

**PREPARATION AND CHARACTERIZATION OF PDLLA-PCL-STARCH
BLENDS PROCESSED UNDER MICROWAVE RADIATION**

*Submitted in partial fulfillment of the requirement for
the award of degree of*

**MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING**

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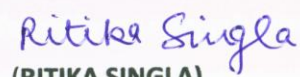
DEPARTMENT OF CHEMICAL ENGINEERING

THAPAR UNIVERSITY

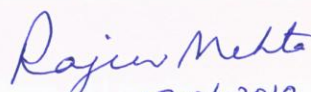
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DECLARATION

I hereby declare that the thesis entitled "PREPARATION AND CHARACTERIZATION OF PDLLA-PCL-STARCH BLENDS PROCESSED UNDER MICROWAVE RADIATION" is an authentic record of my study carried out as requirements for the award of degree of **M.Tech (Chemical Engineering)** at **Thapar University, Patiala**, under the guidance of **Dr. Rajeev Mehta**, Associate Professor in department of Chemical Engineering, Thapar University, Patiala during **July 2009 to June 2010**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.


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This is to certify that above declaration made by the student concerned is correct to the best of my knowledge and belief.


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ABSTRACT

Properties of the biodegradable polymers like PDLLA and PCL can be modified by blending them with each other and with other polymers like Starch. In the present study we have prepared blends of PDLLA, PCL and Starch in different proportions and then subjected to microwave radiation. Using microwave, time of reaction has been reduced to 3-30 min as microwave is associated with more even distribution of heat. To characterize the blends various techniques like FTIR has been used.

On blending the PDLLA, PCL and Starch in various ratios using chloroform as a solvent and subjecting the mixtures to microwave radiation, it becomes clear from FTIR spectra that O-H and C=O regions of the blend show significant variance after microwave irradiation compared to the parent polymers. The results indicate a direct linkage between the polymers indicating the formation of a chemical linkage between the two molecules as opposed to just a physical blend.

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CHAPTER – 1
INTRODUCTION

1.0 BACKGROUND

In recent years, the massive use and disposal of petroleum-based plastics has seriously caused public affairs over the environmental hazards. The main strategies to address these problems are to develop materials that are renewable, degradable, and recyclable, better known as “green materials,” [Chen et al., 2003] as alternatives to the petroleum-based materials. The biodegradable PLA has attracted increasing attention as a candidate for use in industrial applications since it possessed excellent mechanical properties (especially in tensile strength and modulus) and was produced with corn or other starches as the starting raw material. Also these biodegradable polymers have wide applications in an environmentally friendly packaging, biomedical materials, in various industrial applications such as computer and mobile phone industry. The most popular and biodegradable polymers are aliphatic polyesters, such as polycaprolactone (PCL), polylactic acid [Spevacek et al., 2007].

However since these polymers are still expensive and do not match all the technical requirements for possible applications, blends of these polymers with starch, which is a cheap abundant source are used. The PCL, a ductile biodegradable polymer, can be used to tune the PLA from rigid to ductile material. In the present study, to overcome the limitations (brittle and high price) of polylactide (PLA), it is proposed to prepare and characterize ternary blends composed of PLA, PCL, and starch using microwave radiation.

1.1 CONVENTIONAL BLENDS

1.1.1 Mechanical Mixing of Polymer Blends

Most commercial polymer alloys and blends are prepared by mechanical mixing, largely because of its simplicity and low cost. The preferred industrial method of mechanical mixing is to use a screw compounder or extruder that can be run continuously and generate a product in a convenient form for further processing. Not surprisingly, much effort has gone into trying to understand the flow of polymer blends.

1.1.2 Conventional Blending and In-situ Polymerization Blending

Other methods for forming blends such as by evaporation of a solvent or by polymerization of a monomer in the presence of a polymer involve at least three components in the

preparation process. Mixing in a common solvent followed by its removal is a convenient way of making blends on a laboratory scale, but has obvious commercial disadvantages due to the cost and difficulty of solvent recovery as well as the potential environmental hazards associated with handling large volumes of often toxic chemicals. (Source: <http://pubs.acs.org/doi/pdf/10.1021/bk-1989-0395.ch001>).

1.2 Fundamentals of Microwave Radiation

Microwave frequency occupies a place in the electromagnetic spectrum between radio frequencies and infrared radiation with the frequencies of 300 GHz to 300 MHz, which corresponds to the wavelengths of 1 mm to 1 m respectively.

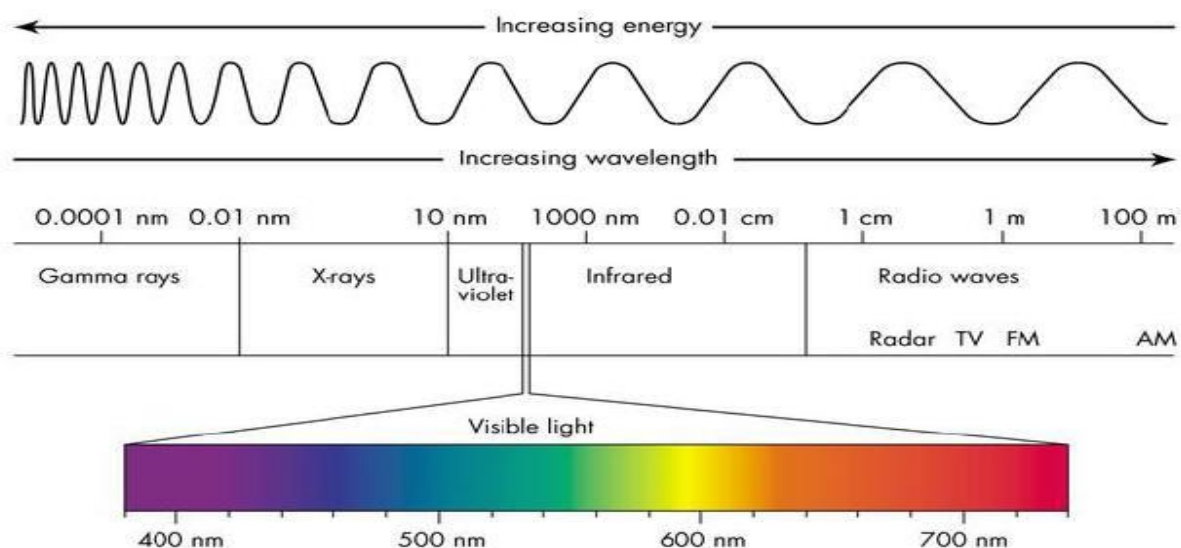


Fig. 1.1 Electromagnetic Spectrum

(Source: www.antonine-education.co.uk/physics_gcse/Unit_1/Topic_5/em_spectrum.jpg)

The most common microwave applicators (i.e. domestic microwave ovens) use the frequency of 2.45 GHz.

1.2.1 Interaction of microwaves with materials

The mechanism of energy transfer in a microwave is significantly different from a heating mantle. Microwave energy heats the sample through direct activation. In the microwave, energy is transferred to the reaction components within the solution.

There are two components of a microwave: an electric field and a magnetic field. The electric field will interact with any molecule that has a dipole or that is ionic. The electric component causes heating by two main mechanisms:

- (i) Dipole polarization
- (ii) Ionic conduction

When exposed to microwave frequencies, the molecular dipoles align in the applied electric field. As the applied field oscillates, the dipole field attempts to follow these oscillations and the energy is lost in the form of heat through molecular friction. The amount of heat generated is directly related to the ability of molecules to align itself with the frequency of the applied field.

The second major heating is by ionic conduction. The dissolved charged particles in a sample oscillate back and forth under the influence of the electric component of microwave radiation. They collide with their neighboring molecules or atoms. These collisions cause agitation or motion creating heat.

1.2.2 Advantages of Microwave heating over conventional Heating

Conventional heating is normally performed through a heated surface and therefore is governed by the temperature of that source. Also heating is limited by the physical properties of the material such as density, heat capacity, thermal conductivity etc. Microwave on the other hand is associated with a more even distribution of heat that leads to easier control over the temperature profile in the heated material.

1.2.3 The extent to which material is heated depends on two parameters

- **Dielectric constant (ϵ')** :- It tells the ease with which a material is polarized by an electric field.
- **Dielectric Loss (ϵ'')** :- It tells the efficiency with which the electromagnetic radiation is converted into heat.

$$\tan\delta = \epsilon'' / \epsilon'$$

where, $\tan\delta$ is the ability to absorb and convert electromagnetic energy into thermal energy at a given temperature and frequency.

1.2.4 Areas where microwave heating is used

- Synthesis of polymers
- Making polymeric blends to get the desired properties, etc
- Process for the disposal of plastic wastes
- Regeneration of activated carbon
- Ceramic industry

1.2.5 Acceleration of polymerization reactions under microwave radiations

The application of microwave is attractive because a number of reactions can be carried out with a substantial reduction of reaction time in comparison to conventional processes. Reactions that usually take many hours or days can, under the influence of microwave radiations be run in a considerably shorter time of several minutes or even seconds. There are various theories regarding this:-

One of the theories says that the kinetics and mechanism of the reactions are still the same. The reduction of reaction time is the result of sudden and sometimes uncontrollable temperature growth of the reaction mixture under microwave radiation, which increases the rate of reaction following the common kinetics laws.

Other theory says that there is an increase in the polarity of the reaction system by development or increase of dipole moment, which results in the acceleration of the reaction due to a stronger interaction of microwaves with the reagents during the course of reaction.

Fig. 1.2 shows a comparison of conventional and microwave heating. In conventional heating, heat flow is initiated on the material's surface and the rate of heat flow into the center is dependent on the material's thermal properties and the temperature differentials.

In microwave there is an even distribution of heat that leads to easier control over the temperature profile in the heated sample.

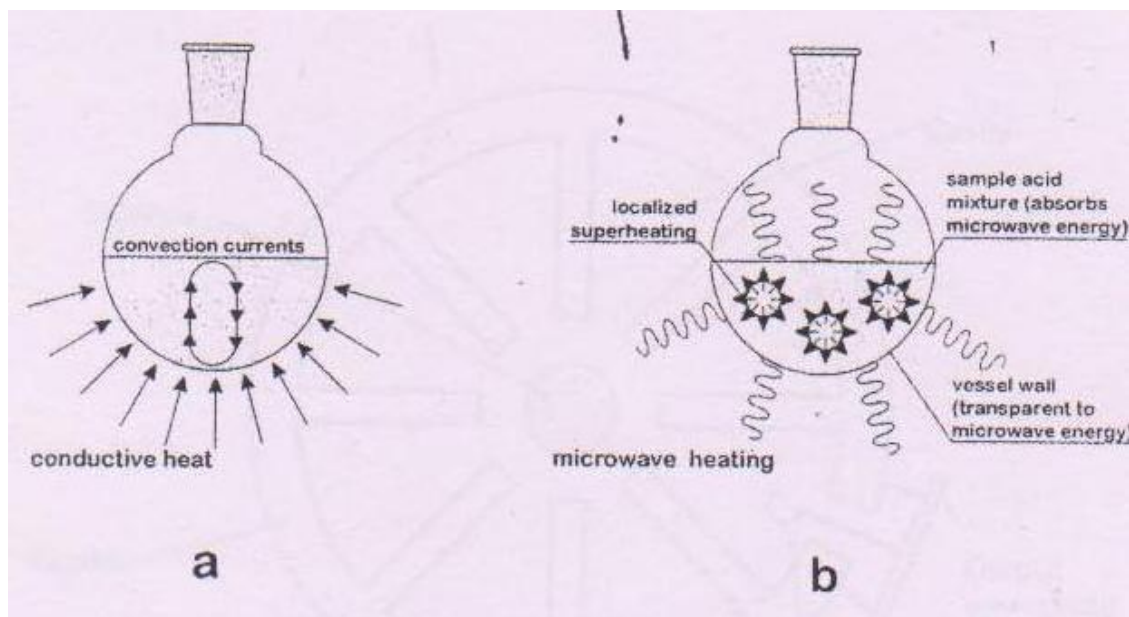


Fig. 1.2 Different Heating mechanisms for (a) conventional and (b) microwave heating

So activation energy is lowered and it is believed that it affects the selectivity by promoting the favorable reactions so it increases the yield of products [Bogdal, et al, 2007]

1.3 Polylactic acid

Poly(lactic acid) (PLA) is a degradable polymer derived from renewable sources (mainly starch and sugar). It is a polymer with a future. Until the last decade, the main uses of PLA have been limited to medical applications such as implant devices, tissue scaffolds, and internal sutures, because of its high cost, low availability and limited molecular weight. Recently, new techniques, which allow economical production of high molecular weight PLA polymer, have broadened its uses. Since PLA is compostable and derived from sustainable sources, it has been viewed as a promising material to reduce the societal solid waste disposal problem. PLA lifecycle is shown in fig. 1.3. Its low toxicity, along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and for other consumer products. The polymer can be processed to replace less environmentally friendly petroleum-based polymers, such as polystyrene or polyethylene. This allows the production of a wide spectrum of PLA polymers to match performance requirements. PLA has reasonably good optical, physical, mechanical, and barrier properties compared to existing petroleum-based polymers [Lim et al., 2008].

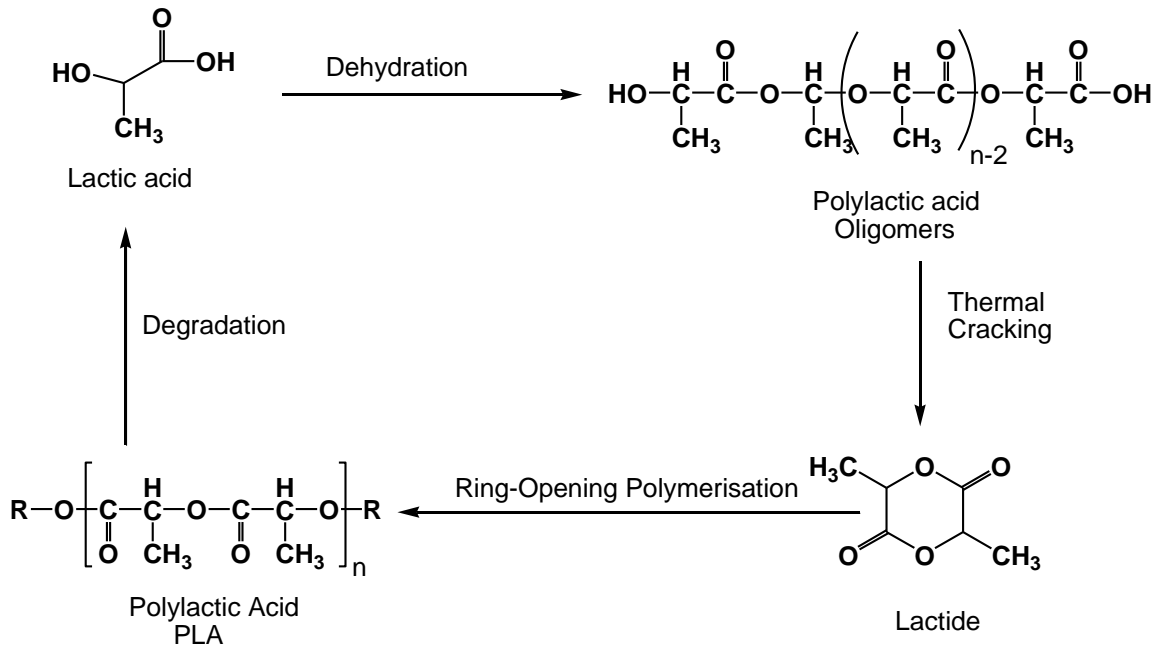


Fig. 1.3 PLA lifecycle

1.4 Polycaprolactone

Polycaprolactone is a biodegradable thermoplastic polymer derived from the chemical synthesis of crude oil. Although not produced from renewable raw materials, it is fully biodegradable. It has good water, oil, solvent and chlorine resistance. It has a low melting point (58-60 °C) and low viscosity, and it is easy to process. It is used mainly in resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopaedic splints, and fully biodegradable compostable bags, sutures, and fibres.

Fully biodegradable, the low melting point makes the material suited for composting as a means of disposal, as the temperature obtained during composting routinely exceeding 60 °C. Degradation time is very short. In Sweden there has been an attempt to produce PCL bags, but they degraded before reaching the customers. Polycaprolactone is often mixed with starch to obtain a good biodegradable material at a low price The mix has been successfully used for making trash bags in Korea (Yukong Company).

(Source: <http://designinsite.dk/htmsider/m0954.htm>)

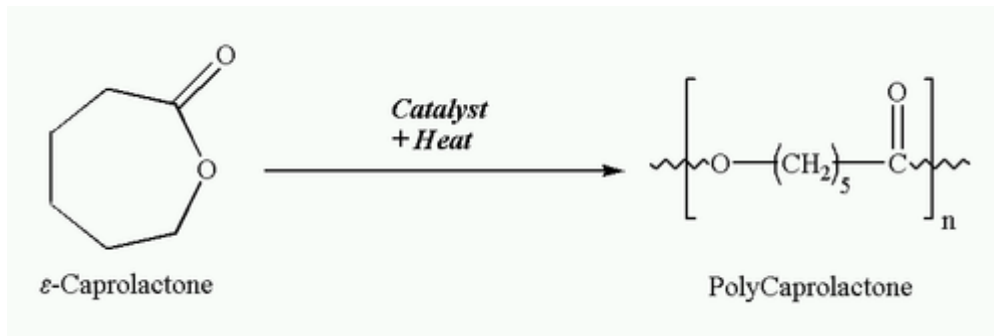


Fig. 1.4 Synthesis of Polycaprolactone

(Source: <http://www.absoluteastronomy.com/topics/Polycaprolactone>)

1.5 Starch

Starch is a natural polymer found in granular form in a variety of plants such as potato and corn. Starch is composed of two glucan chains (amylose and amylopectin). These polymers have the same basic monomer but differ in their length and degree of branching, which ultimately affects their physicochemical properties. Amylopectin consists of granules that are more crystalline, denser and more resistant to penetration by water and to enzymatic action than amylose. The chemical structure of starch varies, depending on its origin, and may contain branched chains of various lengths, phosphate derivatives and peculiar functional states. These structural and functional variations make starch suitable for many applications. Starch is hydrolyzed to glucose, maltose by enzymes [Rosa, et al, 2005].

CHAPTER-2
LITERATURE REVIEW

2.1 Conventional Blending

2.1.1 Conventional Blending of PLLA and PCL

Blend of PCL and PLLA is well investigated which is usually fabricated as a film by solution casting because PCL and PLLA are immiscible in their blend when it is made by a compression moulding method and they degrade at high temperature and pressure [Jin and Liu, 2004].

2.1.2 Conventional Blending of PLA, Polycaprolactone and thermoplastic starch

Study revealed that PLA could be tuned from rigid to ductile by incorporating PCL using the melt blending method, and that the cost of PLA/PCL blends could be further reduced by the addition of starch [Liao and Wu, 2009].

Binary and ternary blends of PLA, PCL and thermoplastic starch (TPS) are prepared using a one-step extrusion process. The ternary blend results in an even greater ductility as compared to pure PLA. The mechanical properties for the ternary blend clearly indicate a synergistic effect that exceeds the results obtained for any of the binary pairs. Overall the ternary blend approach (PLA/PCL/TPS) gives us the expanded property range of PLA materials [Sarazin et al, 2007].

2.1.3 Microwave Blending of PCL and PLLA

PLLA and PCL blends have been fabricated by solution casting under microwave irradiation. The results obtained were totally different from the blends obtained by conventional methods. The blend was more homogeneous and degradation time of a PCL plank by *Pseudomonas lipase* was significantly retarded [Jin and Liu, 2004].

2.2 Characterization

2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

It is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR can be used to

identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques (Source: <http://www.wcaslab.com/TECH/tbftir.htm>).

2.2.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. (Source: http://en.wikipedia.org/wiki/Differential_scanning_calorimetry)

2.2.3 Nuclear magnetic resonance (NMR)

It is a property that magnetic nuclei have in a magnetic field and applied electromagnetic (EM) pulse or pulses, which cause the nuclei to absorb energy from the EM pulse and radiate this energy back out. The energy radiated back out is at a specific resonance frequency, which depends on the strength of the magnetic field and other factors. This allows the observation of specific quantum mechanical magnetic properties of an atomic nucleus. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals and non-crystalline materials through NMR spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI). (Source: http://en.wikipedia.org/wiki/Nuclear_magnetic_resonance)

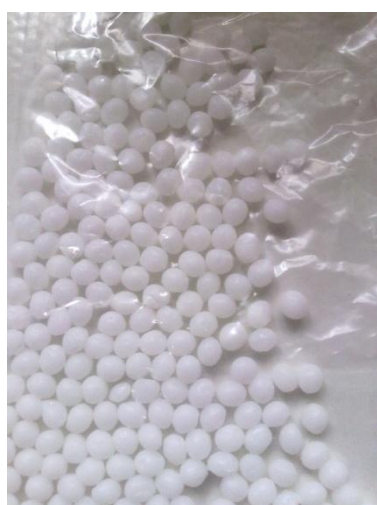
CHAPTER-3
EXPERIMENTAL WORK

3.0 Materials and Experimental procedure

3.1 Materials

The Polycaprolactone(PCL), Poly-D-L Lactic acid (PDLLA) (Viscosity Index 0.18dL/g), Starch and Chloroform is used without further purification or processing.

Polycaprolactone granules are white in color and each Polycaprolactone granule weighs approximately 0.03g. Melting point is around 60°C. Original pictures of PCL and Starch are shown below:



PCL



STARCH

Fig 3.1 Original pictures of PCL and Starch

3.2 Apparatus

The apparatus used for blending was a LG domestic microwave oven.

Specifications:

Model No.- MC 8048 WR

Input- 230 V

Microwave-1350 W

Frequency(ν)- 2450 MHz

It has a variable power levels from 120W to 900W

3.3 Polymer Blending

The PDLLA/PCL/Starch blends were prepared by the following procedure:

PDLLA, PCL and starch were dissolved in chloroform separately. Different groups of solutions were made mixed in different ratios to obtain a wide range of blend composition as listed in table below.

A: Blend composition:

I	PDLLA (100%)
II	PCL (100%)
III	Starch (100%)

B: Blend Composition:

I	PCL (50%) +PDLLA (50%)
II	PCL (50%) + Starch (50%)
III	PDLLA (50%) + Starch (50%)
IV	PCL (33.33%) + PDLLA (33.33%) + Starch (33.33%)

C: Blend Composition:

I	PCL (33%) + PDLLA (67%)
II	PCL (33%) + Starch (67%)
III	PDLLA (33%) + Starch (67%)

D: Blend Composition:

I	PCL (67%) + PDLLA (33%)
II	PCL (67%) + Starch (33%)
III	PDLLA (67%) + Starch (33%)

These solutions were subjected to ~120 W power microwave irradiation for a predetermined amount of time (30min). Chloroform being a solvent that has a low dielectric constant at 2450 MHz is not a good absorber of microwave and hence provides a cooling effect by draining the heat from the microwave absorbing PDLLA, PCL and starch and in this process evaporated rapidly. Solid PDLLA/PCL/Starch blends having a good structural stability were obtained for FTIR measurements.

CHAPTER-4

RESULTS

4.0 Results

The FTIR spectra of neat polymers and their blends with different compositions were obtained.

The FTIR spectra of all the blends with different compositions are shown below

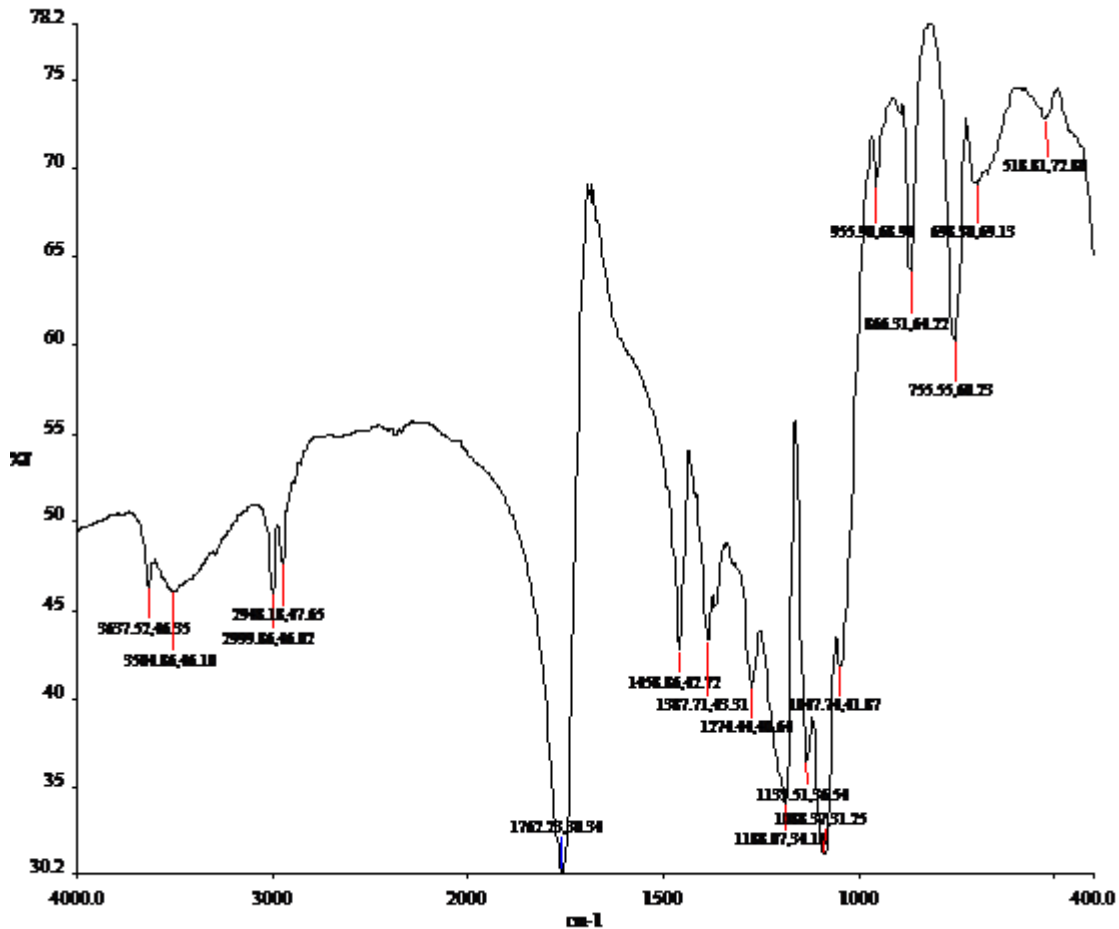


Fig 4.1: FTIR spectra of pure PDLLA after microwave treatment.

The peaks located at 2999, 2948 cm^{-1} were assigned to the stretching vibration of CH_2 ; the peak at 1762 cm^{-1} was assigned to C=O bonds and the peak at 3504 cm^{-1} was assigned to O-H bond of PDLLA.

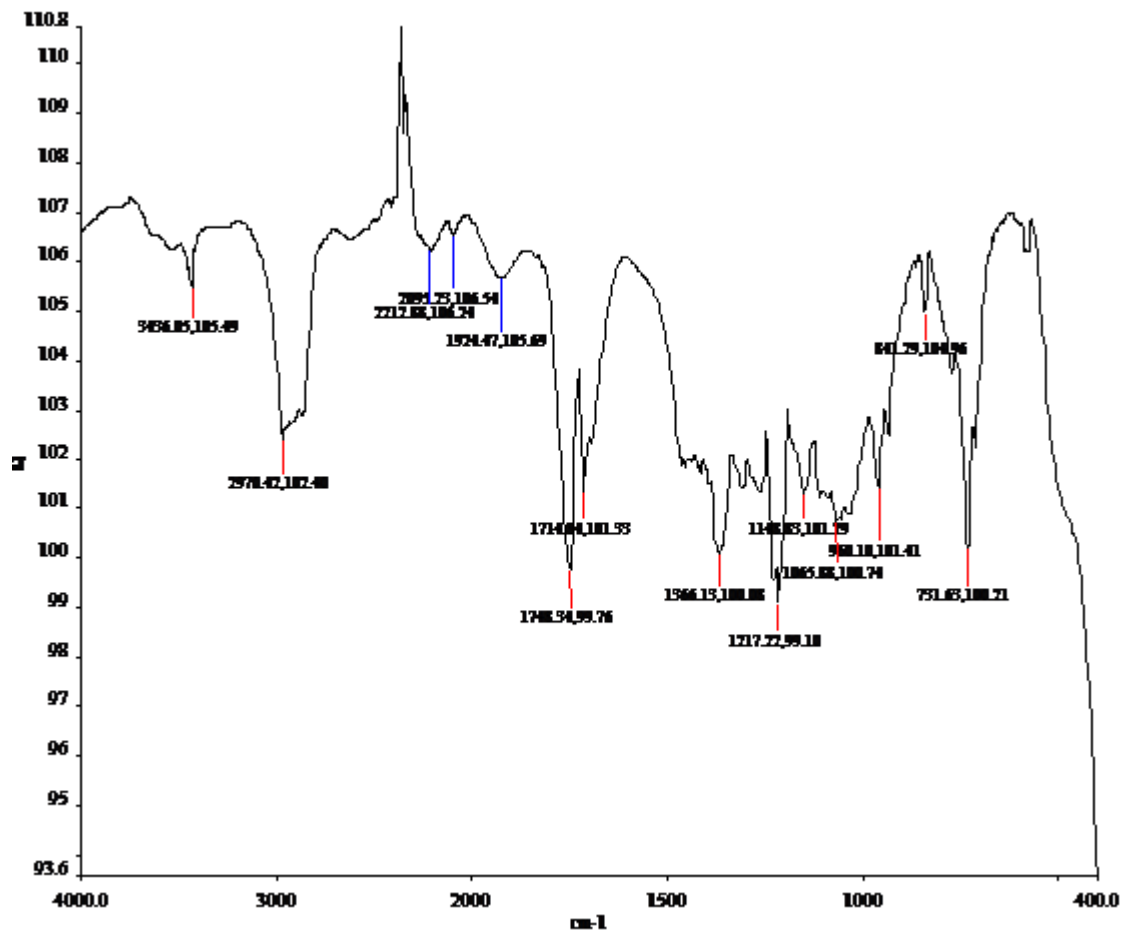


Fig 4.2: FTIR of pure PCL after microwave treatment

The peaks located at 2970, 2864 were assigned to the stretching vibration of CH_2 ; the peak at 1748 cm^{-1} was assigned to $\text{C}=\text{O}$ bonds of PCL.

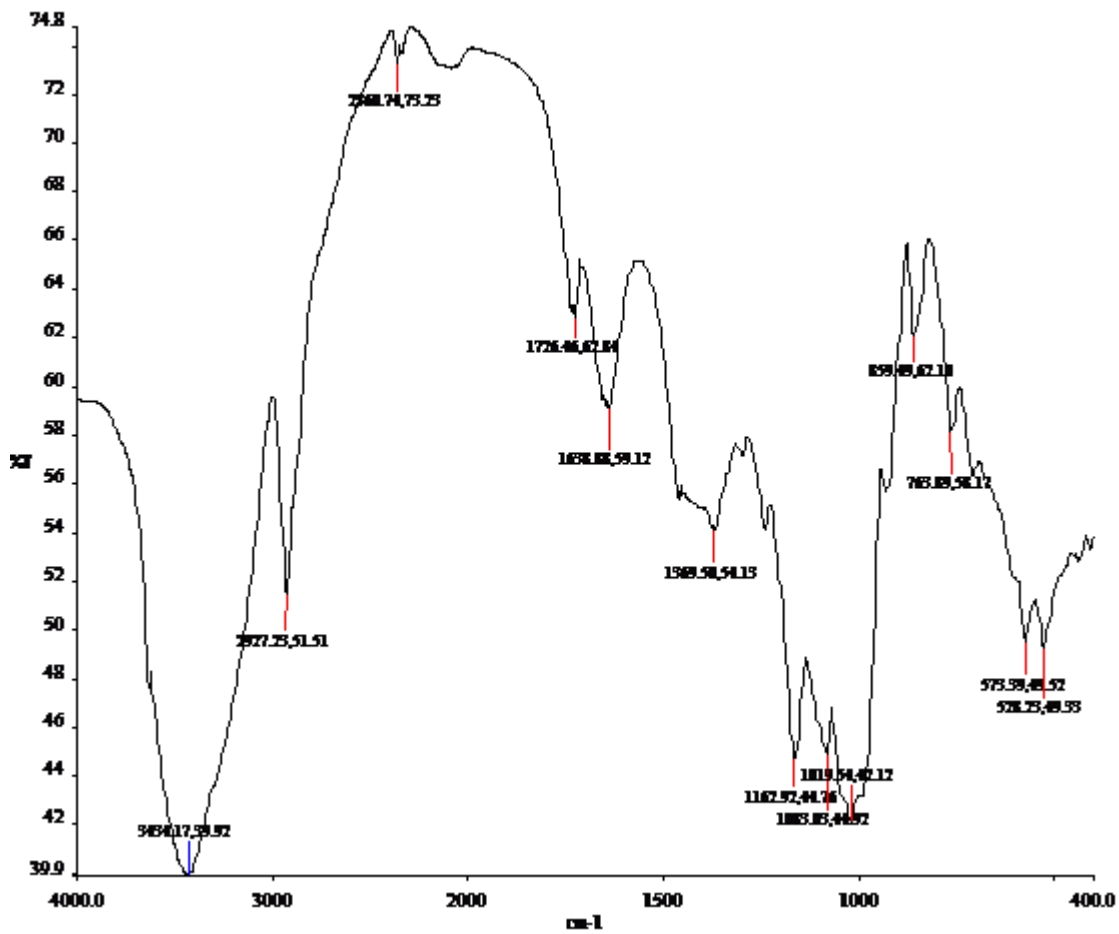


Fig 4.3: FTIR spectra of pure Starch after microwave treatment

The spectrum of the starch showed a strong band at 1019 cm^{-1} which is corresponded to C-O group, and broad bands in $1398\text{-}1369\text{ cm}^{-1}$ region which correspond to symmetrical bands of C-H group.

The peak located at 3434 cm^{-1} was assigned to O-H group.

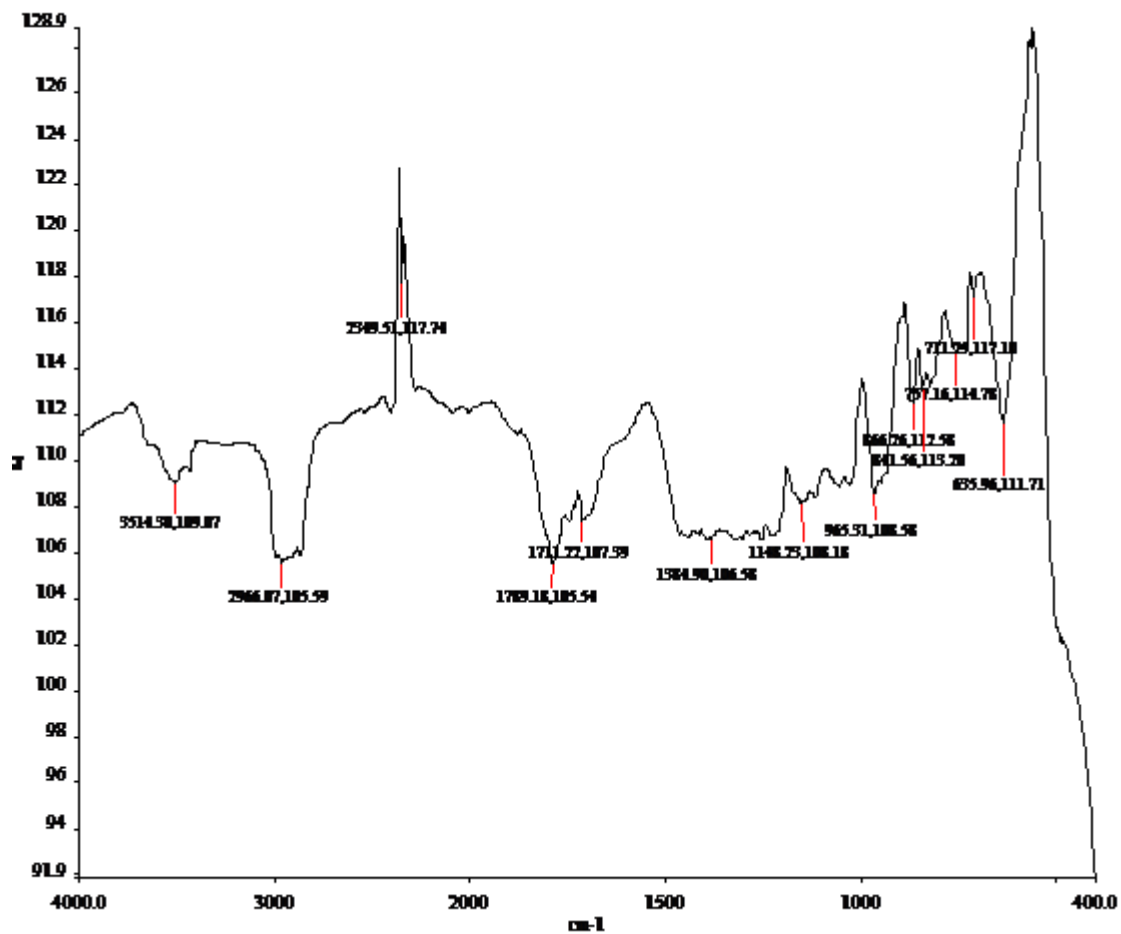


Fig 4.4: FTIR spectra of PDLLA/PCL blend with 50-50% composition after microwave treatment.

The peaks located at 2996, 2998 cm^{-1} were assigned to the stretching vibration of CH_2 ; the peak at 1789 cm^{-1} was assigned to $\text{C}=\text{O}$ bonds and the peak at 3514 cm^{-1} was assigned to $\text{O}-\text{H}$ bond of the blend.

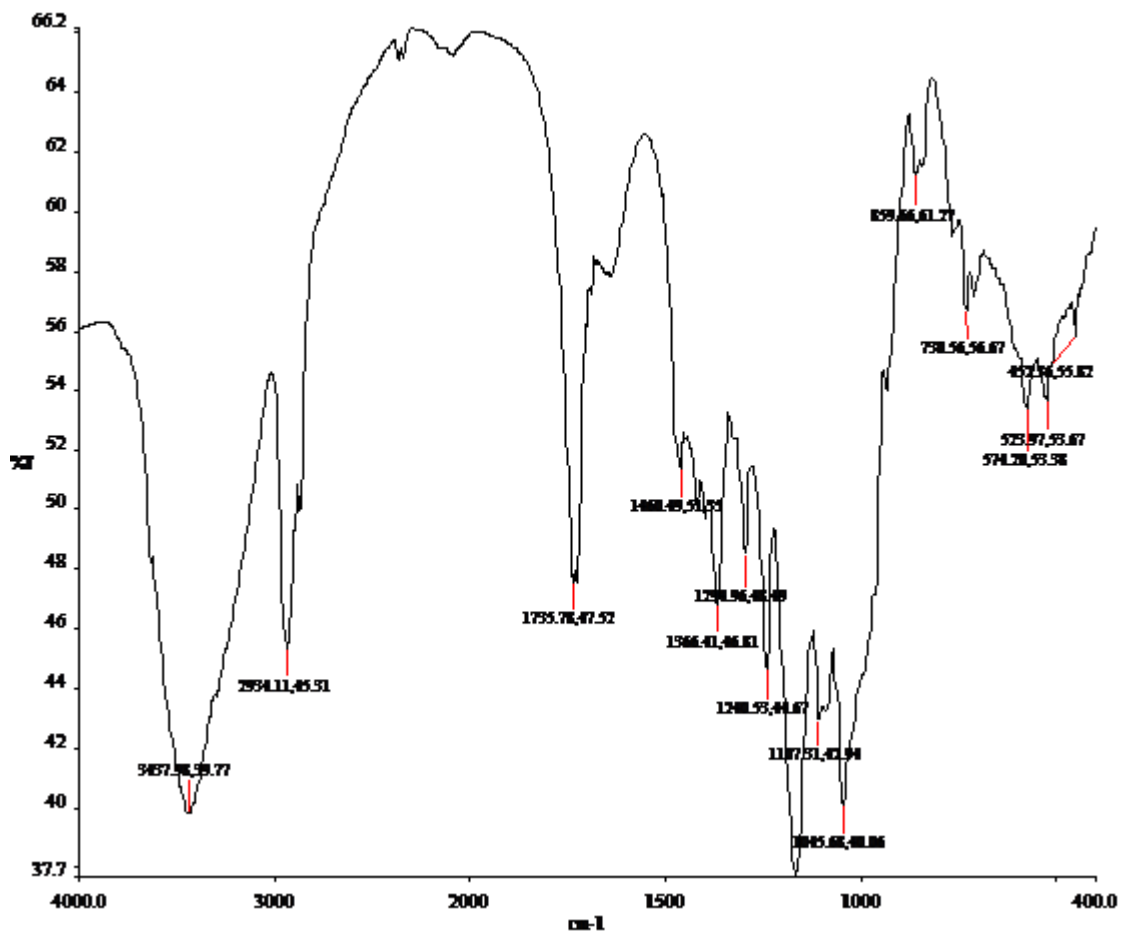


Fig 4.5: FTIR spectra of PCL/Starch blend with 50-50% composition after microwave treatment

The spectra of PCL/Starch blend with 50-50% composition shows a peak of C=O at 1735 cm^{-1} and a peak of O-H at 3437 cm^{-1}

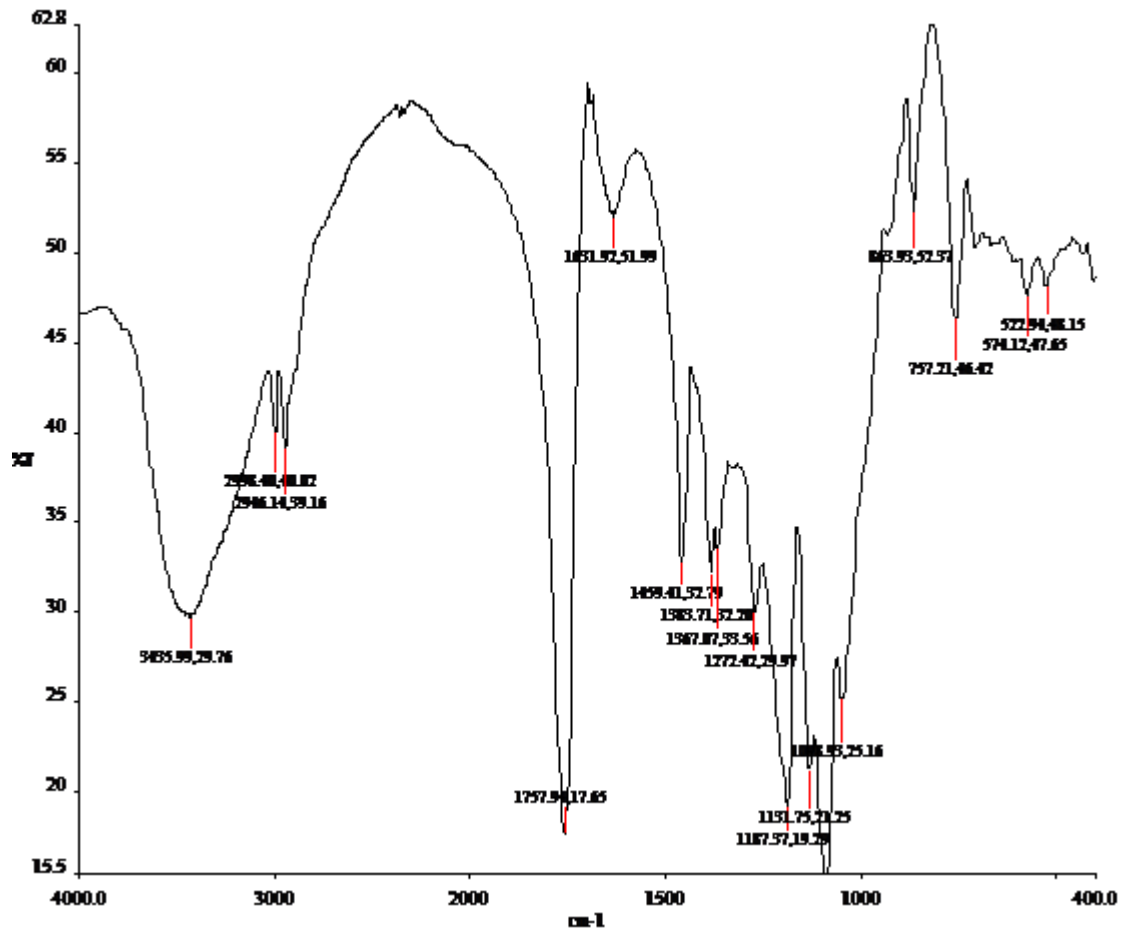


Fig 4.6: FTIR spectra of PDLLA/Starch blend with 50-50% composition after microwave treatment

The spectra of PDLLA-Starch blend with 50-50% composition shows a peak of C=O at 1757 cm^{-1} and a peak of O-H at 3435 cm^{-1}

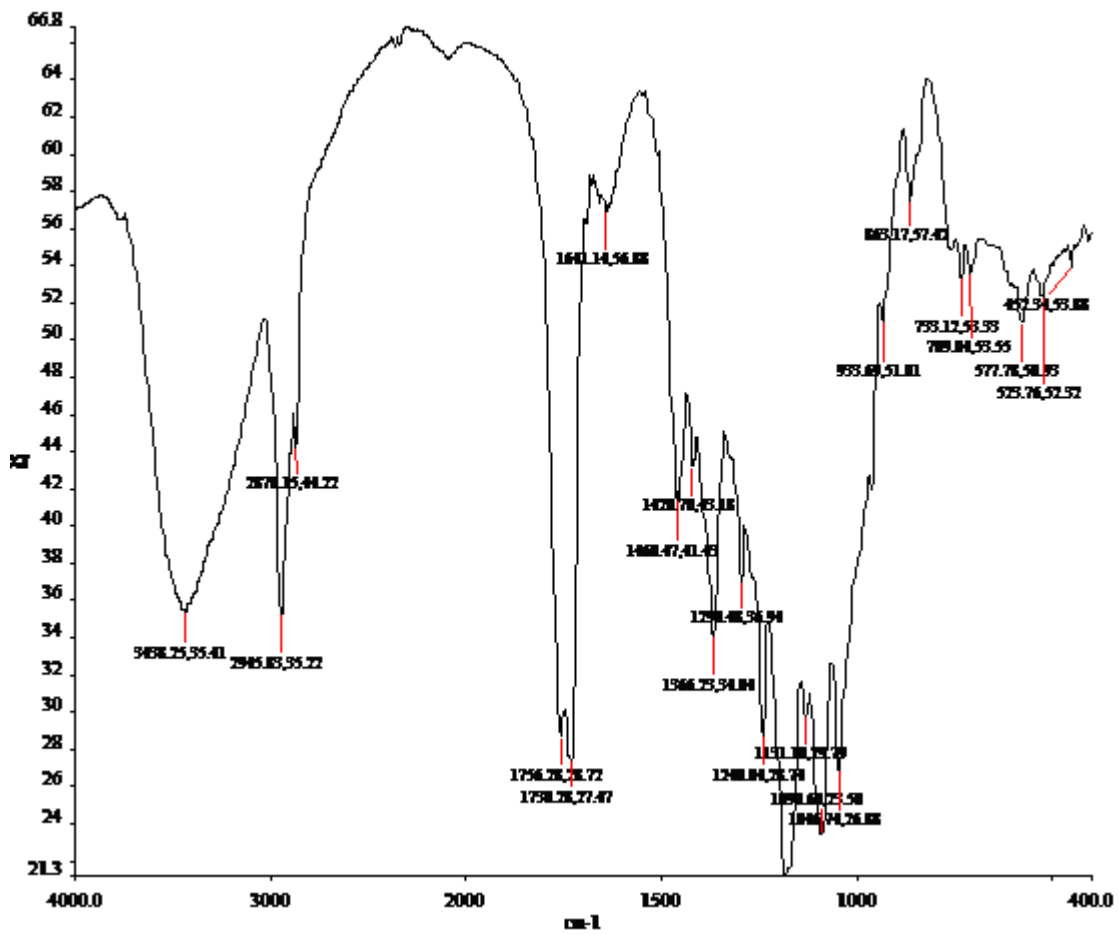


Fig 4.7: FTIR spectra of PDLLA/PCL/Starch blend (one-third each) after microwave treatment

The spectra of PDLLA/PCL/Starch blend shows a peak of C=O at 1730 cm^{-1} and a peak of O-H at 3438 cm^{-1}

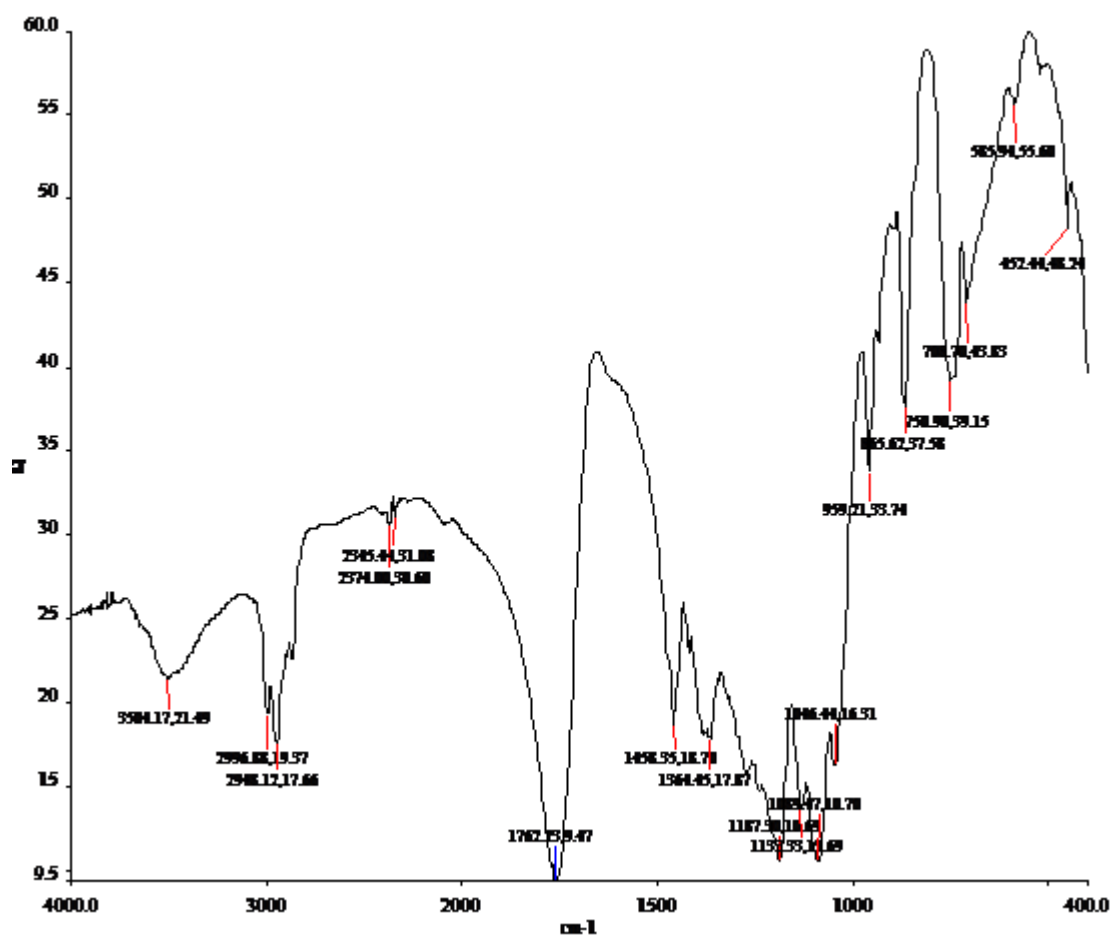


Fig. 4.8: FTIR spectra of PCL (33%)/PDLLA (67%) blend after microwave treatment

The spectra of this blend shows a peak of C=O at 1762 cm^{-1} and a peak of O-H at 3504 cm^{-1}

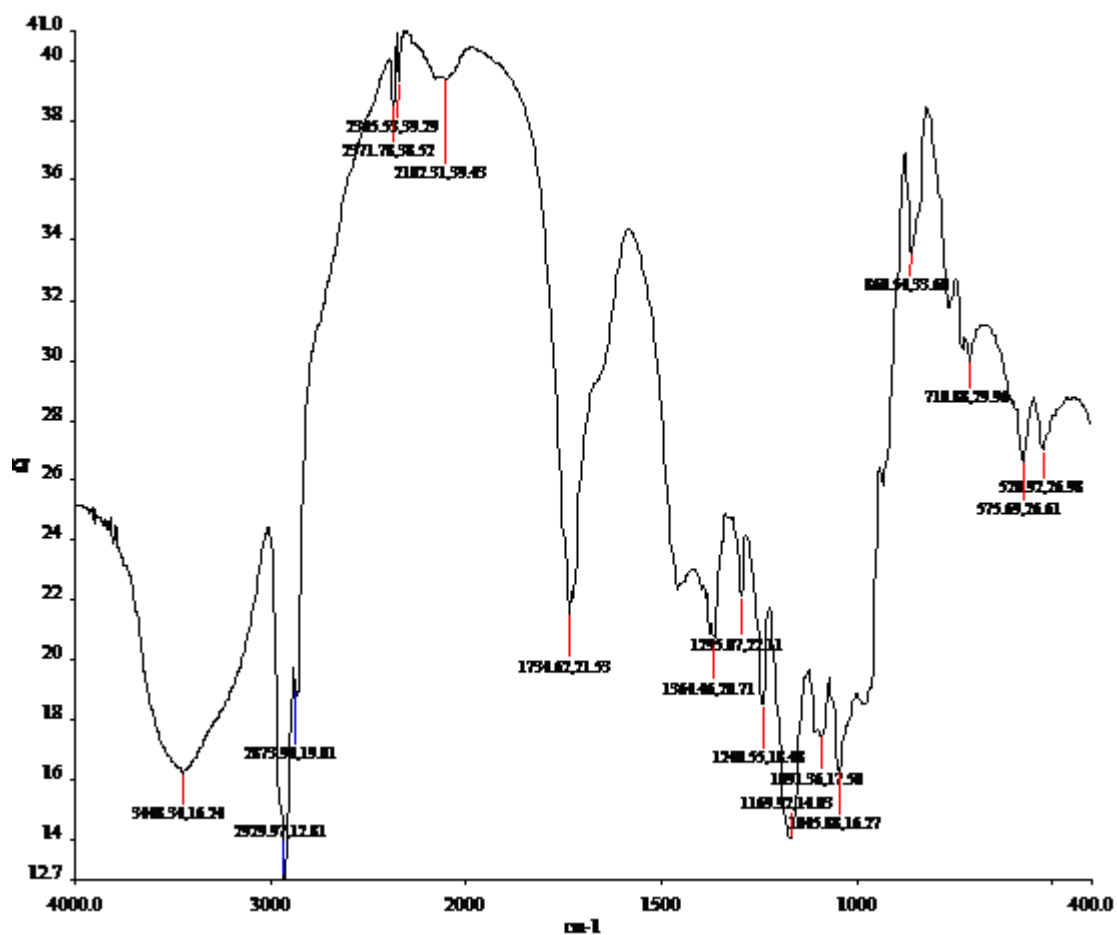


Fig 4.9: FTIR spectra of PCL (33%)/Starch (67%) blend after microwave treatment

The spectra of this blend shows a peak of C=O at 1734 cm⁻¹ and a peak of O-H at 3448 cm⁻¹

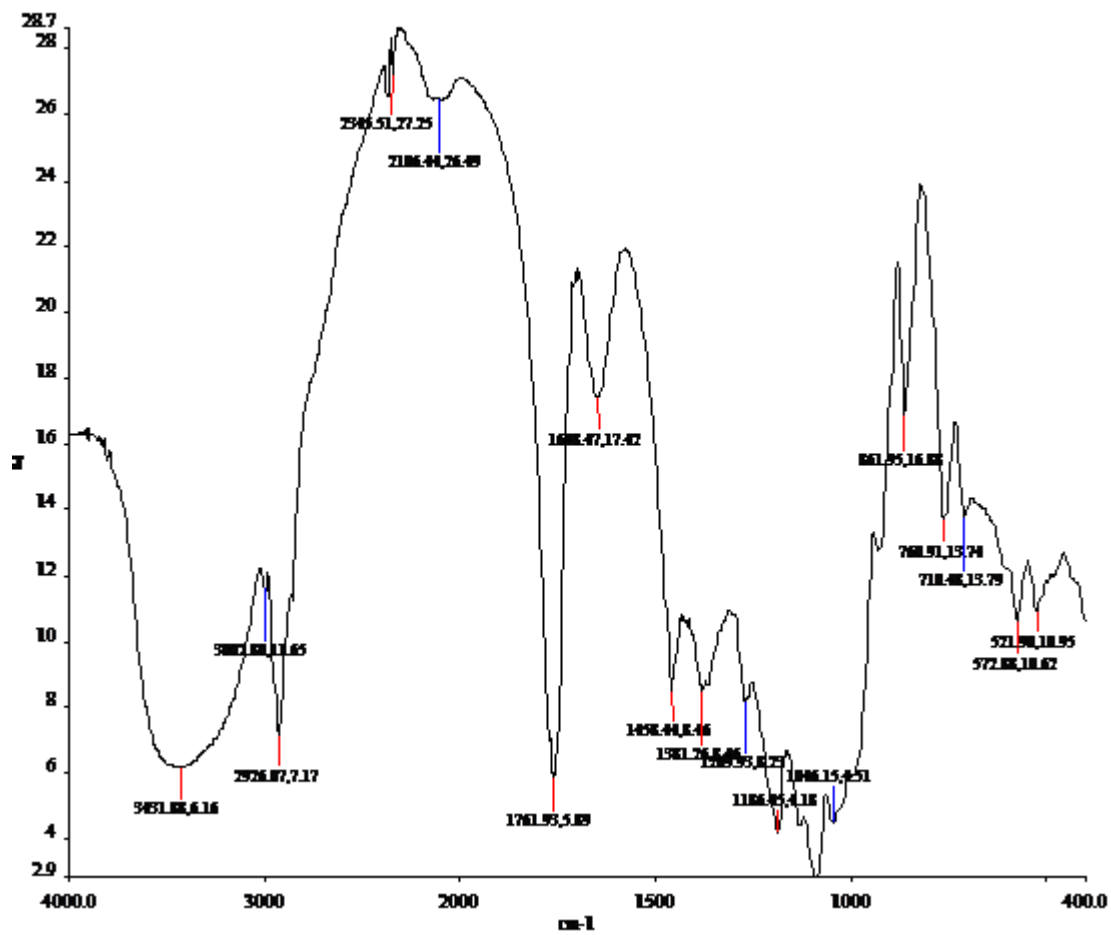


Fig 4.10: FTIR spectra of PDLLA (33%)/Starch (67%) blend after microwave treatment

The spectra of this blend shows a peak of C=O at 1761 cm^{-1} and a peak of O-H at 3431 cm^{-1}

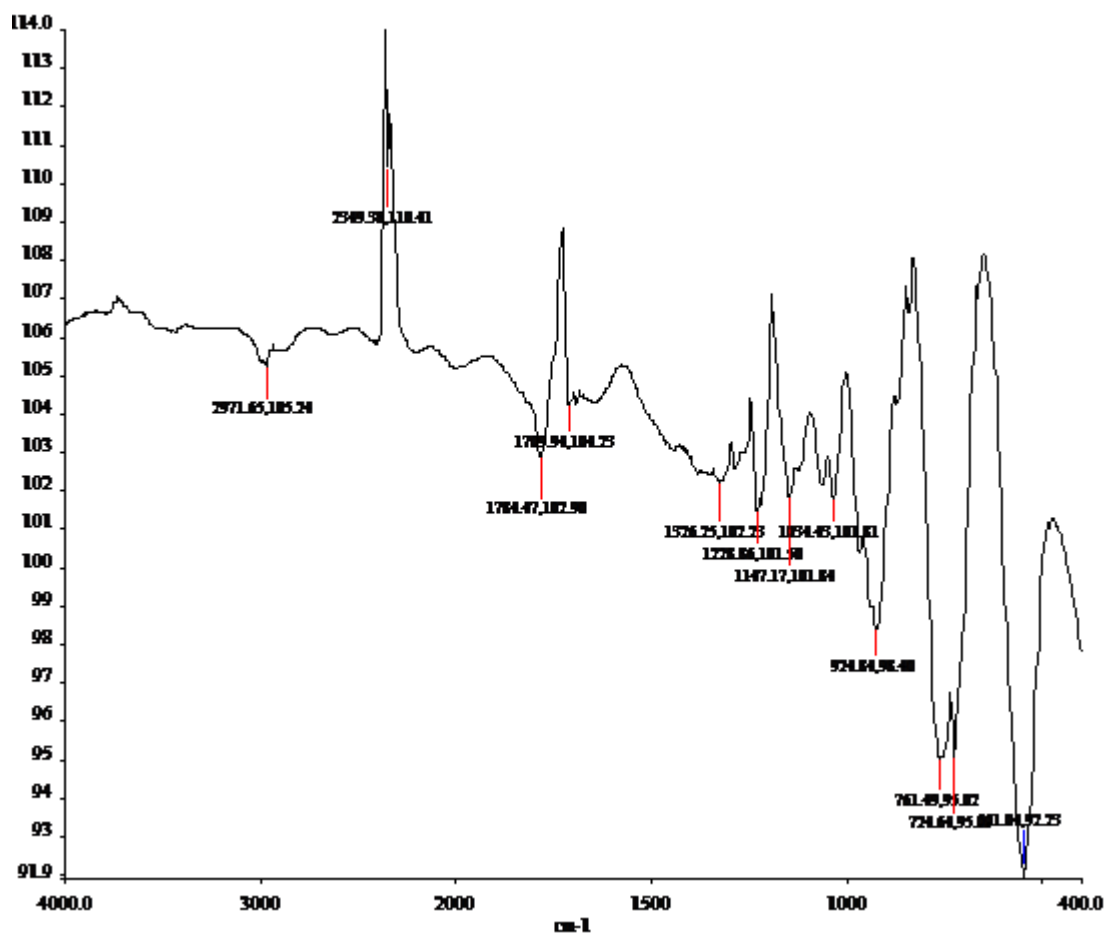


Fig 4.11: FTIR spectra of PCL (67%)/PDLLA (33%) blend after microwave treatment

The spectra of this blend show a peak of C=O at 1784 cm⁻¹ and a peak of O-H is not resolved.

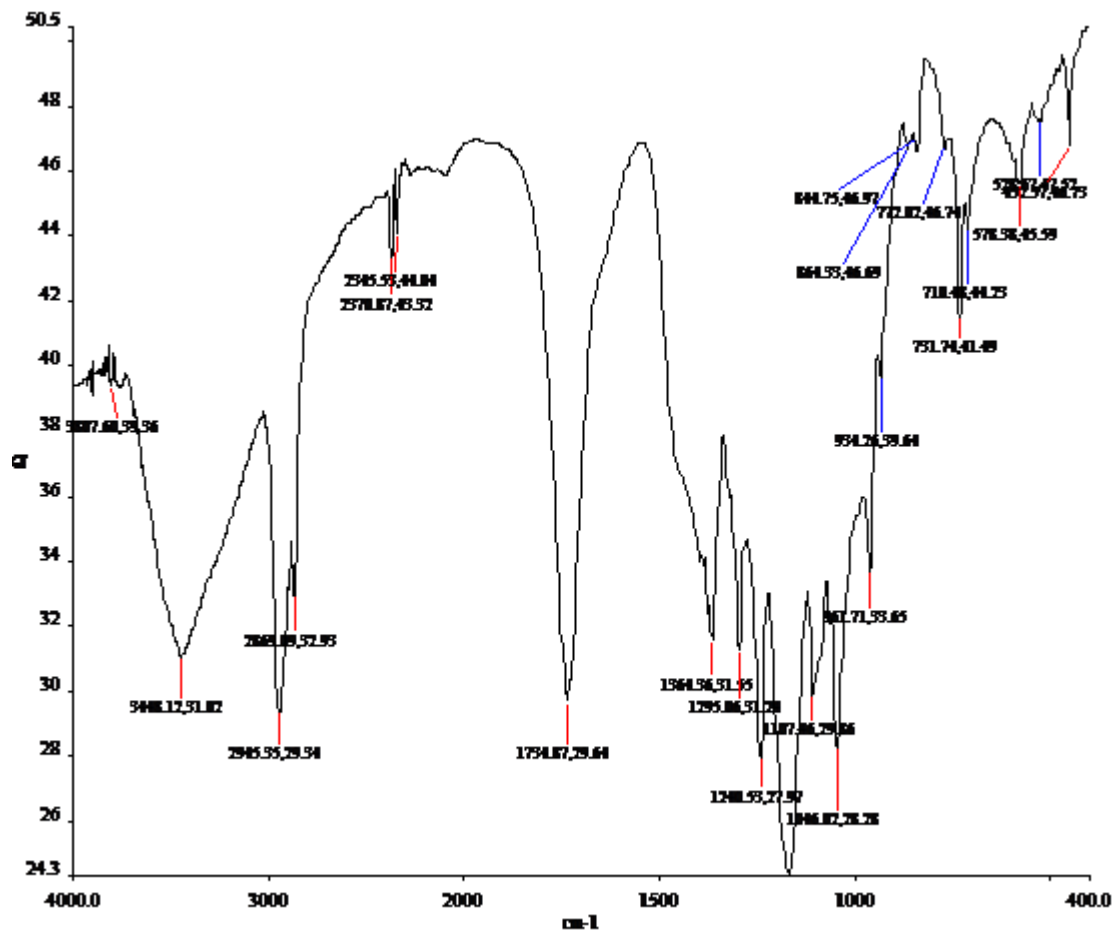


Fig 4.12: FTIR spectra of PCL (67%)/Starch (33%) blend after microwave treatment

The spectra of this blend shows a peak of C=O at 1734 cm^{-1} and a peak of O-H at 3448 cm^{-1}

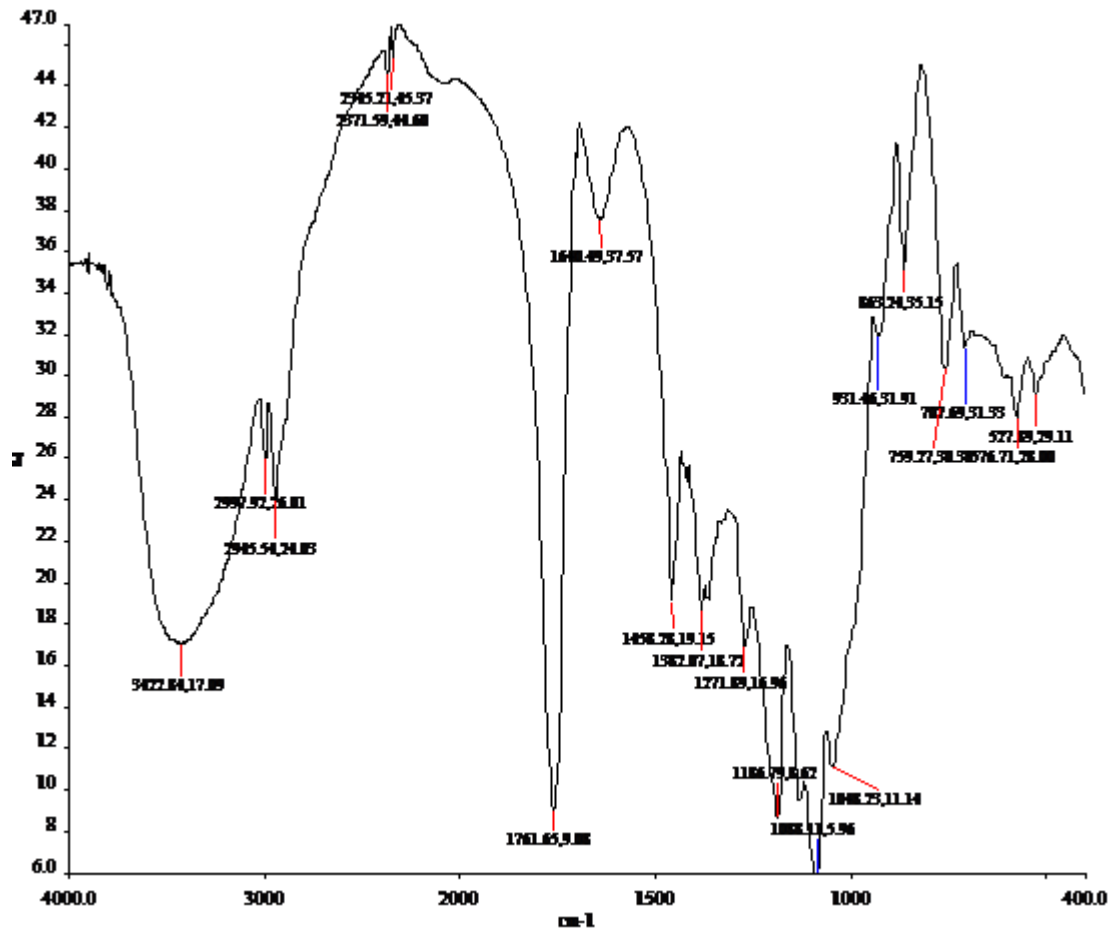


Fig 4.13: FTIR spectra of PDLLA (67%)/Starch (33%) blend after microwave treatment

The spectra of this blend shows a peak of C=O at 1761 cm⁻¹ and a peak of O-H at 3422 cm⁻¹

CHAPTER-5
DISCUSSIONS & CONCLUSIONS

5.1 Discussions

The IR spectral features of both the pure polymers before and after microwave treatment did not show any significant difference [Chen et al., 2003].

The FTIR spectra of PDLLA/PCL blend indicates that there are some molecular interactions between PDLLA and PCL. The interaction between PDLLA and PCL may be due to the possible hydrogen bonding that occurs between the C=O group in PCL and the small amount of terminal hydroxyl groups in the PDLLA main chain [Hoidy et al., 2010]. A proposed possible site for interaction between PCL and PDLLA is shown in Fig.12.1

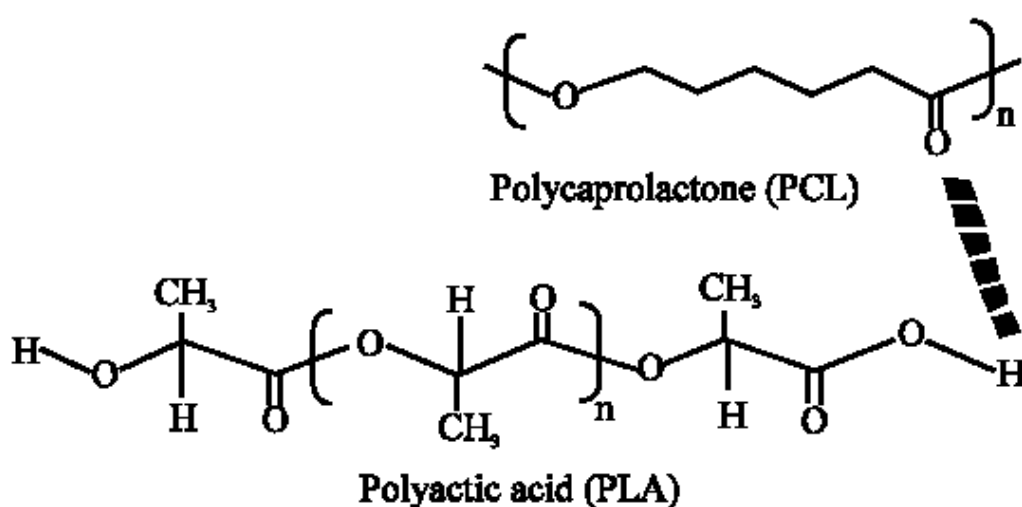


Fig 5.1 Proposed chemical interactions (intermolecular hydrogen bonding) between PDLLA and PCL [Hoidy et al., 2010]

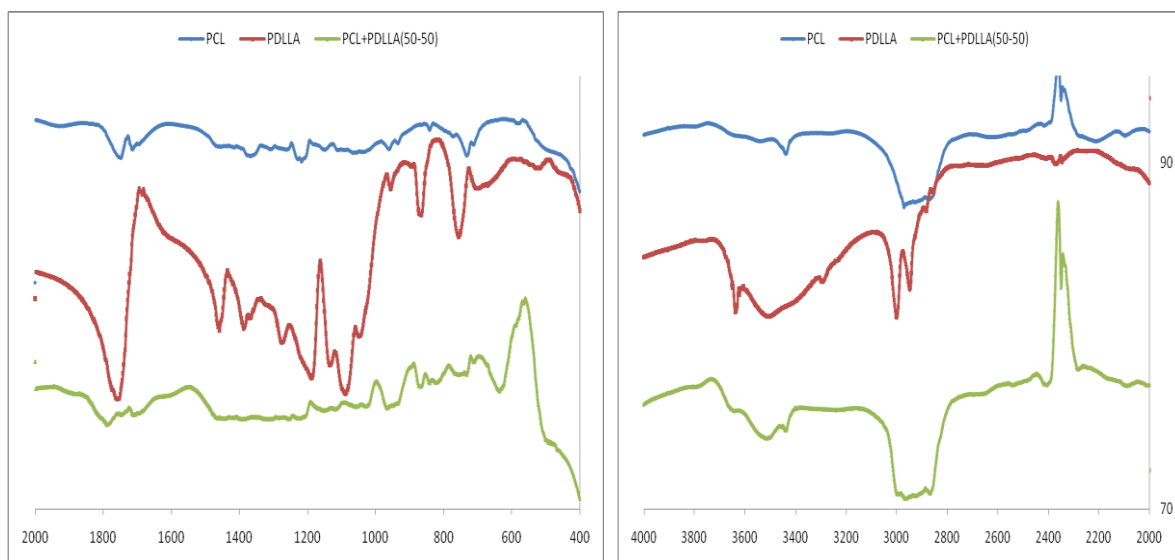


Fig. 5.2 Combined Curves of PDLLA, PCL & PDLLA/PCL Blend with 50-50% composition.

FTIR spectrum of the PDLLA supports this claim which shows a peak at 3504 cm^{-1} (hydroxyl group stretching). It was observed that this characteristic peak of PDLLA has shifted to 3514 cm^{-1} in the PDLLA/PCL blend with 50-50% composition. Also the peaks of C=O has shown a considerable shift from 1762 cm^{-1} in PDLLA and 1748 cm^{-1} in PCL to 1789 cm^{-1} in the blend of PDLLA/PCL with 50-50% composition as shown in Fig. 5.2.



Fig. 5.3 Combined Curves of PCL, Starch & PCL/Starch Blend with 50-50% composition.

The C=O band of PCL/Starch blend with 50-50% composition appeared at 1735 cm^{-1} which was lower than that of pure PCL (1748 cm^{-1}). Also the band of O-H has shown a little shift in the blend (3437 cm^{-1}) than pure starch (3434 cm^{-1}). The shift suggests that some hydrogen bonding might exist between the C=O group of PCL and hydroxyl group of starch (Im et al., 1999) as shown in Fig. 5.3.

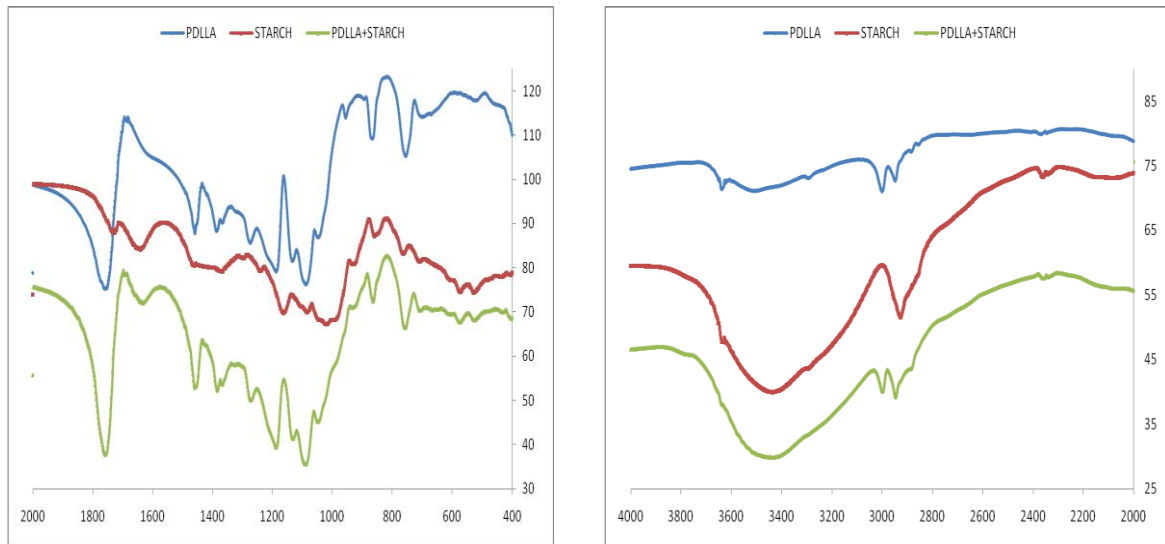


Fig. 5.4 Combined Curves of PDLLA, Starch & PDLLA/Starch Blend with 50-50% composition.

Similarly, The C=O band of PDLLA/Starch blend with 50-50% composition appeared at 1757 cm^{-1} which was lower than that of pure PDLLA (1762 cm^{-1}). Also the band of O-H has shown a little shift in the blend (3435 cm^{-1}) than pure starch (3434 cm^{-1}). The shift suggests that some hydrogen bonding might exist between the C=O group of PDLLA and hydroxyl group of starch (Im et al, 1999) as shown in Fig. 5.4.

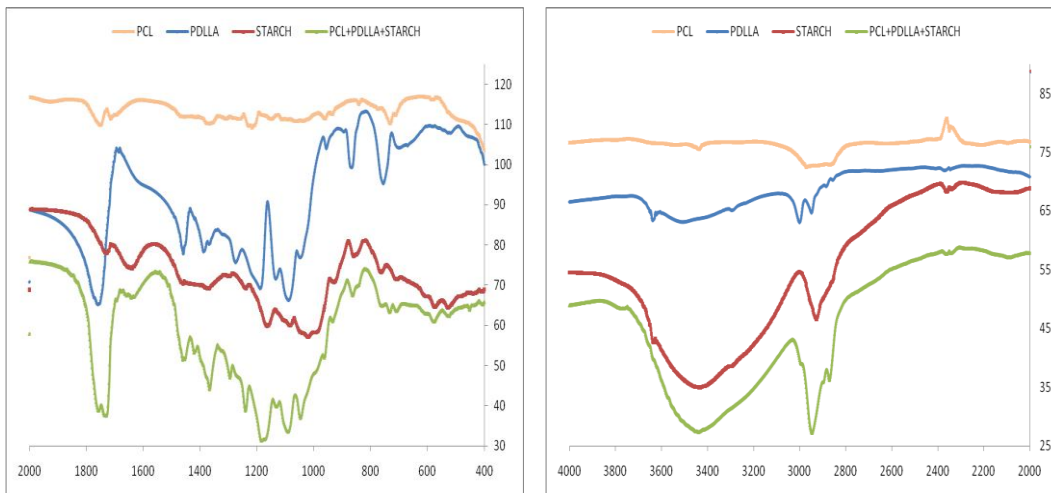


Fig 5.5 Combined Curves of PDLLA, PCL, Starch & PDLLA/PCL/Starch Blend

In the IR spectra of PDLLA/PCL/Starch blend the C=O band was shifted to a lower wave number (1730 cm^{-1}) and the shift was very large. Also there is a slight shift in the O-H group (3438 cm^{-1}). This shows a strong hydrogen bonding between C=O groups of PDLLA, PCL and O-H groups of PDLLA, PCL and starch (Im et al, 1999) as shown in Fig 5.5.

The IR spectra of the blends of PDLLA, PCL & Starch with different compositions also shows considerable variation in the peaks from their parent polymers which proves that chemical linkages are being formed between these polymers but the extent of these linkages could not be determined based just on FTIR. For this another tool like DSC is required.

The above observations indicate a strong possibility of linkages between two/three polymers as a result of treatment with microwave radiations.

5.2 CONCLUSIONS

On blending the PDLLA, PCL and Starch in various ratios using chloroform as a solvent and subjecting the mixtures to microwave radiation, it is clear from FTIR spectra that O-H and C=O regions of the blend show significant variance after microwave irradiation compared to the parent polymers. The results indicate a direct linkage between the polymers indicating the formation of a chemical linkage between the two molecules as opposed to just a physical blend.

CHAPTER-6

FUTURE WORK

6.0 Future work

DSC & NMR techniques could have told more about the quality of blend and whether some esterification reaction has taken place or not and as a future work one can look at the quality of blend by varying power levels, temperature and time.

Effect of varying the concentration can be studied by DSC.

Also, if any cross-linking takes place in the blend, it can be confirmed using DSC & NMR and comparing the behaviour of blends with respective copolymers.

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