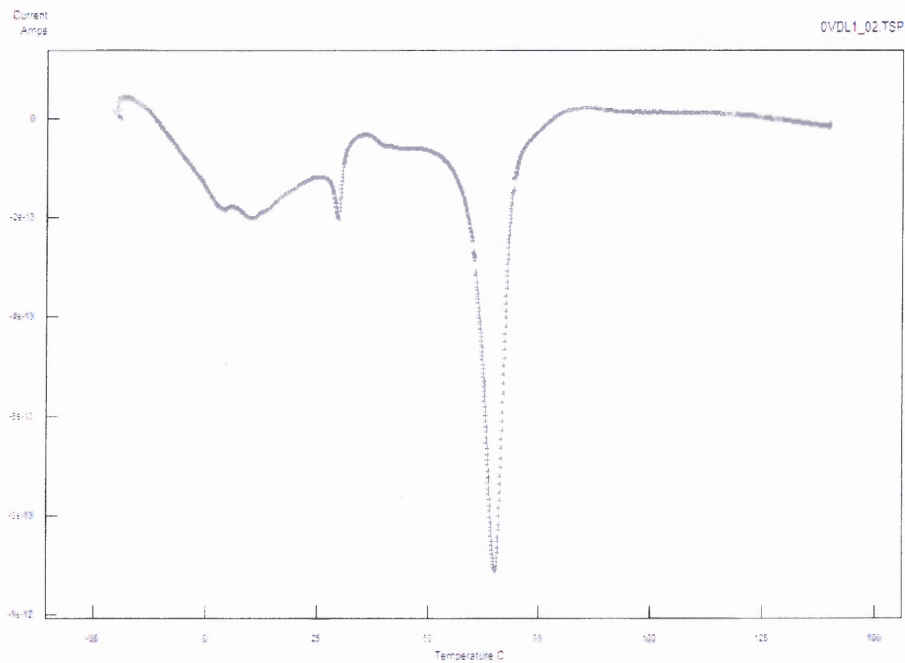
**Figure 4.20** TSPC analyses for the second heating of poly(DTE) carbonate with no field.

The same experiment was run for P(LcoDL)LA and the results are represented in figures 4.21 and 4.22 below.



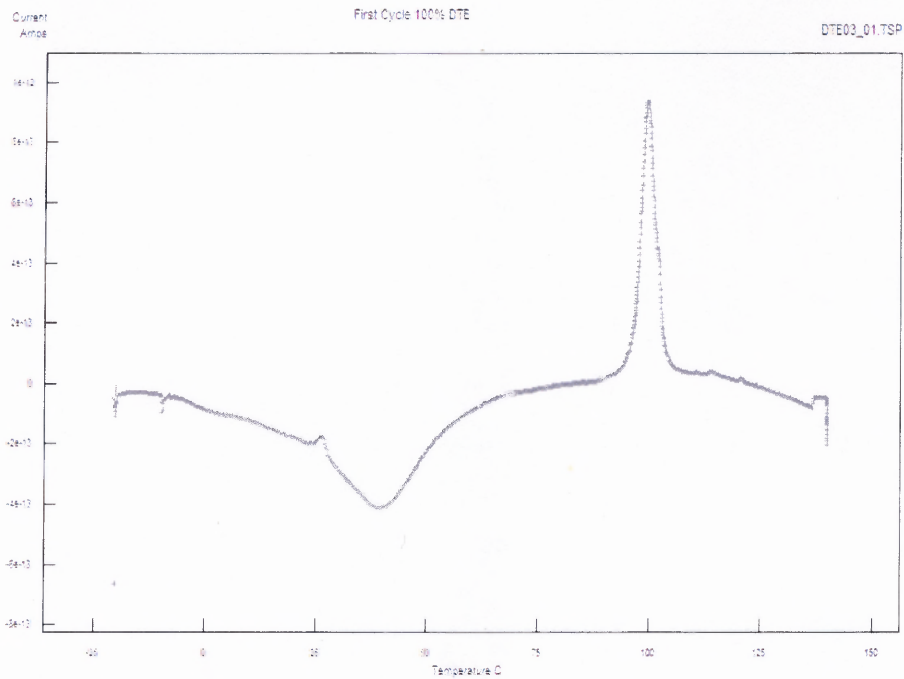
**Figure 4.21** TSPC analysis for the first heating of P(LcoDL)LA with no electric field.

Figure 4.22 below also shows dissimilarities in thermal behavior for the P(LcoDL)LA film.



**Figure 4.22** TSPC analysis for the second heating of P(LcoDL)LA with no electric field.

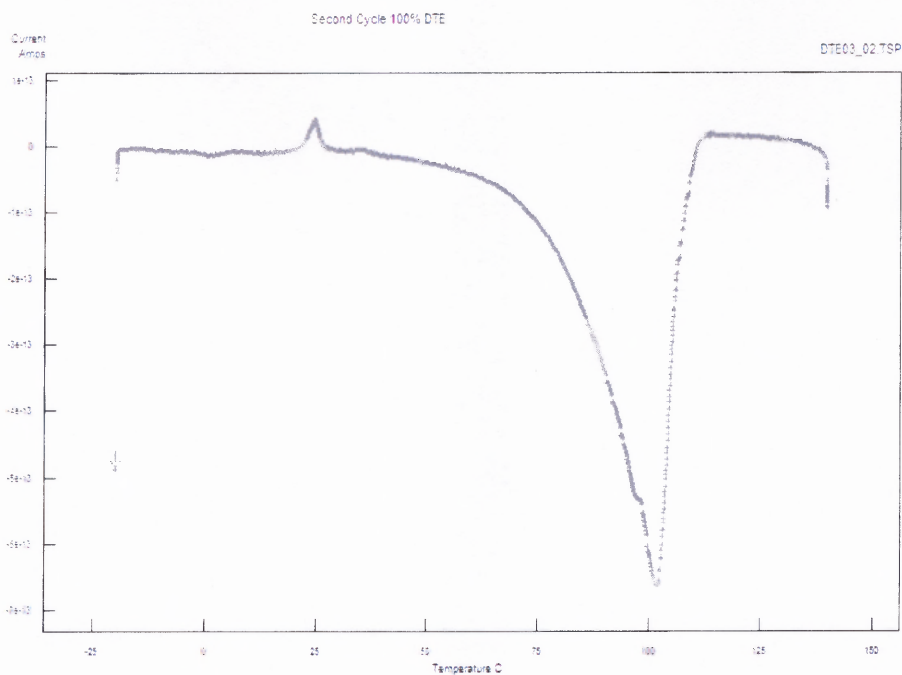
The material was then exposed to an electric field and the results generated for poly(DTE) carbonate and P(LcoDL)LA are represented in figures 4.23-4.26.



**Figure 4.23** TSPC analyses for the first heating of poly(DTE) carbonate with an electric field.

When the second heating of the material was analyzed, the thermal activities generated as a result of the polymer being exposed to heat are not similar with the first heating of the material. In figure 4.24 a significant change in the behavior of the polymer is seen around 100 °C. There is also a difference in the direction of peak observed around 100 °C when the material is heated a second time.



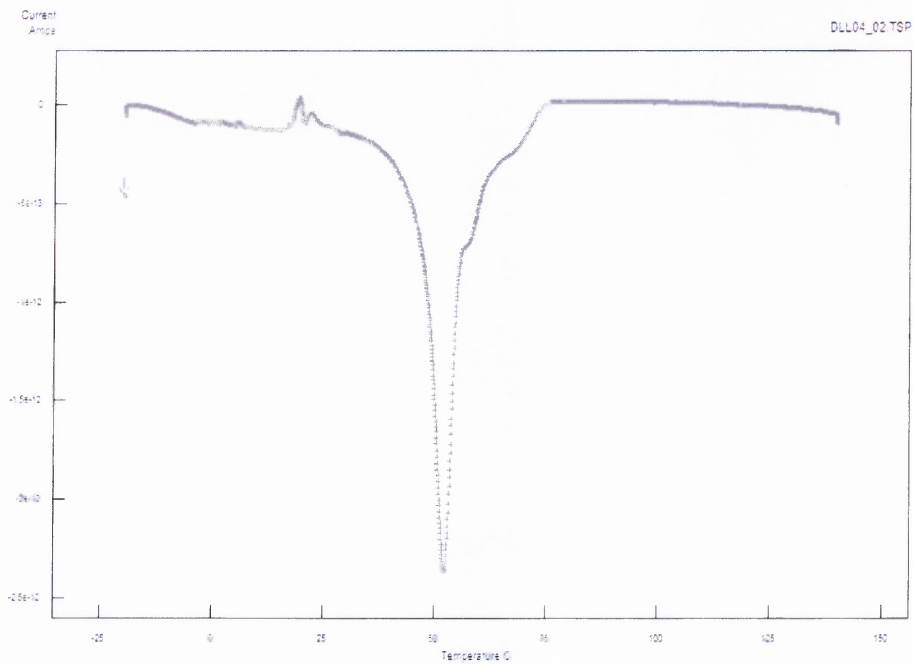


**Figure 4.24** TSPC analyses for the second heating of poly(DTE) carbonate with an electric field.

In figure 4.25 and 4.26 difference in behavior is also observed for the copolymer P(LcoDL)LA. In figure 4.25 complexities are observed between 25 °C and 100 °C. The pattern of the thermal events is different and opposite direction of the peaks is also observed for the material after it is reheated.

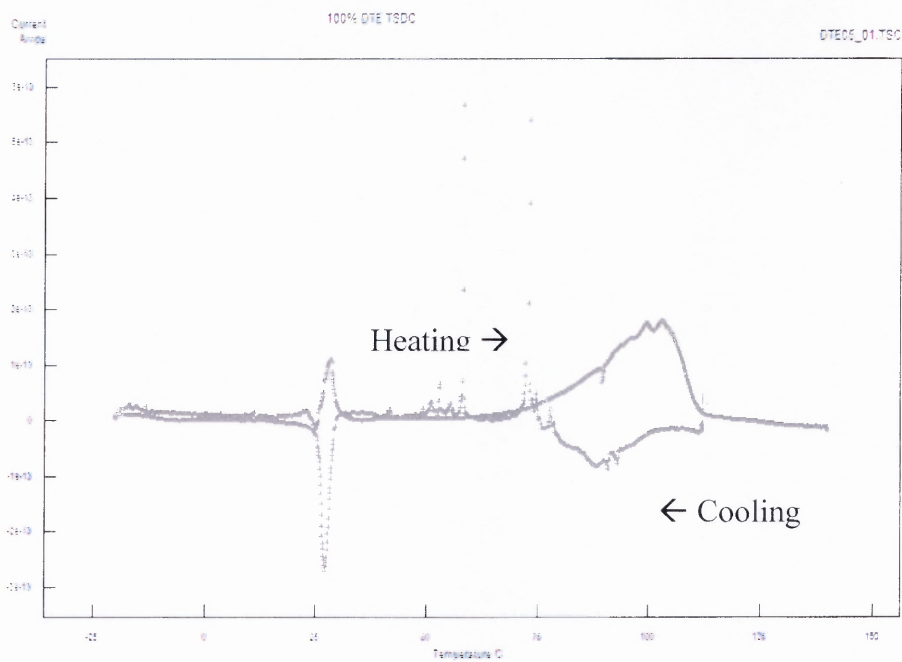


**Figure 4.25** TSPC analysis for the first heating of P(LcoDL)LA with an electric field.



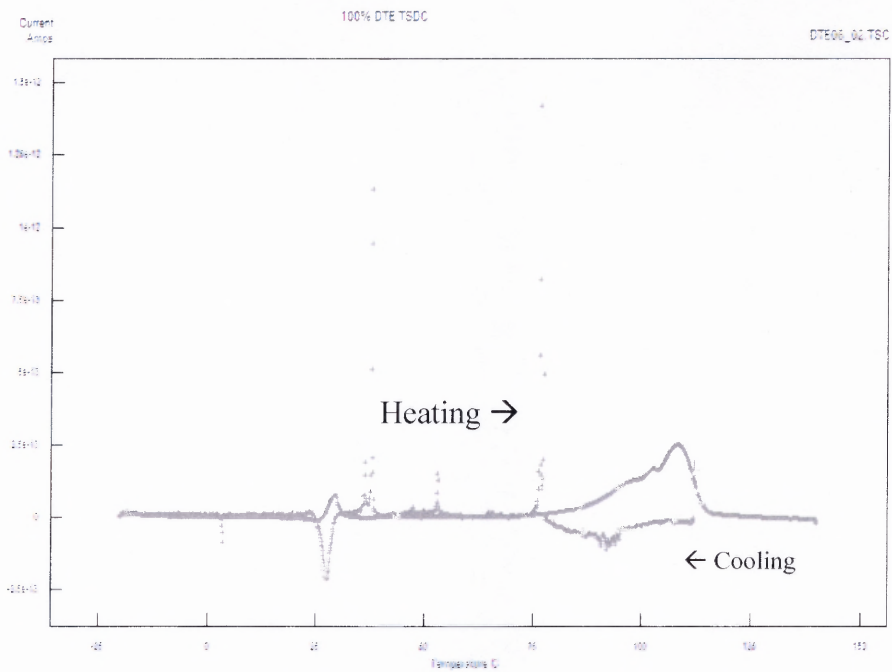
**Figure 4.26** TSPC analysis for the second heating of P(LcoDL)LA with an electric field.

The results from the TSPC analysis are not conclusive in determining the thermal events taking place within the materials. In trying to understand what is taking place within the polymer, the TSDC method was used. The polar groups of the polymer film were aligned and the temperature lowered so the material is in a state where the kinetic energy is low enough for the polar groups to become immobile. The temperature position where current was generated was obtained. The following figures also show the complexities in the behavior for poly(DTE) carbonate and P(LcoDL)LA. In figure 4.27 the generation of current begins for the poly(DTE) carbonate film between 75 and 100 °C while the material is exposed to an electric field and is being cooled.



**Figure 4.27** Modified TSDC analysis of poly(DTE) carbonate.

In figure 4.28 there is also motion between 75 °C and around 100 °C for the cooling phase of the test when same poly(DTE) carbonate film is tested a second time. The temperature positions where the events are happening are similar to the first test done for the material.



**Figure 4.28** Modified TSDC analysis of poly(DTE) carbonate second test.

The response to the TSDC test for P(LcoDL)LA is similar to poly(DTE) carbonate. Both produce thermal behaviors that are not readily explained. Like poly(DTE) carbonate, P(LcoDL)LA thermal peaks patterns and the positions where they occur are similar for both times ran. Figure 4.29 represents the first time that P(LcoDDL)LA is tested. Significant thermal activities are observed between  $-20\text{ }^{\circ}\text{C}$  and  $75\text{ }^{\circ}\text{C}$  during the cooling cycle. Thermal peaks in either direction relative to the ordinate are observed. In Figure 4.30 the behavior of the film is similar when the same piece of film is tested a second time.

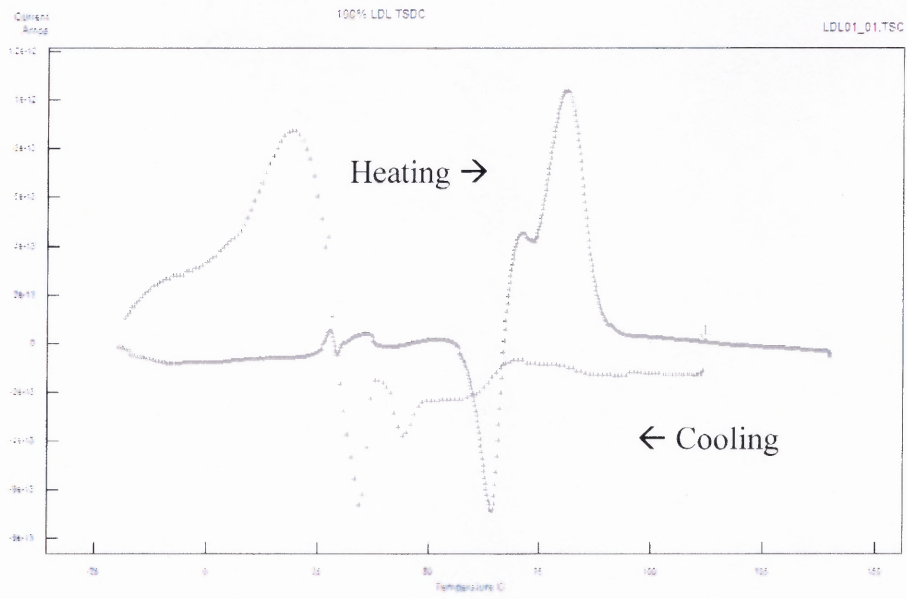


Figure 4.29 Modified TSDC analysis of the first run of P(LcoDL)LA film.

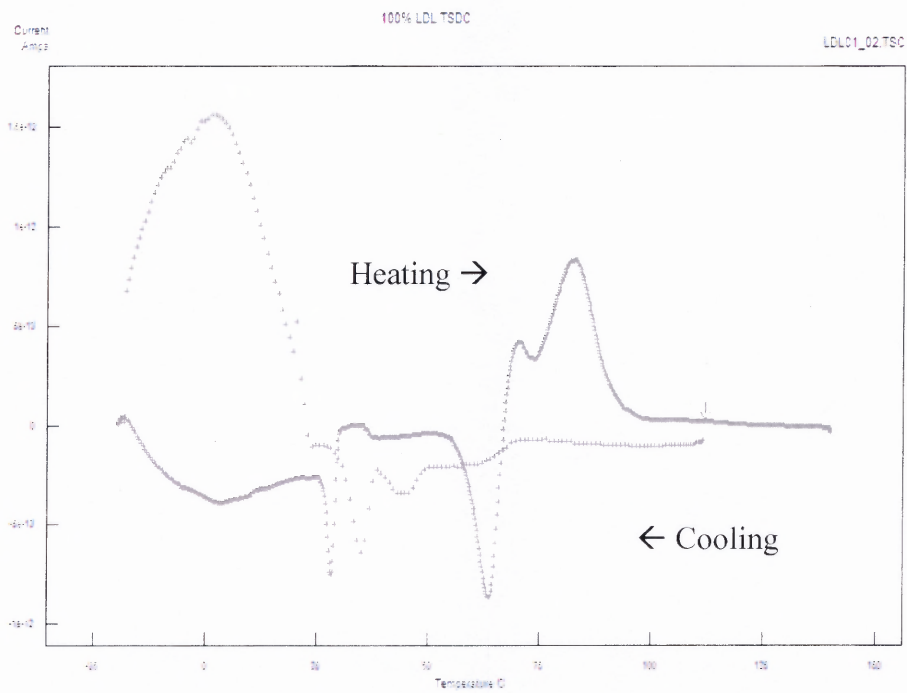
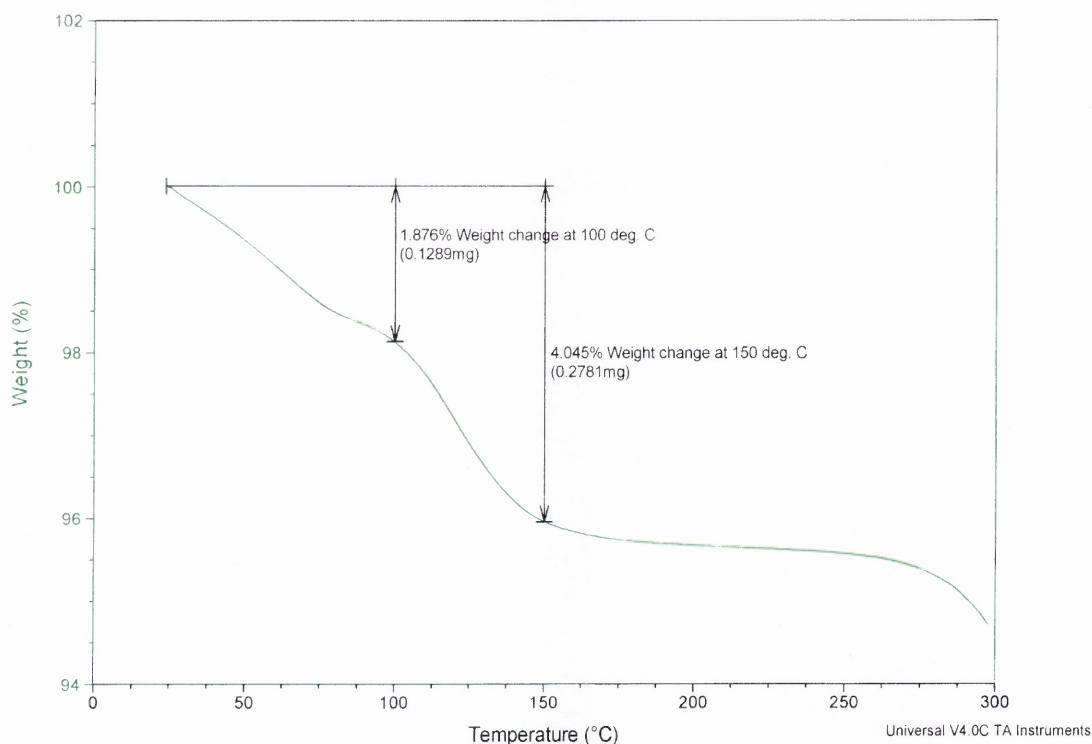


Figure 4.30 Modified TSDC analysis of the second run of P(LcoDL)LA film.

#### 4.1.4 TGA Results for Polymer Blends

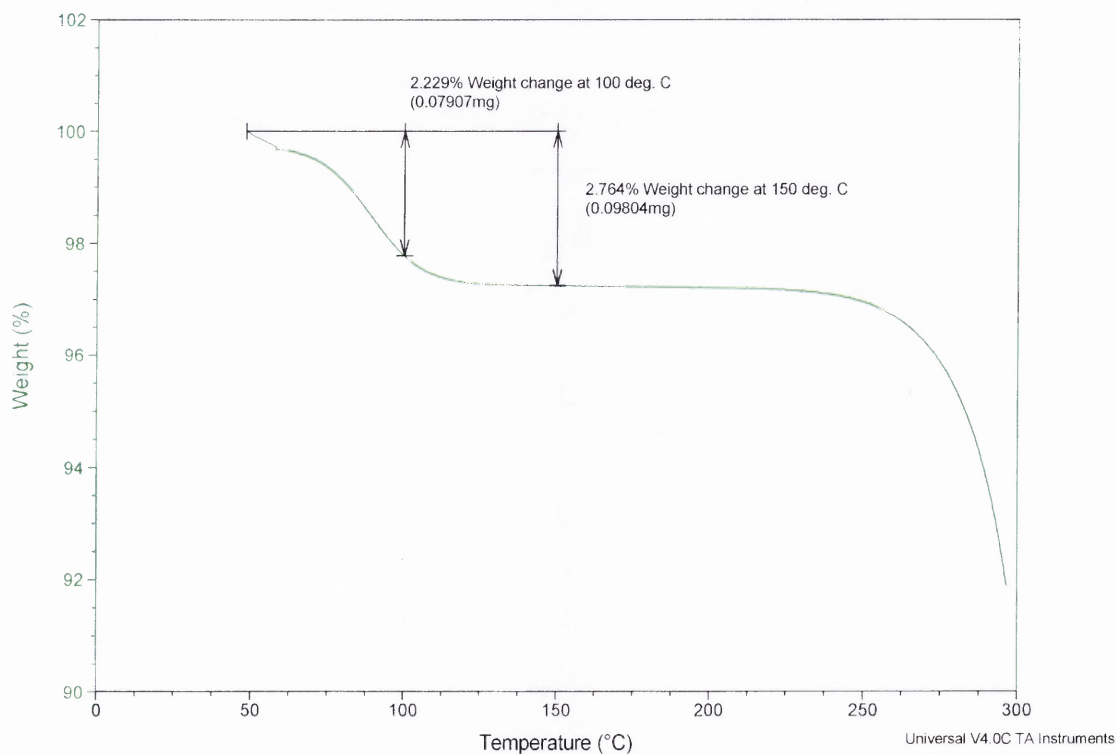
The TGA results are used to determine the weight loss of the polymer blends as a function of temperature by analyzing the materials' thermal stability and composition. Figure 4.31 and 4.32, respectively are the thermographs for poly(DTE) carbonate solvent cast film and P(LcoDL)LA solvent cast film, respectively. For poly(DTE) carbonate, the weight reduction process occurred in two steps. In the first step, 1.88% weight loss was observed at 100 °C. Additional weight reduction occurred during the second step until there was 4.04%, a total loss of 0.28 mg at the 150 °C.



**Figure 4.31** TGA analysis for the weight loss of the 100% poly(DTE) carbonate film.

P(LcoDL)LA weight reduction over the same temperature range is not as significant as that observed for poly(DTE) carbonate. Weight reduction may have occurred in two steps as observed for poly(DTE) carbonate. Compared to the

temperature where poly(DTE) carbonate first step ended, P(LcoDL)LA first step stopped around 60 °C. At 100 °C more than 2.00% weight loss is observed. At 150 °C temperature point, there is a 2.76% decrease in the polymer weight, lower than the weight reduction for poly(DTE) carbonate at that temperature.



**Figure 4.32** TGA analysis for the weight loss of the 100% P(LcoDL)LA film.

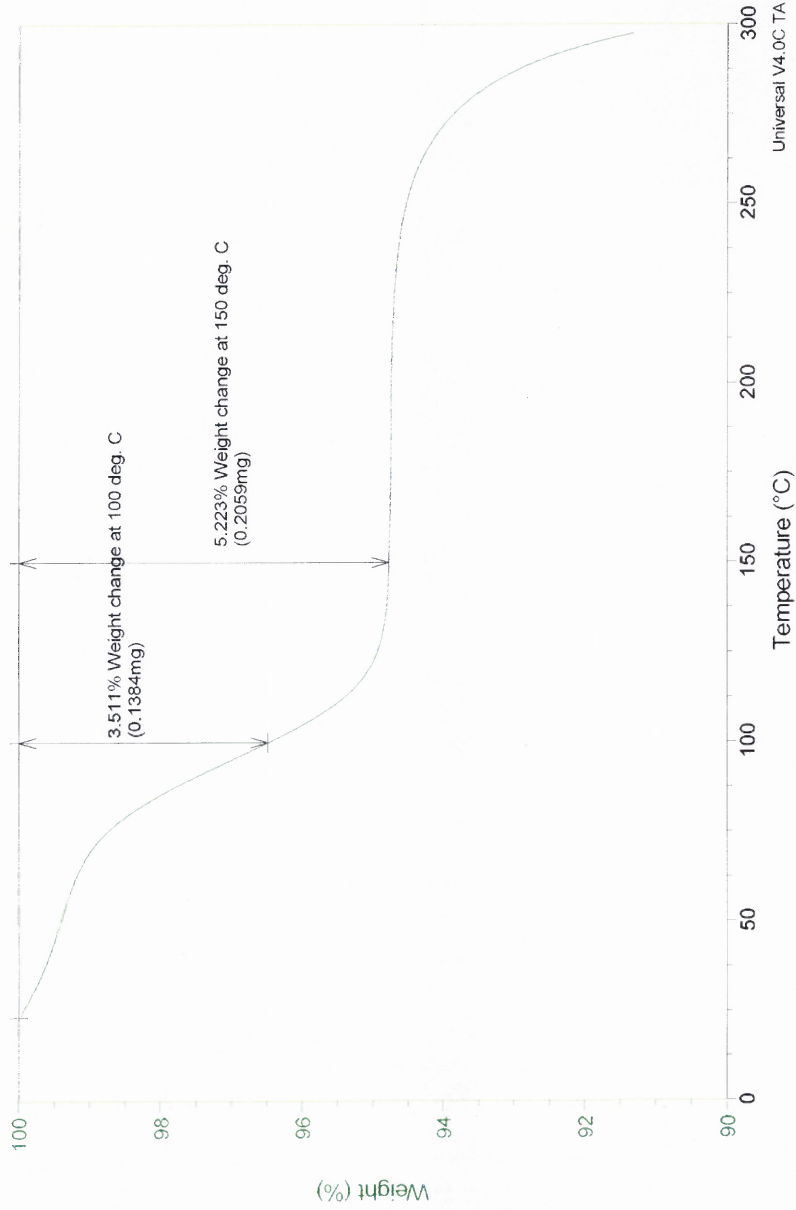
Significant weight loss is also observed for the poly(DTE) carbonate/P(LcoDL)LA blends. Figure 4.33 and 4.34 represents the 40:60 and 60:40 blends ratios, respectively. Higher weight loss is observed than for either of the component polymers. The 40:60 film decreased 5.22%; 0.21mg in weight at 150 °C. At the same temperature, the 60:40 film decrease 5.89%; 0.32 mg in weight.



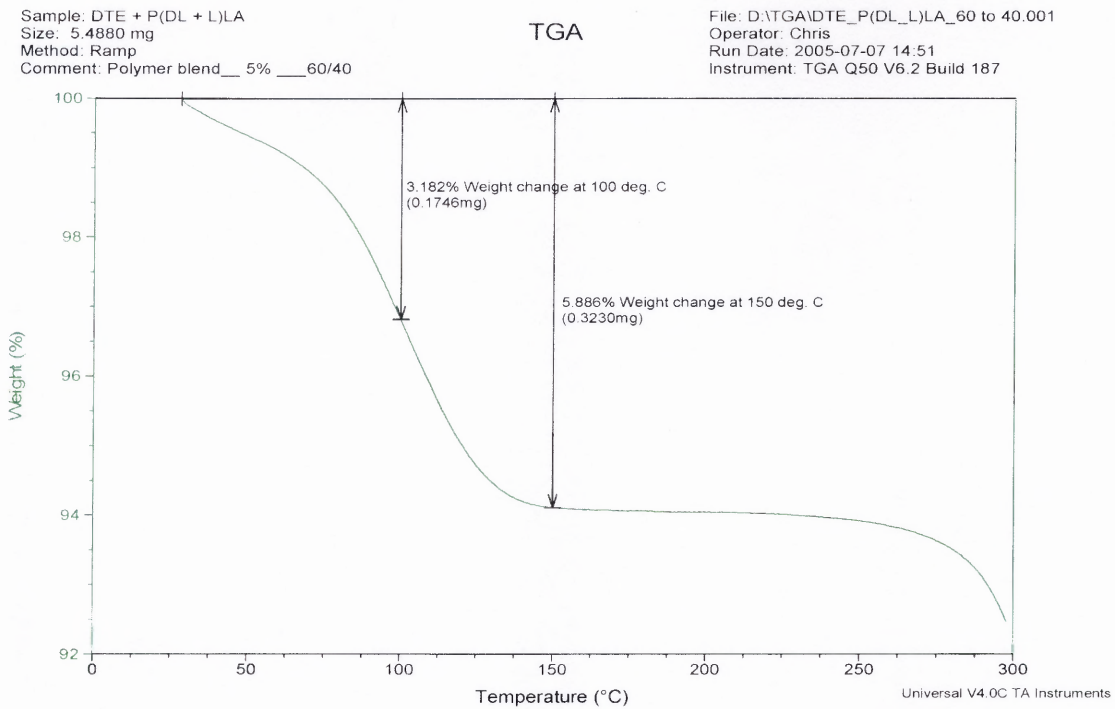
File: D:\TGA\DTE\_P(DL\_L)LA\_40 to 60.001  
Operator: Chris  
Run Date: 2005-07-08 12:40  
Instrument: TGA Q50 V6.2 Build 187

### TGA

Sample: DTE\_P(DL\_L)LA\_40 to 60  
Size: 3.9420 mg  
Method: Ramp  
Comment: Polymer blend\_ 5% \_\_\_ 40/60

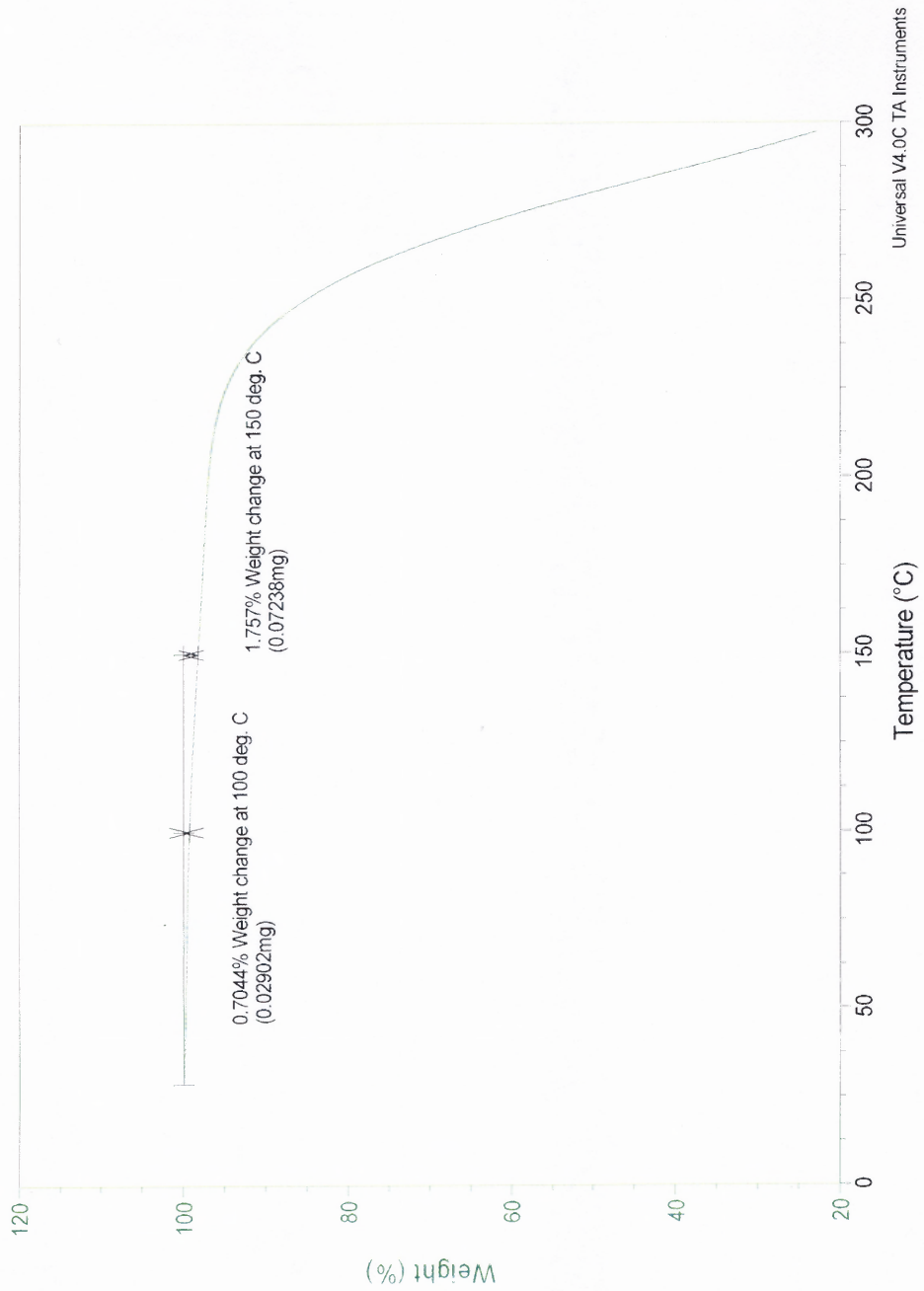


**Figure 4.33** TGA analysis for the weight loss of the 40:60 poly(DTE) carbonate/P(LcoDL)LA film

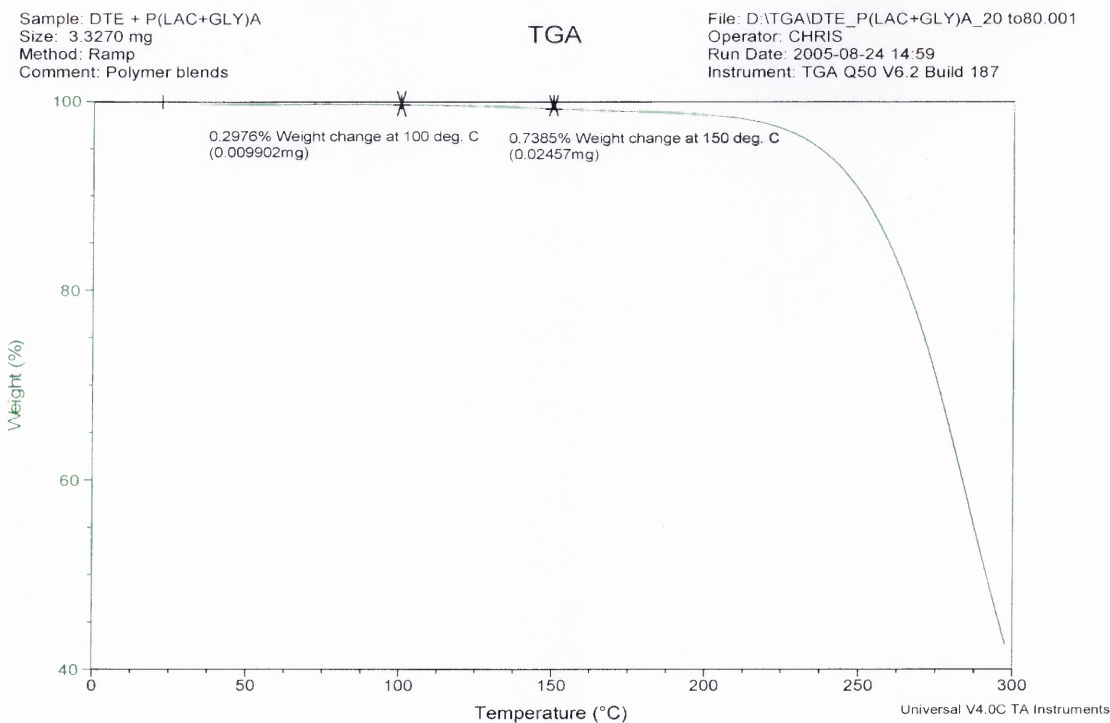


**Figure 4.34** TGA analysis for the weight loss of the 60:40 poly(DTE) carbonate/P(LcoDL)LA film.

The polymer blends comprised of poly(DTE) carbonate with PLGA and poly(DTE) carbonate with PLLA respectively, were also analyzed using the TGA method. The weight loss is lower than what was observed for the poly(DTE) carbonate/P(LcoDL)LA films. Figure 4.35 represents the TGA thermograph for the pure PLGA solvent cast film. A 1.76% reduction in weight at the 150 °C is observed. The 100% PLGA film has the most weight loss, when compared with the PLGA and poly(DTE) carbonate blends. The lowest weight loss is seen for the 20/80 blend of poly(DTE) carbonate and PLGA is depicted in Figure 4.36. A weight loss of 0.74%, 0.024 mg is present at 150 °C.



**Figure 4.35** TGA analysis of 100% PLGA film.



**Figure 4.36** TGA analysis for the weight loss for the 20:80 poly(DTE) carbonate/PLGA film.

The PLLA blends also show a lower weight loss at 150 °C compared to the poly(DTE) carbonate/P(LcoDL)LA blends. Figure 4.37 depicts the weight loss observed for the 100% PLLA film at 150 °C. 1.95% reduction in weight is observed at this temperature.

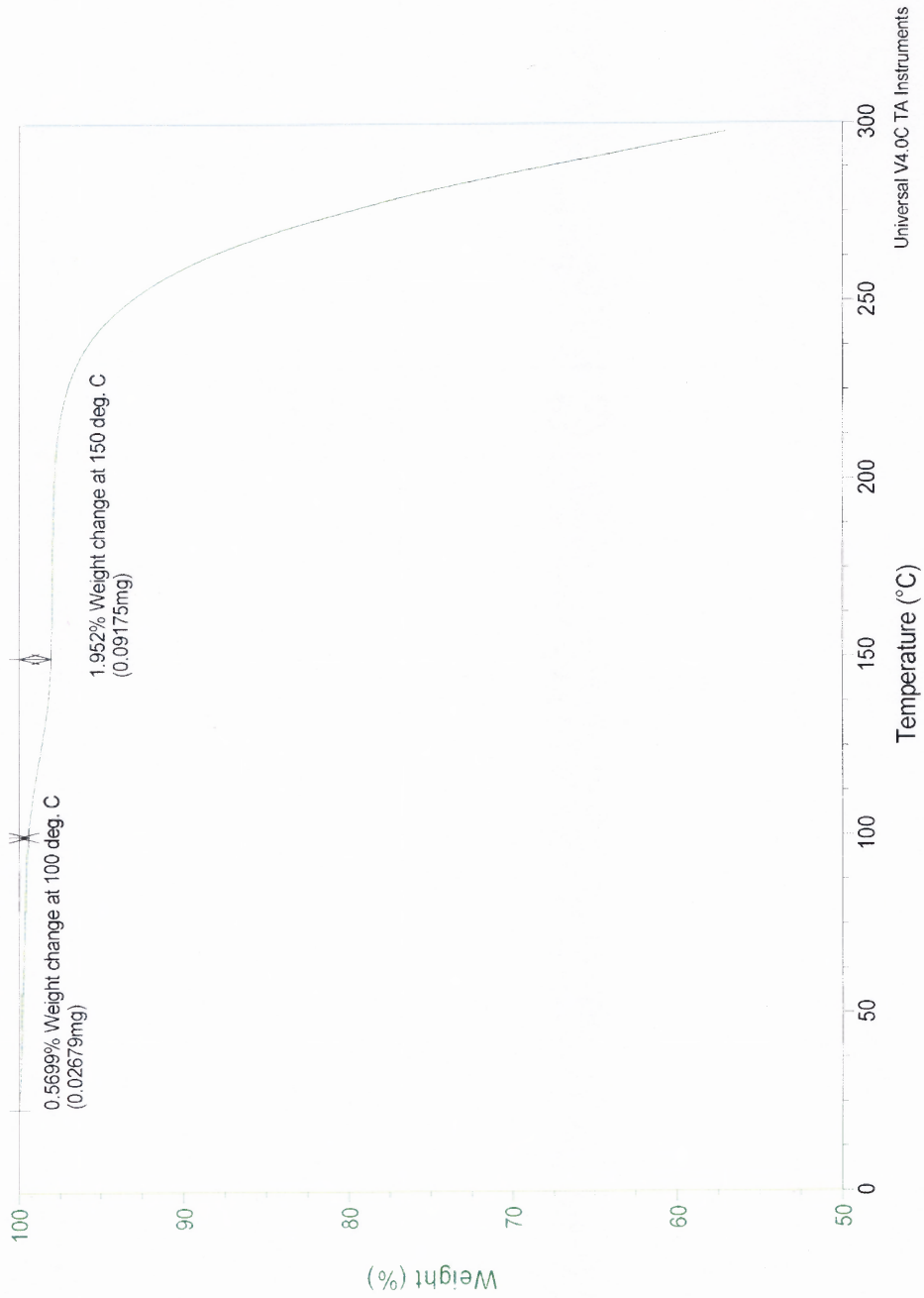
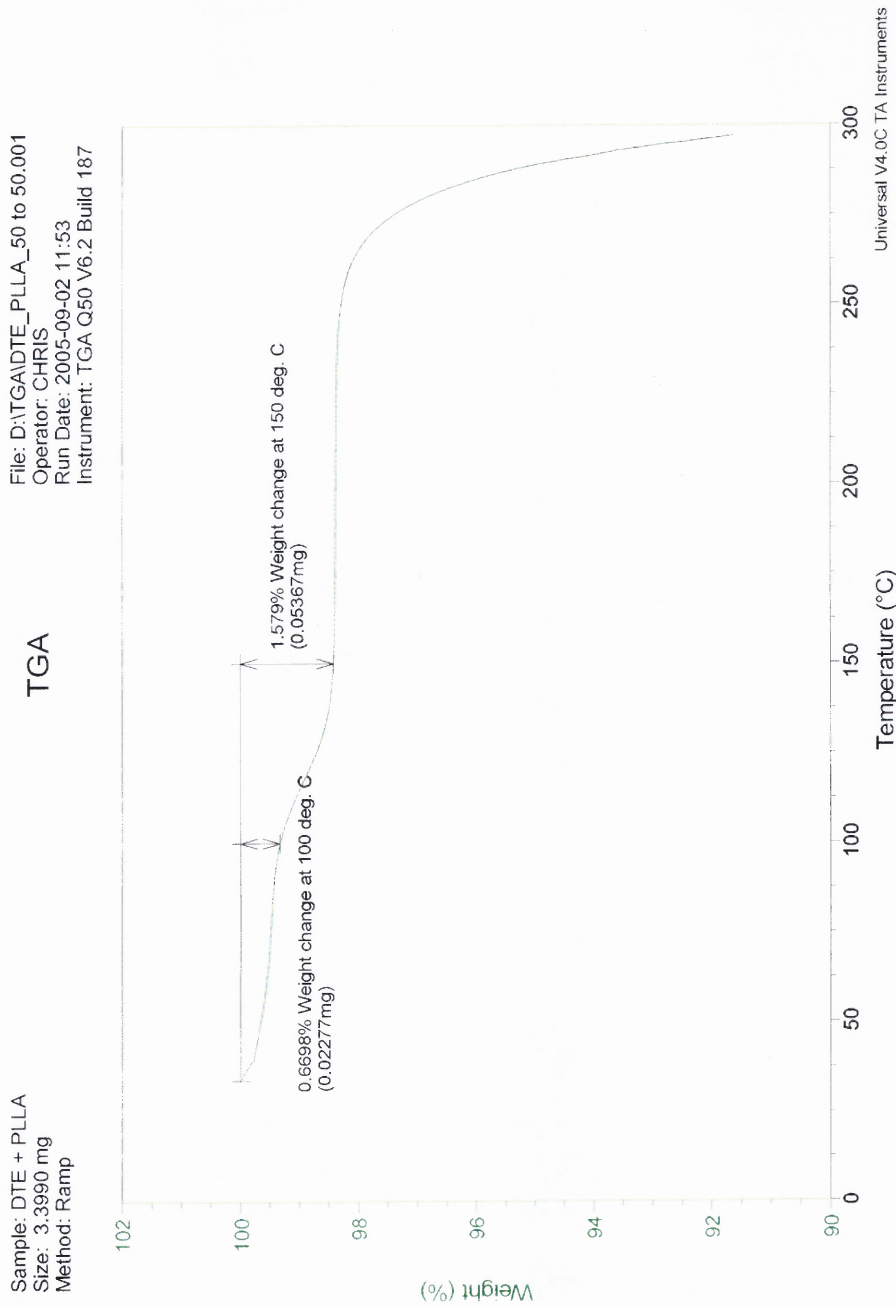
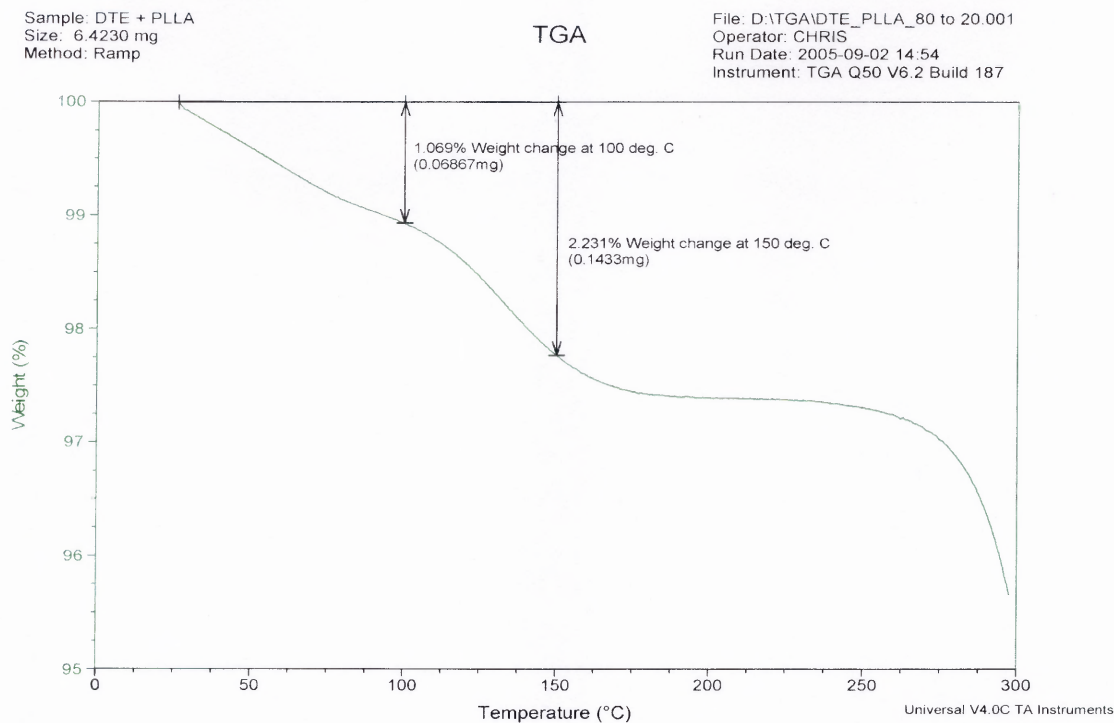


Figure 4.37 TGA analysis of 100% PLLA film.

The PLLA blends with poly(DTE) carbonate weight losses vary from 1.58% (50:50) to 2.23% (80:20), respectively as depicted in Figure 4.38 and 4.39 below.



**Figure 4.38** TGA analysis for the weight loss of the 50:50 poly(DTE) carbonate/PLLA film.



**Figure 4.39** TGA analysis for the weight loss of the 80:20 poly(DTE) carbonate/PLLA film.

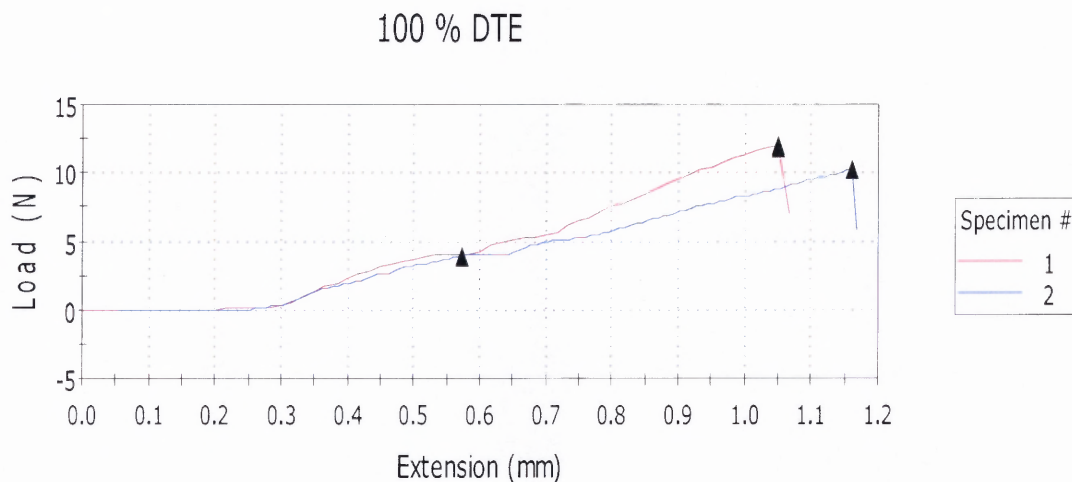
## 4.2 Mechanical Analysis

The mechanical properties of the poly(DTE) carbonate blends were investigated by using an Instron machine. The average modulus, tensile strain at break, and the tensile stress at maximum load were determined. The modulus was calculated by determining the highest slope between the starting point and the yield point. The data was divided into six equal regions with no overlap and a least square fit algorithm was applied to find the slope in each region. The algorithm determines the pair of consecutive regions that has the highest slope sum and from this pair the region with the highest slope is assigned the modulus.

#### 4.2.1 Poly(DTE) carbonate and P(LcoDL)LA Films

Figure 4.40 and 4.41 represents the tensile curve for poly(DTE) carbonate and P(LcoDL)LA, respectively. An average Young's modulus in the range of 1 giga Pascal (GPa) for poly(DTE) carbonate and 1.4 GPa for P(LcoDL)LA polymer was determined.

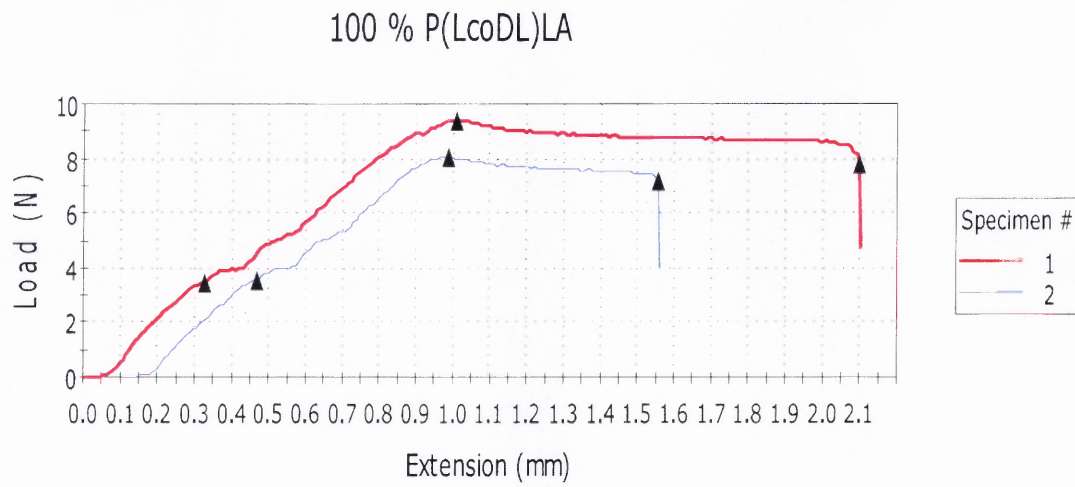
The results for the blends are represented in Table 4.2.



	Modulus (Automatic) (MPa)	Tensile strain at Break (Standard) (%)	Tensile stress at Maximum Load (MPa)
1	1070.24914	8.06971	50.27
2	943.36894	5.5375	32.163
Mean	1006.80904	6.8036	41.216
STD	89.71785	1.79054	12.80358

**Figure 4.40** Mechanical analysis for 100% poly(DTE) carbonate film.





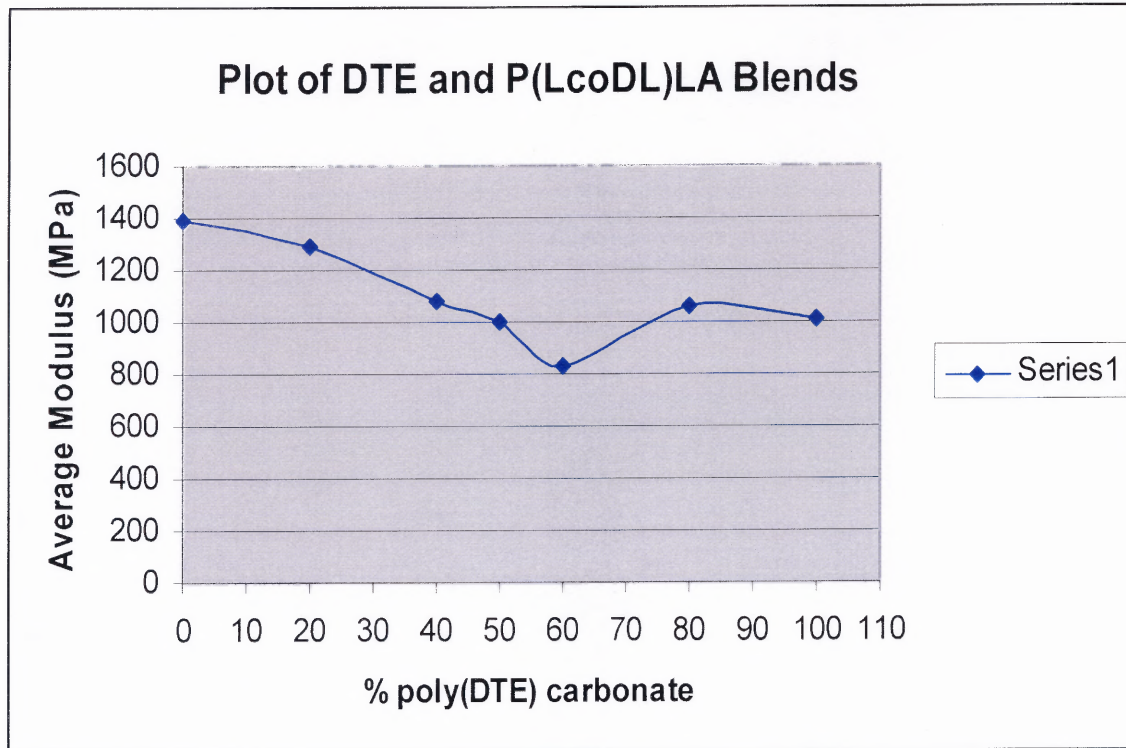
	Modulus (Automatic) (MPa)	Tensile strain at Break (Standard) (%)	Tensile stress at Maximum Load (MPa)
1	1130.45678	10.49765	33.928
2	1657.99745	7.24766	48.027
Mean	1394.22712	8.87265	40.977
STD	373.02758	2.2981	9.96992

**Figure 4.41** Mechanical analysis for 100% P(LcoDL)LA film.

**Table 4.2** The Instron Analysis Results for Poly(DTE) Carbonate/P(LcoDL)LA Blends

<b>% of DTE</b>		<b>Modulus (Automatic) (MPa)</b>	<b>Tensile strain at Break (Standard) (%)</b>	<b>Tensile stress at Maximum Load (MPa)</b>
<b>100</b>	1	1070.24914	8.06971	50.27
	2	943.36894	5.5375	32.163
	Mean	1006.80904	6.8036	41.216
	STD	89.71785	1.79054	12.80358
<b>0</b>	1	1130.45678	10.49765	33.928
	2	1657.99745	7.24766	48.027
	Mean	1394.22712	8.87265	40.977
	STD	373.02758	2.2981	9.96992
<b>20</b>	1	1180.94492	4.83906	38.03
	2	1407.07897	4.74687	39.326
	Mean	1294.01194	4.79297	38.678
	STD	159.90092	0.06519	0.91635
<b>40</b>	1	1122.31845	4.36953	35.668
	2	1032.5811	3.95625	29.966
	Mean	1077.44977	4.16289	32.817
	STD	63.45389	0.29223	4.03162
<b>50</b>	1	900.65558	4.12578	17.779
	2	1108.20227	3.83047	28.272
	Mean	1004.42893	3.97812	23.026
	STD	146.75767	0.20882	7.41978
<b>60</b>	1	854.54294	3.99844	19.289
	2	812.93722	4.7125	17.223
	Mean	833.74008	4.35547	18.256
	STD	29.41969	0.50492	1.46046
<b>80</b>	1	932.00511	6.20937	19.91
	2	1183.6561	4.37187	25.958
	Mean	1057.83061	5.29062	22.934
	STD	177.94412	1.29931	4.27649

In Figure 4.42, a plot of the average modulus compared with poly(DTE) carbonate/P(LcoDL)LA blends, the modulus decrease as the percent of poly(DTE) carbonate increase. The exception is the 80/20 blend where the average modulus was 1057 MPa.

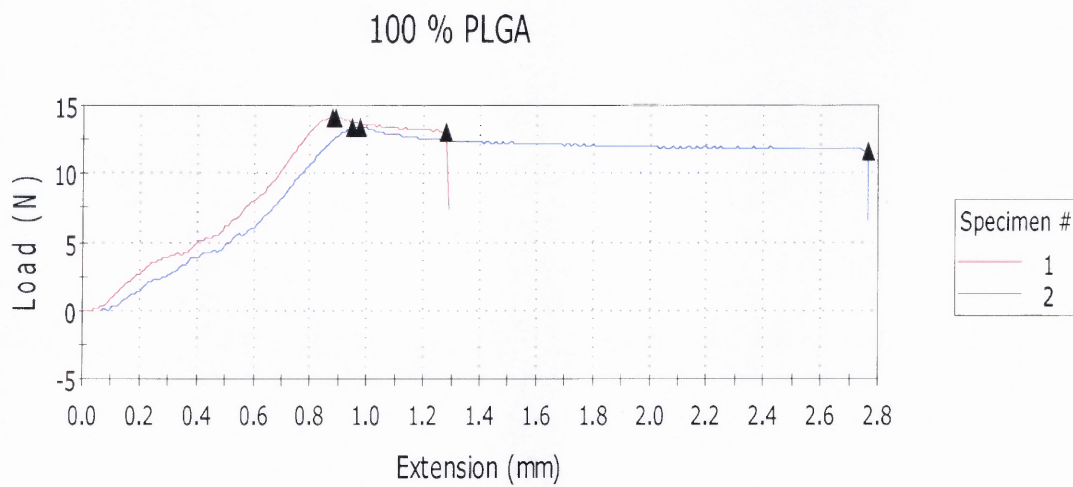


**Figure 4.42** A depiction of the change in modulus of poly(DTE) carbonate/P(LcoDL)LA blends. As the percent of carbonate increase the modulus decreases.

#### 4.2.2 Poly(DTE) carbonate and PLGA Films

The stress-strain profile obtained from the 100% PLGA is represented in figure 4.43.

The average result is 1.4 GPa and a maximum load of 39 MPa. The results for the blends are represented in table 4.3.



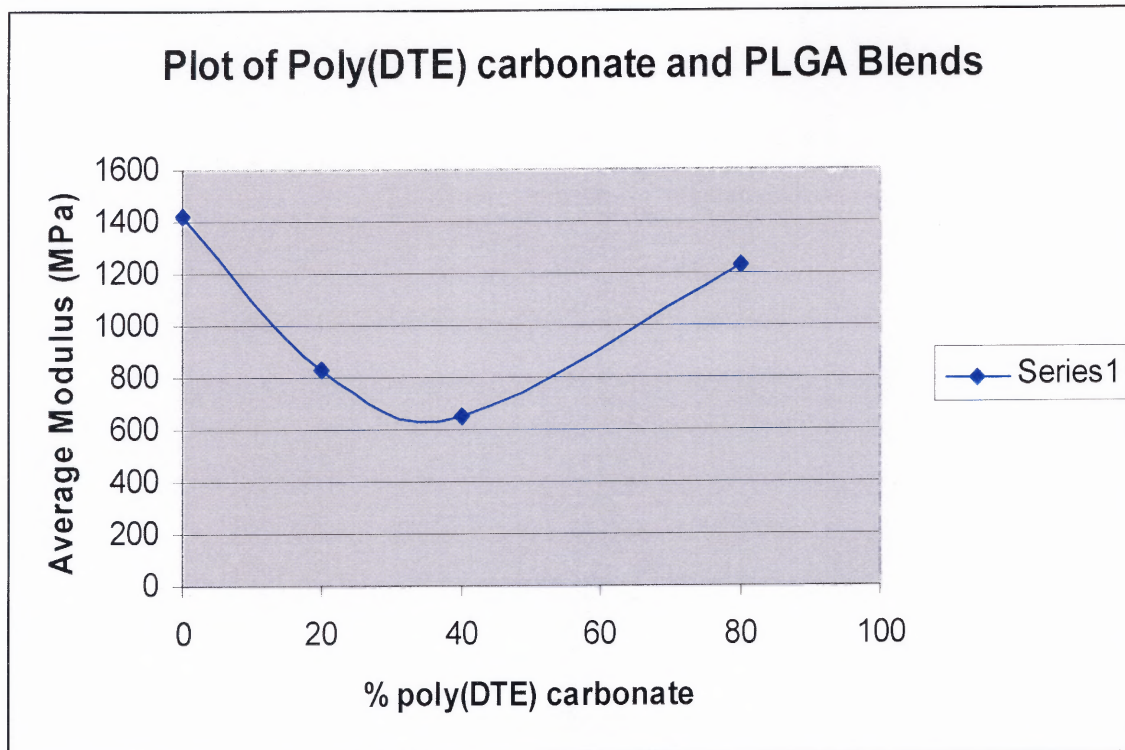
	Modulus (Automatic) (MPa)	Tensile strain at Break (Standard) (%)	Tensile stress at Maximum Load (MPa)
1	1342.41978	6.41172	37.5
2	1491.54209	13.5039	40.683
Mean	1416.98094	9.95781	39.091
STD	105.44539	5.01493	2.25084

**Figure 4.43** Mechanical analysis for 100% PLGA film.

**Table 4.3** The Instron Analysis Results for Poly(DTE) Carbonate/PLGA Blends

<b>% of DTE</b>		<b>Modulus (Automatic) (MPa)</b>	<b>Tensile strain at Break (Standard) (%)</b>	<b>Tensile stress at Maximum Load (MPa)</b>
<b>0</b>	1	1342.41978	6.41172	37.5
	2	1491.54209	13.5039	40.683
	Mean	1416.98094	9.95781	39.091
	STD	105.44539	5.01493	2.25084
<b>20</b>	1	819.02733	3.51016	14.433
	2	842.00055	3.49531	14.755
	Mean	830.51394	3.50273	14.594
	STD	16.24452	0.0105	0.2279
<b>40</b>	1	723.78908	1.29141	6.227
	2	568.07937	3.82969	5.414
	Mean	645.93423	2.56055	5.821
	STD	110.10339	1.79484	0.5746
<b>80</b>	1	908.62124	4.66484	3.516
	2	1547.33156	4.1625	38.909
	Mean	1227.9764	4.41367	21.212
	STD	451.6364	0.35521	25.02695

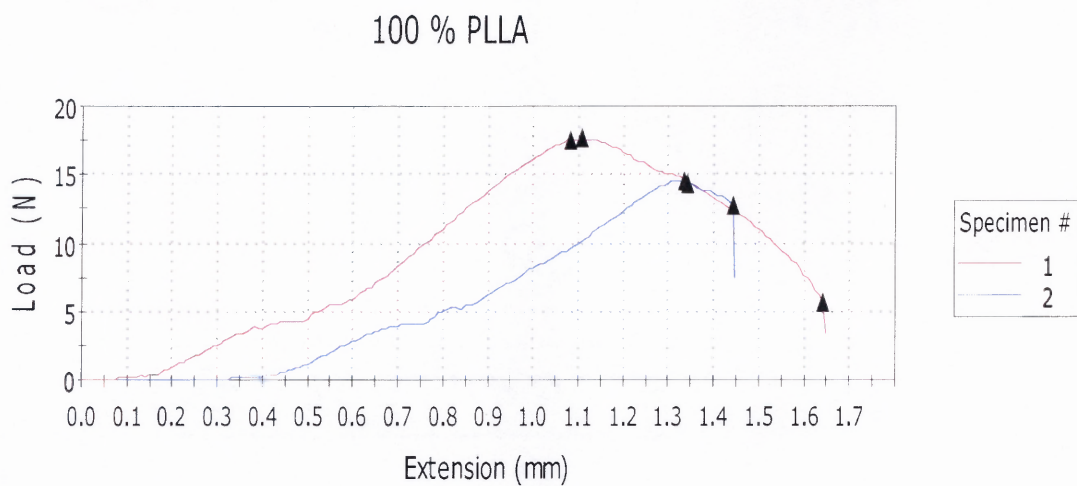
Figure 4.44 is a graphical representation of the modulus obtained for the poly(DTE) carbonate/PLGA blends. The modulus of the blends formed are lower than the blends of poly(DTE) carbonate and P(LcoDL)LA. The 50/50 and 60/40 blends modulus was not determined as a result of the parent polymers inability to form a strong adhesion at their interface.



**Figure 4.44** A depiction of the change in modulus of poly(DTE) carbonate/PLGA blends. As the percent of carbonate increases the modulus decreases.

#### 4.2.3 Poly(DTE) carbonate and PLLA Films

Figure 4.45 is a representation of the stress-strain profile for the 100% PLLA solvent cast film. The film made from only the PLLA component has a Young's modulus of 1.4 GPa and a maximum load of 48 MPa.



	Modulus (Automatic) (MPa)	Tensile strain at Break (Standard) (%)	Tensile stress at Maximum Load (MPa)
1	1554.78372	8.21484	51.218
2	1330.35936	6.79531	45.705
Mean	1442.57154	7.50508	48.462
STD	158.69198	1.00376	3.89823

**Figure 4.45** Mechanical analysis for 100% PLLA film.

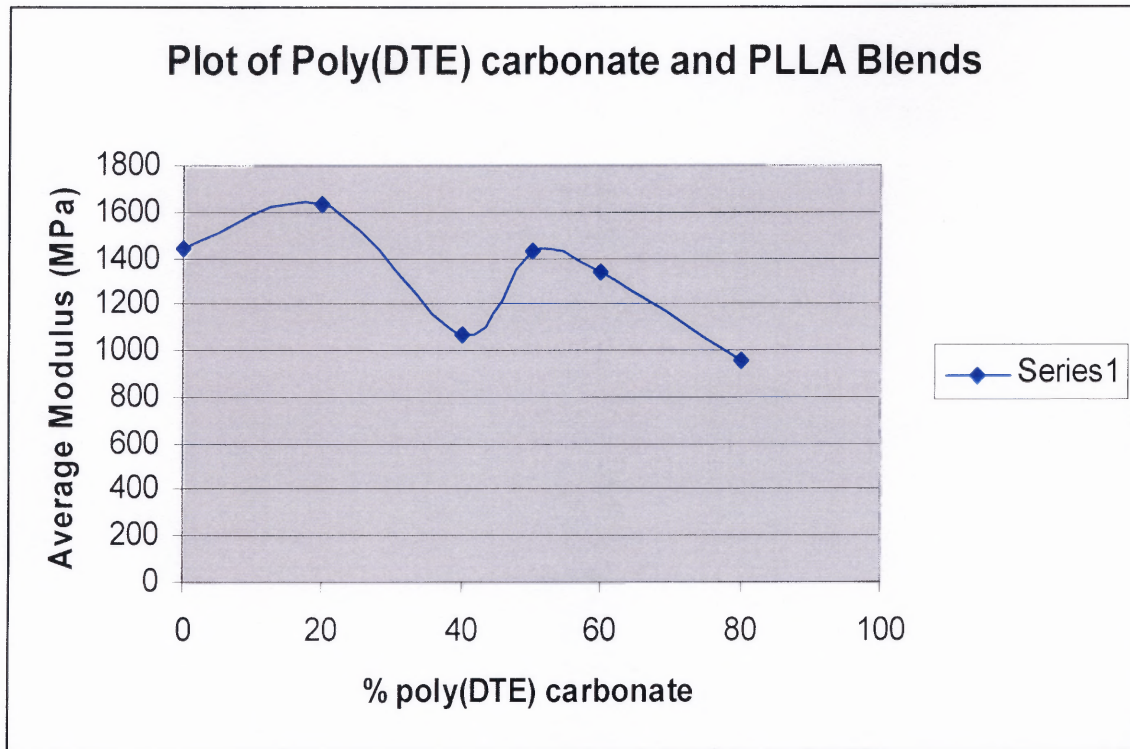
The blends comprised with poly(DTE) carbonate have a Young's modulus between 1-1.6 GPa. The lowest Young's modulus obtained is 955 MPa for the 80/20 blend as represented in table 4.4.

**Table 4.4** The Instron Analysis Results for Poly(DTE) Carbonate/PLLA Blends

<b>% Of DTE</b>		<b>Modulus (Automatic) (MPa)</b>	<b>Tensile strain at Break (Standard) (%)</b>	<b>Tensile stress at Maximum Load (MPa)</b>
<b>0</b>	1	1554.78372	8.21484	51.218
	2	1330.35936	6.79531	45.705
	Mean	1442.57154	7.50508	48.462
	STD	158.69198	1.00376	3.89823
<b>20</b>	1	1593.51758	4.91484	46.141
	2	1664.50416	5.04766	53.792
	Mean	1629.01087	4.98125	49.966
	STD	50.1951	0.09391	5.41009
<b>40</b>	1	1117.17109	3.46406	26.314
	2	1025.39832	3.87266	24.534
	Mean	1071.28471	3.66836	25.424
	STD	64.89315	0.28892	1.25844
<b>50</b>	1	1245.65538	4.74609	37.23
	2	1613.21519	5.04609	50.061
	Mean	1429.43529	4.89609	43.646
	STD	259.90403	0.21213	9.07272
<b>60</b>	1	1423.80195	4.25625	39.972
	2	1263.7812	6.07891	36.658
	Mean	1343.79158	5.16758	38.315
	STD	113.15176	1.28881	2.34296
<b>80</b>	1	1117.1224	4.4125	32.143
	2	794.46375	3.91172	23.769
	Mean	955.79308	4.16211	27.956
	STD	228.15412	0.35411	5.92144

Figure 4.46 is a representation of the plot of the modulus against the percentage of poly(DTE) carbonate was in consistent with the results determined for the previous blends. There is no correlation to the decrease in modulus as the percentage of poly(DTE) carbonate increase. The modulus fluctuates between 1 and 1.5 GPa.





**Figure 4.46** A depiction of the change in modulus of poly(DTE) carbonate/PLLA blends.

## CHAPTER 5

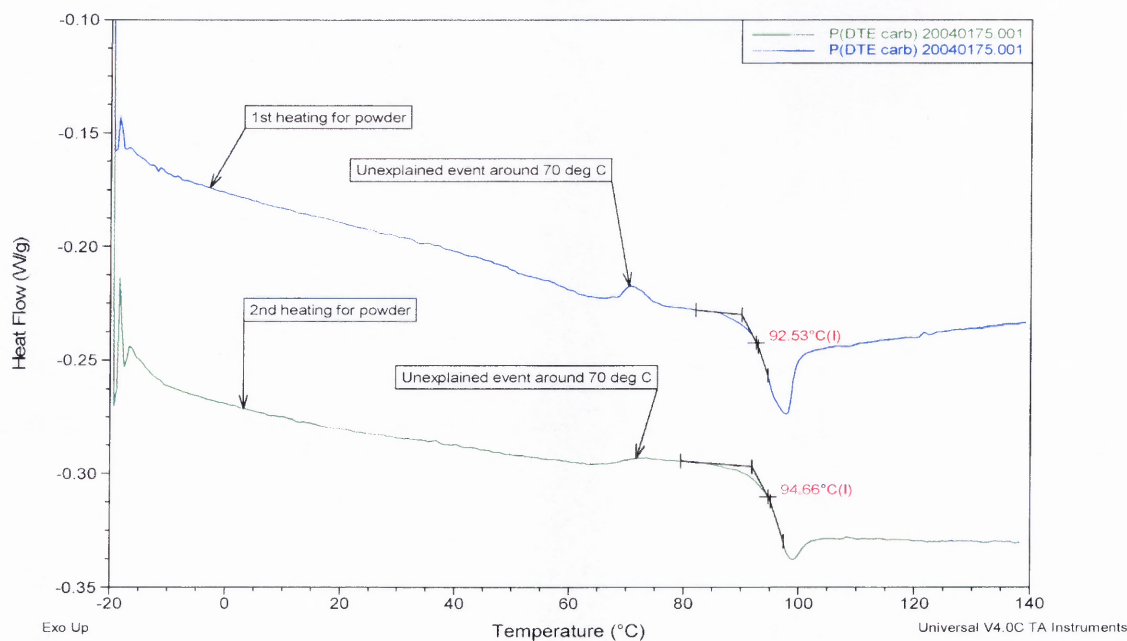
### DISCUSSION

#### 5.1 DSC of the Component Polymers

Poly(DTE) carbonate and P(LcoDL)LA showed complex behavior. What is observed from the thermal analyses, suggests that the materials are more complex than was anticipated. The DSC studies for the poly(DTE) carbonate identified differences in the position where thermal events occur for the powdered form and the film made by solvent casting. It seems as though the processing history of the material plays a key role in the observed behavior of the polymer. Similar outcomes were determined for the P(LcoDL)LA polymer. The temperature where the onset of the glass transition temperature is located for the pellets and solvent cast film is different as observed from the DSC studies.

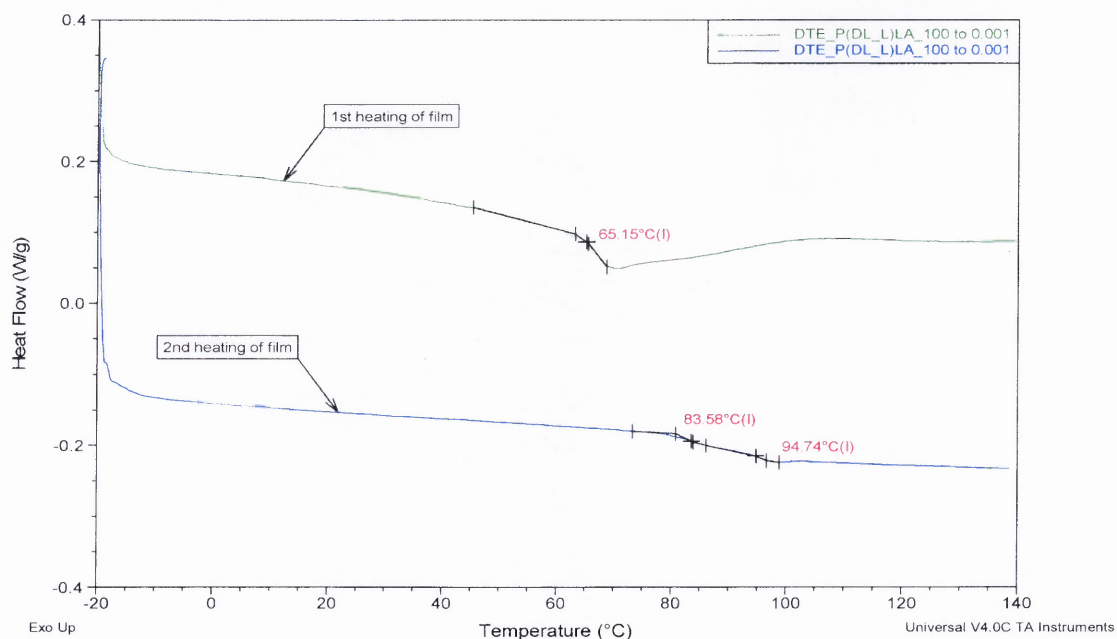
##### 5.1.1 DSC for Poly(DTE) carbonate

As represented in Figure 5.1, the powdered form of poly(DTE) carbonate, the first and second heating cycle have an undefined thermal phenomenon around 70 °C. There was a decrease in heat capacity at the location of the unexplained event for the second heating cycle. This could be a result of the structure of the polymer reorganizing as a consequence of heating to 140 °C.



**Figure 5.1** DSC representation of the thermal events for poly(DTE) carbonate powder and film.

When compared with the solvent cast film, depicted in figure 5.2, the outcome from the DSC studies are different. No evidence of the unexplained event was observed for the first or second heating cycle. For the first heating cycle the solvent seems to have a plasticizing effect on the polymer. When the first heating cycle of the solvent cast film is analyzed, the position where the unexplained thermal event and the 92 °C was observed was displaced and a single thermal event around 65 °C is observed. Even though there is no evidence of the undefined thermal event for the poly(DTE) carbonate film, the second heating cycle shows a region where two thermal events are present. The temperatures where the two events are present are around 83 and 94 °C, respectively.

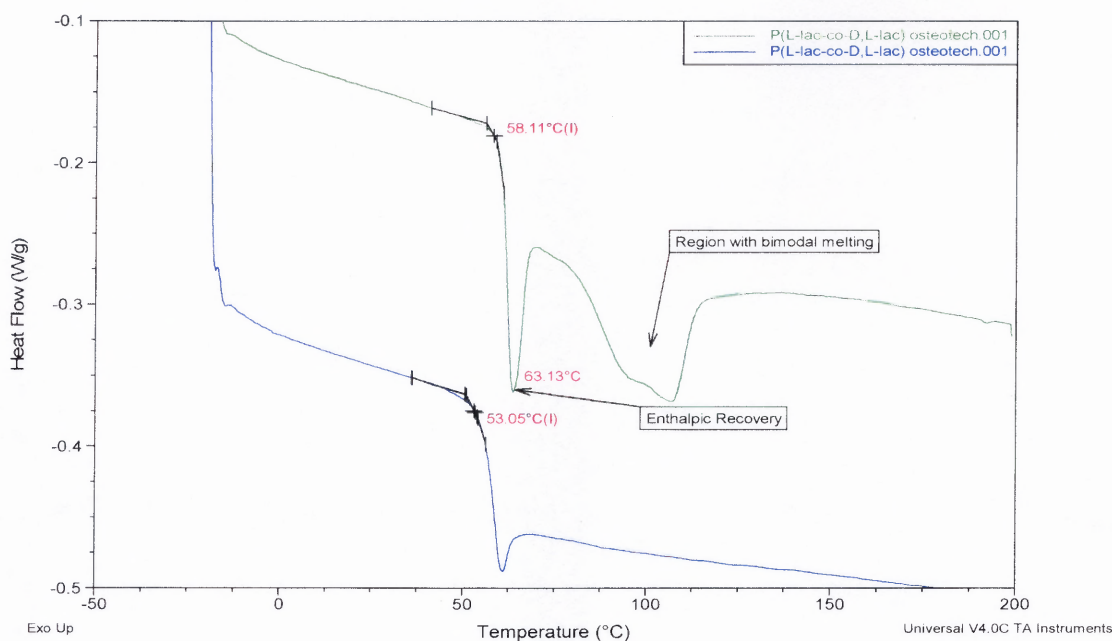


**Figure 5.2** DSC analysis of the first heating of poly(DTE) carbonate film.

The difference in temperature where thermal activity was observed in the DSC result between the first and second heating of the solvent cast film could possibly help to explain the two step weight reducing process observed when the poly(DTE) carbonate film was analyzed using the TGA method. In Figure 4.25 for the poly(DTE) carbonate film, there was significant weight loss before 100 °C followed by another step where the polymer weight was reduced further after that temperature. The first step in the TGA analysis could be a reduction in weight as solvent is given off.

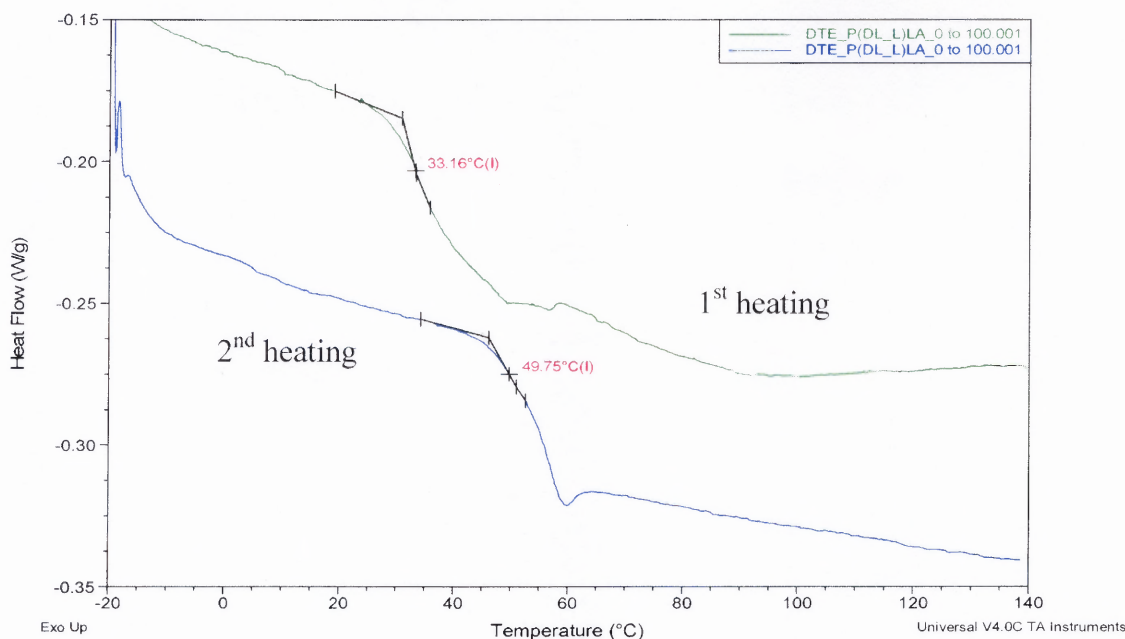
### 5.1.2 DSC for P(LcoDL)LA

P(LcoDL)LA is also a complex polymer; little is known about its properties. Like poly(DTE) carbonate, the polymer also shows difference in the pattern of behavior when heated and solvent cast. The pellet form of the polymer was first analyzed using the DSC. Significant difference between the first and second heating is observed. For the first heating a T<sub>g</sub> around 60 °C is observed, followed by an enthalpic recovery peak and an area defined by a complex phenomenon. Within the complex region, there seem to be some form of bimodal melting process taking place. The copolymer is made up of poly (DL lactide) (PDLLA) and poly (L lactide) (PLLA). PDLLA is an amorphous polymer that is possibly comprised of a random stereo sequence. The T<sub>g</sub> for PDLLA is about 57 °C [11]. PLLA is semi-crystalline with a T<sub>g</sub> of about 65 °C and a melting temperature within 170-180 °C. The complexity observed in the first heating might be a result of the copolymer process history and it developed complex block copolymer morphology. Figure 5.3 is a representation of the pattern of behaviors observed for the P(LcoDL)LA pellets. For the second heating cycle, the complex behavior has been removed after the first heating.



**Figure 5.3** DSC analysis of the first and second heating of P(LcoDL)LA pellets.

The solvent used in casting the film also affects the properties determined for the P(LcoDL)LA copolymer. The temperature where the  $T_g$  is located is much lower ( $30\text{ }^\circ\text{C}$ ) than the position for the pellet form of the polymer. This is suggesting that the solvent is acting like a plasticizer for the material, shifting the  $T_g$  to a lower temperature. Figure 5.4 is a representation of the DSC result for the solvent cast P(LcoDL)LA film. The first heating cycle of the DSC imposes a new process history, and a different  $T_g$  at about  $50\text{ }^\circ\text{C}$  is observed. The higher  $T_g$  is consistent with solvent being driven off. The temperature observed for the first heating is significantly lower than what is observed for the  $T_g$  of the pellet form of the polymer.



**Figure 5.4** DSC analysis of the first and second heating of P(LcoDL)LA film. The top curve represents the first heating.

## 5.2 TSC of the Component Polymers

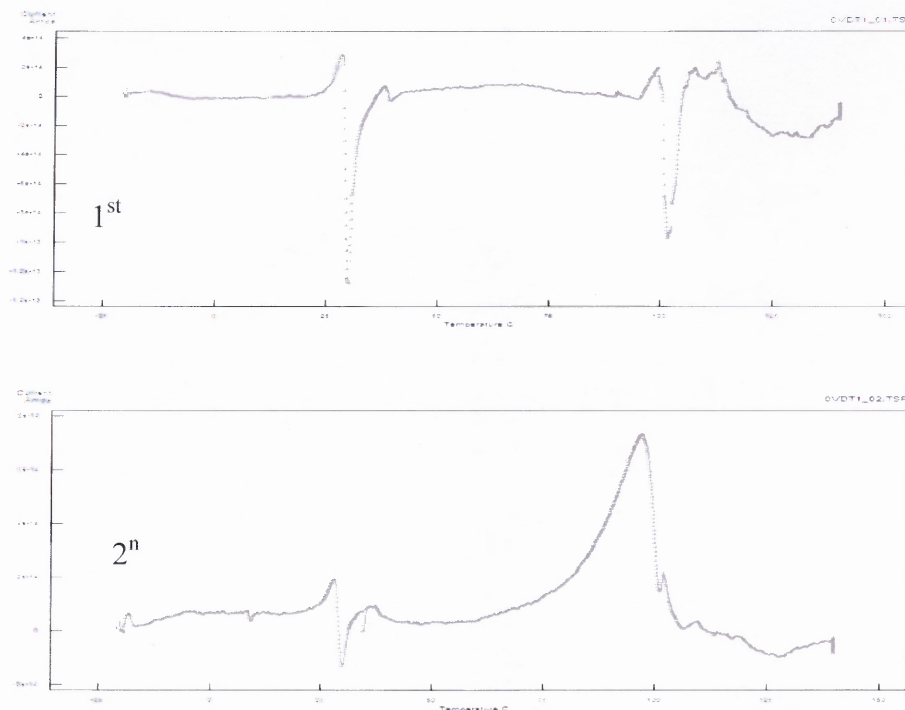
The behavior of the blend components was further investigated using TSC analysis. This method is employed because it can be more sensitive than DSC in detecting subtle relaxations within a material. The technique is sensitive to any relaxation that occur as a consequence of molecular motions such as glass transition and any conformational motions. Both the TSPC and a modified TSDC methods were used to examine the complex behavior seen in both poly(DTE) carbonate and P(LcoDL)LA. The TSPC method was first used to characterize the thermal properties of the poly(DTE) carbonate

and P(LcoDL)LA polymers. The polymers are first heated from -20 °C to 140 °C with no electric field. This experiment was performed to have an idea of the position where relaxations are taking place.

### 5.2.1 TSPC for Poly(DTE) Carbonate

Figure 5.5 represents the TSPC experiments for poly(DTE) carbonate with no electric field. There is no field to immobilize the dipoles; therefore the movement could be a result of spontaneous reorganization. For poly(DTE) carbonate films little activity was observed in the lower temperature region below 25 °C, but is observed from 75 °C upwards. Any peak observed in the 25-30 °C range is a result of solid-solid transition of the Teflon that is used as an insulator and can be ignored. This peak does not represent relations in the sample specimen. When the experiment was repeated for the same specimen of film, events are observed in the same temperature regions, but the direction of the peaks generated in the 75 °C range is not the same. The current peak in the vicinity of 75 °C is in the opposite direction when the first and second runs are compared. In the absence of the driving force that would be provided by the electric field, any current generated in the specimen would have to be the result of thermally induced relaxations. These results may represent relaxations where the material is going through some kind of spontaneous reorganization.



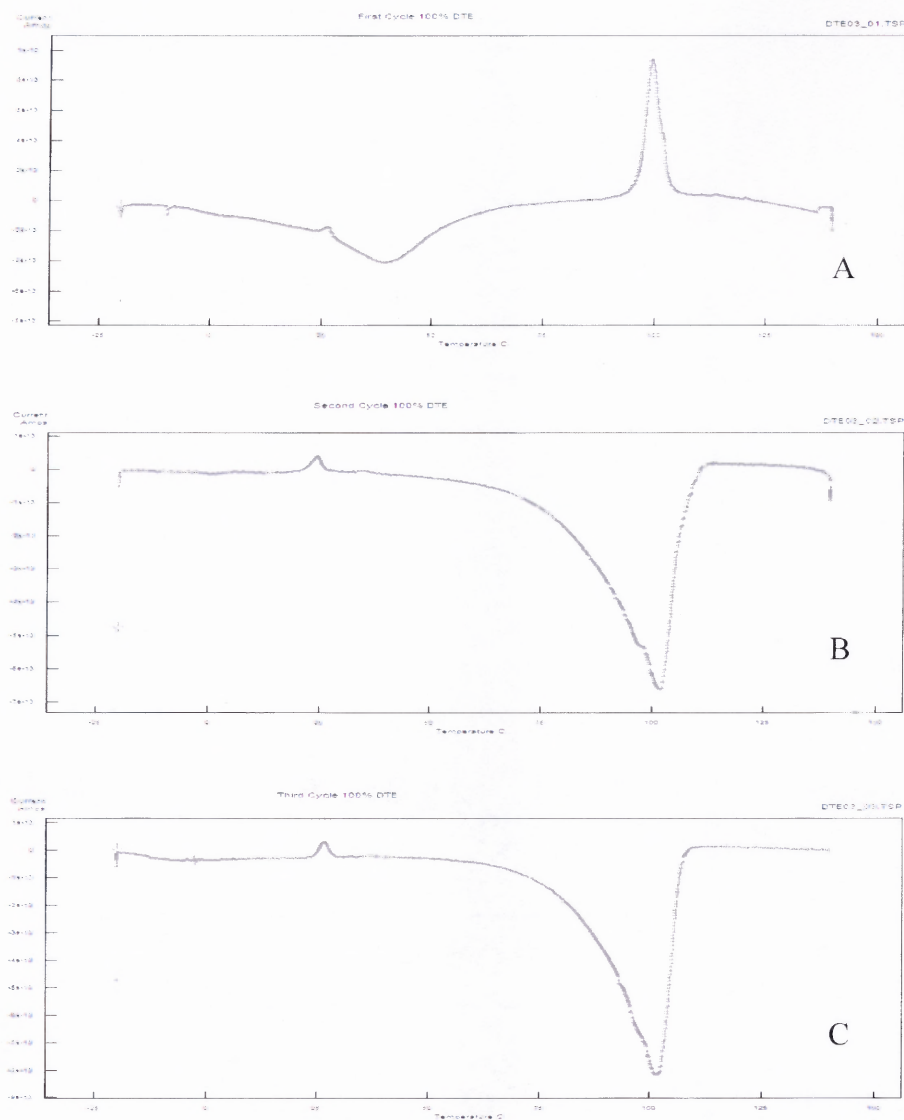


**Figure 5.5** TSPC analyses for two consecutive tests done for the same specimen of poly(DTE) carbonate with no electric field applied. The peak at 100 °C is in opposite direction.

The observed current peak(s) about 100 °C is consistent with the temperature where the complex events were observed in the DSC experiments for poly(DTE) carbonate film.

When the TSPC experiments were run with the application of an electric field, similar behavior of poly(DTE) carbonate is observed. Figure 4.23 and 4.24 represent the shift in the direction of the peak at the 100 °C. The change in the position of the peak at 100 °C might be a result of the material going through mechanical relaxation. Since the polar groups are aligned during the experiment as a consequence of the field, any movement of the polar groups should generate a current. In the TSPC mode dipolar alignment would generate a negative current. Movement due to glass transition should generate a smooth polarization current peak. The peak at 100 °C in the first run is sharp

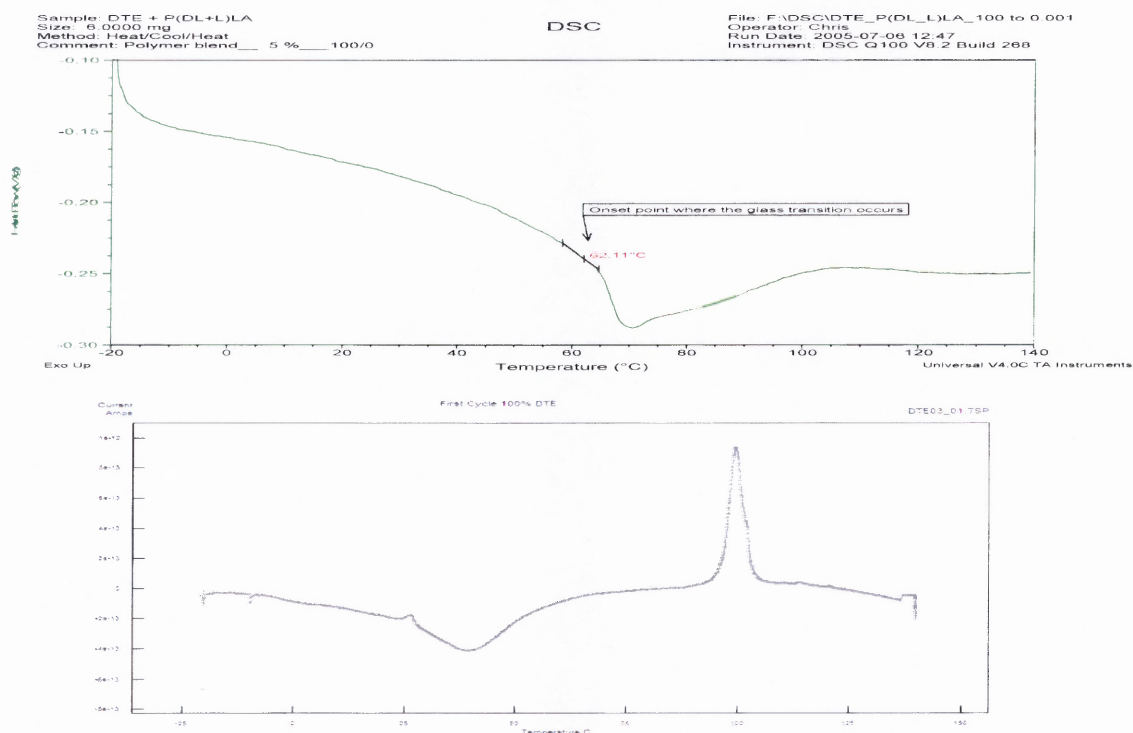
and in the negative direction. However for the second run the current peak at 100 °C is in the positive direction indicating that this may represent a spontaneous reorganization. Figure 5.6 represents three consecutive runs between -20 °C and 140 °C in the presence of 100V across the thickness of the film specimen. In Figure 5.6A a broad negative is observed at about 40 °C and a sharp positive current is observed at about 100 °C. The broad 40 °C current could be related to plasticized Tg of the polymer after it was solvent cast. The 40 °C current peak could suggest that the reduction in weight observed for poly(DTE) carbonate in figure 4.31 for the TGA experiment is a result of solvent being driven off. The 100 °C current peak is similar to where the Tg is reported in literature [20]. In Figure 5.6B the peak at 100 °C is in the negative direction and is now consistent with the direction of current polarization for TSPC experiment. No peak is present at 40 °C, further suggesting that solvent is driven off as a result of plasticize relaxation. Figure 5.6C is similar to Figure 5.6B.



**Figure 5.6** TSPC analysis for poly(DTE) carbonate after the same specimen is tested three consecutive times.

The first time the material is tested using any of the thermal analysis techniques seems to facilitate the reorientation of the polymer chain. These findings are consistent with the results seen for the powder and film form of poly(DTE) carbonate. In figure 5.1 the enthalpic peak appears around 100 °C for the DSC experiment; the location where the thermal peaks are also seen for the TSPC experiment. Figure 5.7 shows the comparison

of DSC and TSC results for the first heating of the carbonate film. The DSC results indicate that the onset point of the glass transition is around 60 °C and the TSPC results show a broad negative peak between 30 and 50 °C. The correlation can be made that the broad negative peak observed in the plot of TSPC could be the position where the  $T_g$  is located for poly(DTE) carbonate after it is solvent cast.

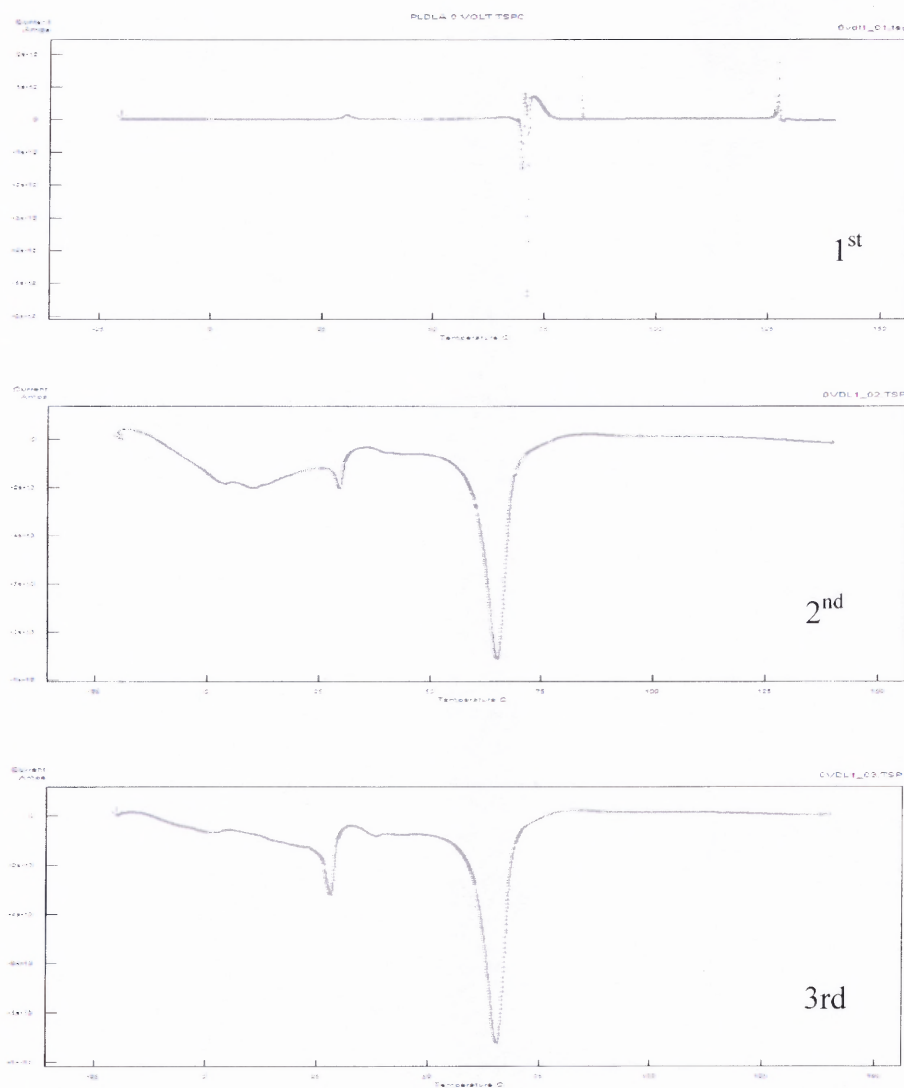


**Figure 5.7** DSC and TSPC analysis of first heating of poly(DTE) carbonate film.

### 5.2.2 TSPC for P(LcoDL)LA

Figure 5.8 represent the TSPC experiment ran for P(LcoDL)LA with no electric field. A similar pattern of behavior was observed like poly(DTE) carbonate where the first run produced different current pattern than the subsequent run. Current peaks are observed between 60 and 90 °C and again around 125 °C. The two runs that followed the first run

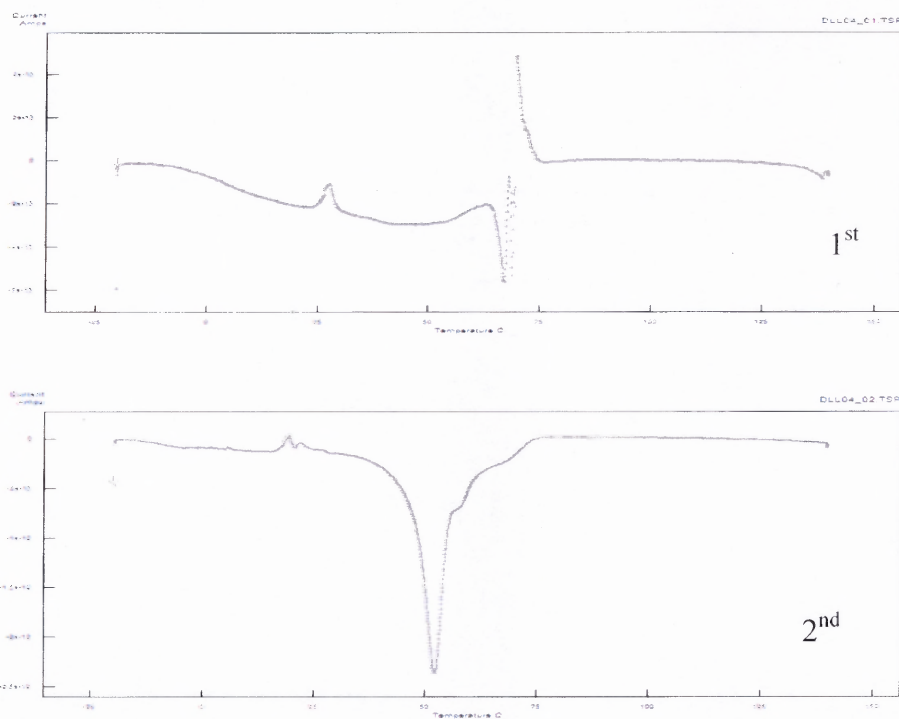
are different. The current peak observed at the 125 °C temperature position is not present. A current peak is observed below 25 °C for the second and third run.



**Figure 5.8** TSPC analysis of P(LcoDL)LA without an electric field.

The thermal event near 25 °C represents the solid-solid transition that occurs in Teflon film. When an electric field is used in the TSPC experiment in Figure 5.9, the locations

where the complex behaviors occur are similar to what is observed for the experiments without the electric field.

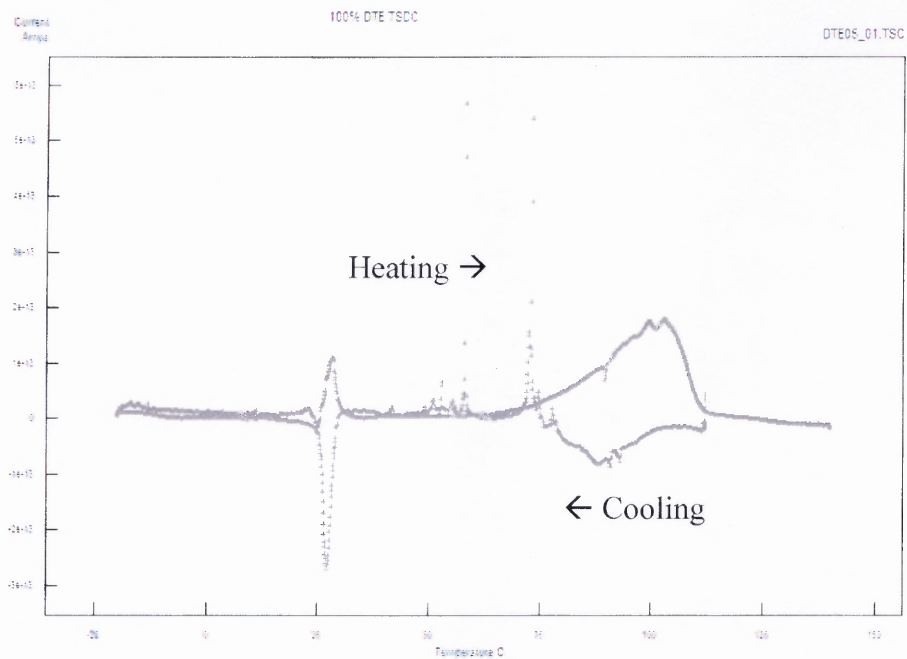


**Figure 5.9** First and second TSPC analysis of P(LcoDL)LA film with an electric field applied.

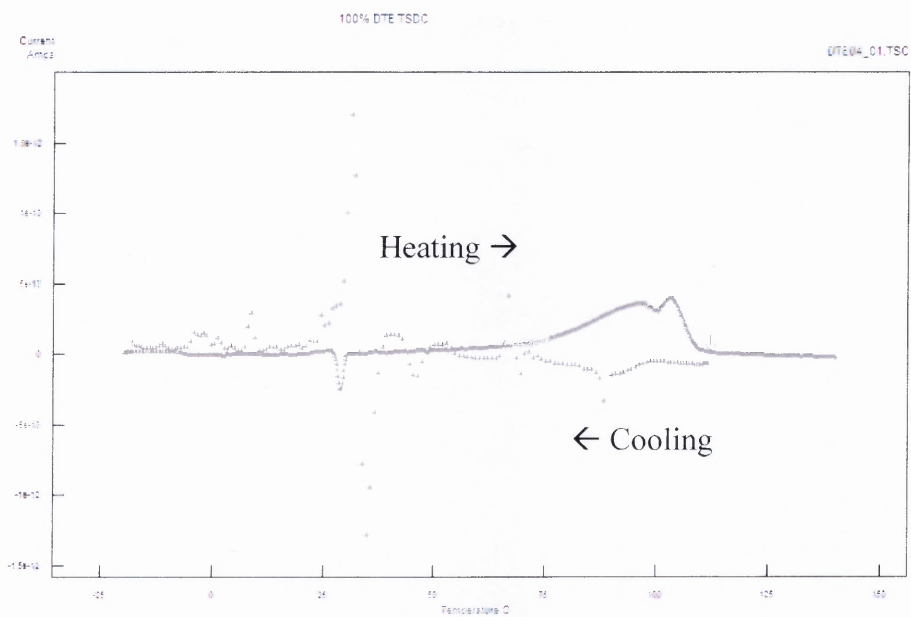
The similarity between the second run for the case where there is an electric field applied and the second and third run for the case where there is no electric field suggests that the behavior observed for the film might not depend totally on the motion of the dipole structure under the influence of an electric field, but has some dependence on the spontaneous rearrangement of the material's structure as it is heated.

### 5.2.3 Modified TSDC for Poly(DTE) Carbonate

The modified TSDC method was also used to characterize the behavior of poly(DTE) carbonate and P(LcoDL)LA. The results obtained from these experiments further confirm that the two components used to make blends are complex in their behavior. In the modified TSDC method, the current generated is read in the presence of the electric field as the material is being cooled and with the field removed as it is reheated. Cooling the presence of the field immobilizes the dipoles so that any current observed originates from some process other than dipole relaxation. This type of current can be considered as spontaneous current. In Figure 5.10A on cooling poly(DTE) carbonate film generated significant amount of current within 100-75 °C range. If two different specimens of film from the same sample are compared, the thermal events observed may vary slightly in detail, but overall they appear similar. Figure 5.10A and 5.10B compare the modified TSDC results for two specimens taken from the same film. In both cases there is an observable negative current on cooling and a positive current on heating.



**Figure 5.10a** The first run of the modified TSDC analysis for poly(DTE) carbonate film.



**Figure 5.10b** The second run of the modified TSDC analysis for poly(DTE) carbonate film.

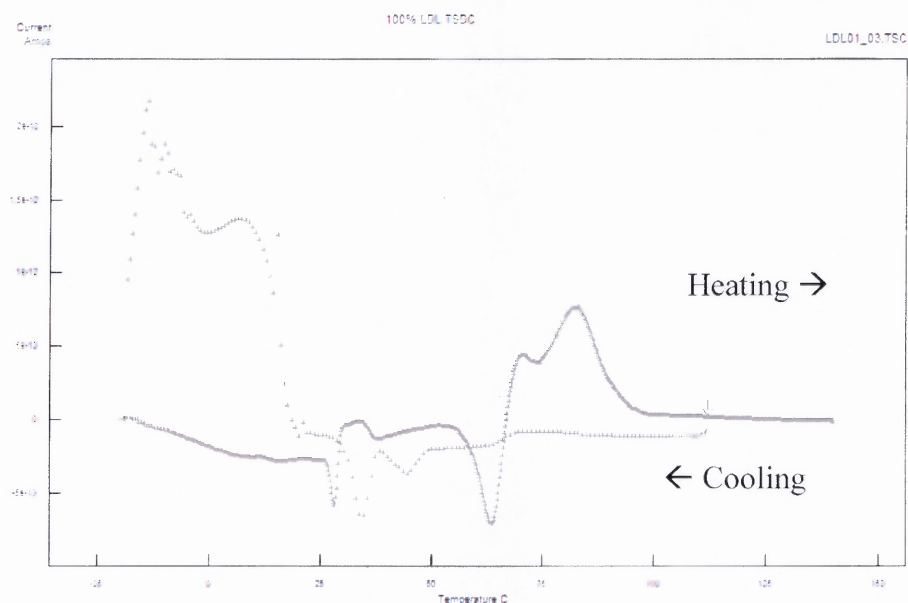


The occurrence of a current on cooling with the field immobilizing the dipoles suggests that either the dipoles spontaneously rearrange or that the material undergoes a mechanical relaxation. In order to distinguish between these two possibilities, a sample of poly(DTE) carbonate film was subjected to the modified TSDC program in successive runs. It is expected that mechanical stresses would be relieved on heating. As a consequence, if the spontaneous current observed on cooling originates from mechanical relaxation, it should not appear on the second run of the same specimen. Figure 4.27 and Figure 4.28 show the results of the same specimen subjected to two successive modified TSDC runs. In both a negative current is observed on cooling which suggests the spontaneous current originates from reorganization of the dipoles.

For the heating segment of the modified TSDC experiments a double peak is observed in the 75-100 °C range for all experiments on poly(DTE) carbonate. The DSC results for poly(DTE) carbonate film similarly showed a region where two thermal events could be observed. V. Tangpasuthadol et al. reported that the  $T_g$  for poly(DTE) carbonate was around 93 °C. The  $T_g$  was determined after the polymer was aged [20]. The enthalpic relaxation studies done by Tangpasuthadol et al. suggests that for poly(DTE) carbonate to reach its equilibrium state it has to be aged for about 108 min. Considering these results, an aging process might be necessary in order to attenuate or eliminate the complexities observed in the thermal analysis experiments.

### 5.2.4 Modified TSDC for P(LcoDL)LA

The results obtained for P(LcoDL)LA are also complex. Figure 5.12 shows the results when P(LcoDL)LA is subjected to the modified TSDC experiment.



**Figure 5.11** Modified TSDC analysis of P(LcoDL)LA film. Current is being generated in the lower temperature region of the cooling cycle. The peaks are also in either polarization position.

Figure 4.21 shows the result of the TSPC experiment in the absence of an electric field. Aside from the small peak in the range of 25-30 °C which is associated with the Teflon insulating film, there is a complex process that occurs in the range of 65-70 °C that is associated with the P(LcoDL)LA sample. When the same specimen is rerun as shown in Figure 4.22, the process in the 65-75 °C range now appear as a distinct, sharp negative peak. The fact that such a distinct process is observed in the absence of a field suggests that this is a spontaneous reorganization process. In Figure 4.29 and 4.30 the results are

shown for two successive modified TSDC experiments performed on the same specimen. In both cases on cooling a negative deflection in current in the vicinity of 65 °C followed by a small but distinct negative peak just above 50 °c. There is also a large positive current peak in the region between 20 °C and -25 °C. While it is difficult to assign these current peaks to specific molecular processes, it is apparent that substantial spontaneous current is generated in the sample on cooling. Figure 4.29 and 4.30 also show the current generated when the P(LcoDL)LA specimen was heated and the field was removed after being polarized. The observed behavior for the two runs is quite similar. A distinct negative peak at about 65 °C appears in both runs. The peak is strikingly similar to the spontaneous current peak observed in figure 4.22 for TSPC with no field. Above 65 °C a positive current event is observed as two closely spaced peaks. In the absence of a field the TSPC experiment is not expected to show any current generation at the T<sub>g</sub> unless there is a spontaneous reorganization process. When the TSPC results in Figure 4.22, the second heating in the TSPC experiment is compared with the second heating in the DSC experiment for P(LcoDL)LA in Figure 5.4, the small enthalpic recovery peak in the DSC just above the glass transition is in the same temperature range as the spontaneous current peak in the TSPC. The small enthalpic recovery peak observed in the DSC represents the calorimetric manifestation of the reorganization process; however, since the molecular motion responsible for that reorganization involves many dipolar structures, the current signature could be much larger.

In the TSDC experiments, it was observed that substantial spontaneous current was generated in the P(LcoDL)LA samples on cooling. If current observed in the TSPC experiments is indeed associated with the enthalpic recovery process, then the

spontaneous current observed on cooling in the modified TSDC experiments may be associated with the densification process produces enthalpic recovery. In the heating segment of the modified TSDC experiments, the current peak associated with enthalpic recovery can be observed. In addition, positive current peaks consistent with depolarization processes can be observed above the enthalpic recovery peak. In the DSC of the film sample of P(LcoDL)LA, there is nothing that can be associated with those TSDC processes. However, in the DSC of the P(LcoDL)LA pellets, complex processes are observed above the temperature of the enthalpic relaxation. It may be that these processes are calorimetrically weak in the film and cannot be observed but the motion of these processes produces detectable current in the TSDC.

### **5.3 Behavior of Blends**

The previous section focused on the component polymers, poly(DTE) carbonate and P(LcoDL)LA. The complex behavior seen for the component polymers that are used to make the poly(DTE) carbonate/P(LcoDL)LA blends are an indication of the behavior that might be expected for the blends. A closer look at the behavior of the individual polymers was warranted. Table 4.1 of the previous chapter compared the DSC results obtained when poly(DTE) carbonate was blended with P(LcoDL)LA, PLGA, and PLLA, respectively. The results obtained of the poly(DTE) carbonate/P(LcoDL)LA blends are an indication of the complexities of the component polymers. Two batches of the blends were made and compared for reproducibility. The results observed for batch one and two are dissimilar. For example, from table 4.1, the 50/50 blend of poly(DTE) carbonate and

P(LcoDL)LA, there are five temperature positions where thermal events are observed for the first batch. For the second batch, with the same blend ratio there were only two locations where thermal events are detected. Another key observation is the temperature where a number of the apparent "Tgs" are detected in some of the blends are well below and above where the apparent glass transition are determined for the component polymers. Two suggestions as to what might be happening in these cases are: one, a plasticizing and anti-plasticizing effects are taking place simultaneously with some of the blends as a result of the two polymers being partially miscible in each other. The results could indicate that one of the polymers is phase separating into block components and blending with the other in a non-uniform way to give different properties. The other possibility is that one of the component polymers are dominating the results obtained. The pieces of film used in the DSC experiment are small in size and selected from a film that is visibly non-uniform. It is likely that the composition varies for each separate specimen that is being tested. It is difficult to determine the plasticization of the blends are a result of poly(DTE) carbonate or P(LcoDL)LA. As observed from the modified TDSC the two polymers generate current peak at low and high temperatures.

Figure 9 represents the first and second heating of PLGA. Even though the polymer is composed of 75% lactide and 25% glycolide only one thermal event is observed when the DSC experiment was run. In Figure 4.10 for the PLGA solvent cast film, two thermal events are observed for the first heating in the DSC experiment indicating that the polymer is able to phase separate. The ability for the PLGA polymer to phase separate when solvent cast may have contributed to the results observed when it is blended with poly(DTE) carbonate. Similar outcomes are observed for the PLGA

blends if compared with the blends made of poly(DTE) carbonate and P(LcoDL)LA. The plasticizing/anti-plasticizing effects are seen for the 80/20 blend film. The number of temperature position where the apparent “Tgs” are located is different from batch one and batch two. If PLGA is phase separating into smaller composition of its constituent polymers, it may be that these smaller constituents are blending in a non uniform way resulting in the plasticization and anti-plasticization observed.

The PLLA blends are reproducible and showed none of the complexities previously observed for P(LcoDL)LA and PLGA. The results between batch 1 and batch 2 for poly(DTE) carbonate blended with PLLA are nominally the same. The number of apparent “Tgs” observed for each blend is the same for the two batches. The apparent “Tgs” determined are relatively the same except for the 60/40 blend. The PLLA polymer showed no complexities when solvent cast.

#### **5.4 Weight Loss Investigation for Poly(DTE) Carbonate and P(LcoDL)LA**

The component polymers and their blends showed rapid weight loss in TGA experiments. Weight loss was investigated for the Poly(DTE) carbonate, P(LcoDL)LA and the 40/60 and 60/40 blends that had the greatest weight loss. The results from the TGA experiment for the two component polymer and the two blend ratios selected were compared to the original TGA results. The specimens are heated at a rate of 5 °C/min to 200 °C for two consecutive runs. The second run is to observe any additional weight loss.

The original specimens weight losses observed are within the 4 to 5% range at the 150 °C. Table 5.1 shows the comparison of the duplicate specimen weight loss to the

originals. The duplicate specimens' weight loss falls within the 0.5 and 0.8 % range at this same temperature. The difference observed could be used in determining that the significance of the weight loss observed is the result of solvent from solvent cast process.

**Table 5.1** TGA Results for Weight Loss of Poly(DTE) carbonate/P(LcoDL)LA Polymer Blends

		Original Result		Duplicate 1 <sup>st</sup> Run		Duplicate 2 <sup>nd</sup> Run	
DTE	100 °C	1.88%	0.129mg	0.70%	0.031mg	0.13%	0.006mg
	150 °C	4.05%	0.278mg	0.72%	0.032mg	0.14%	0.006mg
P(LcoDL)A	100 °C	2.24%	0.080mg	0.27%	0.020mg	0.05%	0.004mg
	150 °C	2.77%	0.100mg	0.50%	0.037mg	0.05%	0.004mg
60% DTE	100 °C	3.20%	0.176mg	0.59%	0.053mg	0.07%	0.006mg
	150 °C	5.89%	0.323mg	0.74%	0.066mg	0.05%	0.004mg
40% DTE	100 °C	3.53%	0.139mg	0.48%	0.048mg	0.15%	0.014mg
	150 °C	5.22%	0.206mg	0.86%	0.085mg	0.15%	0.015mg

The table suggests that the rapid weight loss observed for poly(DTE) carbonate/P(LcoDL)LA blends are a result of significant amount of residual solvent within the films made.

### 5.5 Tensile Properties of Polymer Films

From the literature, it was observed that the storage modulus for poly(DTE) carbonate compressed mold films are about 2 GPa [20]. The dynamic mechanical analysis (DMA) was used in calculating the storage modulus as the temperature of the experiment was ramped from 0 °C to 140 °C. The dimensions of the films made were about 9x5x0.4 mm. The average modulus determined for poly(DTE) carbonate solvent cast film was 1 GPa. While the modulus determined from the solvent cast film is half what was determined for the compressed mold film, the result indicates that high tensile strength is possible with

the polymer. The difference in the value of the modulus is possibly a result of the difference in technique used for determining the modulus. The Instron machine computes the modulus for the material as the material is stretched beyond its yield point at room temperature. The DMA test was done over a broader temperature range while the polymer goes through flexural bending at a frequency of 1 Hz. From the DSC analysis in Figure 5.2, the first heating, the  $T_g$  observed was significantly lower than the powder form after the film was made. The  $T_g$  for the powder form was about 92 °C and after it was solvent cast the  $T_g$  dropped to about 62 °C. The lower  $T_g$  could suggest that the material has mechanically rearranged to another equilibrium state and as such is in a lower energy state. The average modulus determined for P(LcoDL)LA solvent cast film was about 1.4 GPa and that for PLLA and PLGA were both 1.4 GPa.

For the blends of poly(DTE) carbonate and P(LcoDL)LA the modulus range from 0.8 GPa for the 60/40 combination to 1.3 GPa for the 20/80 film. The blends made from the two component polymers decreased in modulus as the composition of poly(DTE) carbonate was increased. This could be a result of weak adhesion forces at the surface of the two polymers. The blend combinations of poly(DTE) carbonate and PLLA also generated tensile properties similar to the parent polymers. Modulus as high as 1.6 GPa was determined from the Instron experiments. The lowest modulus determined for the PLLA blend combination was 0.95 GPa for the 80/20 combination. The PLGA blends had the lowest modulus from the tensile tests. Modulus as low as 0.65 GPa was recorded. The modulus for the 50/50 and 60/40 poly(DTE)/PLGA blends were not possible because the mechanical integrity of the films were compromised by the poor adhesion of the parent polymers at their interface. The films consisted of circular



aggregates of the polymers that break apart from the film. The low modulus determined for the PLGA blends is a result of the weak adhesion force between the two polymers.

The results obtained from the tensile test for all the blends are an indication that there are some combinations of the parent polymers that have strong adhesion at their interfaces to give mechanical results similar to the parent polymer that make the blends. The PLGA blends can be said to be least likely to form miscible or partially miscible blends with poly(DTE) carbonate. The results are confirmed from the observation made that agglomerates of one polymer to the other is the result when PLGA is combined with poly(DTE) carbonate by the solvent cast method.

## CHAPTER 6

### CONCLUSION

Poly(DTE) carbonate is an ideal polymer for many biomedical applications. Research have determined that the polymer possess good osteoconductive properties [1]. From mechanical studies done by Tangpasuthadol et al, the polymer mechanical properties would make its contribution to the orthopedic field very valuable. The compression mold films were determined to generate modulus in the range of 2 GPa [20]. With the high strength that is characteristics of the material, it is likely that the polymer could be use in medical device application where high stresses would be imposed on the material, for example in bone replacement devices.

The high cost for the polymer is a set back to the research and development of novel ideas and products for the material. One idea to reduce the expenses is to blend the polymer with other polymers that are known for their osteoconductive properties, biocompatibility and all around known to be “generally regarded as safe” (GRAS) materials by the FDA. These GRAS materials are the polyesters made from lactic and glycolic acids.

The DSC results for the two batches of blends suggest that there are reproducibility issues in obtaining similar results when the same blends combination from the two batches are compared for most of the blends. For instance the 50/50 blend for batch 1 of the poly(DTE) carbonate/P(LcoDL)LA blends showed as much as five thermal events occurring for the film. When the same blend ratio for batch 2 is compared to batch 1, only two thermal events are seen. The PLGA blends are behaving in a similar

manner where the number of thermal events varies for similar blend ratio for the two batches and the temperature where the events occurred are not the same in most cases. Only the PLLA blends have the same number of events occurring and at similar temperature for the two batches.

Poly(DTE) carbonate is a complex polymer. The DSC results for the powder form showed a two event occurring at 70 °C and above 90° C for the first and second heating of the polymer. When the polymer was solvent cast, the event at 70 °C was not observed in the first heating of the solvent cast film, only one event at about 65 °C is observed. This observation suggests that poly(DTE) carbonate is easily plasticized to lower energy state. For the second heating cycle of the DSC experiment the material rearranges and two events at 83 °C and 94 °C is observed. For the modified TSDC experiment, on cooling, the electric field is on to immobilize the dipoles. The results of the same specimen subjected to two successive modified TSDC runs in both cases a negative current is observed on cooling which suggests the spontaneous current originates from reorganization of the dipoles. On removing the field and heating the specimen a twin current peak is generated in close proximity of each other, similar to what is observed in the DSC results for the second heating cycle of the film.

The tensile properties determined for most of the blends made from P(LcoDL)LA and PLLA are similar to what was determined for 100% poly(DTE) carbonate. Economically it is an advantage to use the blends, however, reproducibility of the blends are an issue. There is no advantage in making blends with PLGA because of the poor adhesion with poly(DTE) carbonate.

## **FUTURE WORK**

Further characterization studies is needed to fully understand the behavior of poly(DTE) carbonate. It was suggested that poly(DTE) carbonate dipoles are rearranging spontaneously during the cooling cycle of the modified TSDC experiment. To prove if this is correct the modified TSDC experiment can be run multiple times and increasing the voltage across the face of the film in each run. Increasing the voltage will increase the intensity of the electric field on the specimen. The field will cause more dipoles to be in the vicinity where spontaneous activity is observed. More dipoles in the vicinity will result in the increase in length of the current peak.

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