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Synthesis of Biodegradable Polylactic Acid Polymer By Using Lactic Acid Monomer

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Abstract

Biodegradable polymer polylactic acid was synthesized by using lactic acid. FT-IR technique was used for confirmation of LA and PLA. Thermal behavior of PLA was carried out using DSC analysis. DSC thermogram of PLA showed Glass Transition temperature (T_g) at 58.0˚C, endothermic peak at 119.4°C and Sharp exothermic peak at 151.7°C. PLA Film was prepared by using solvent casting method. The biodegradability of the PLA Film was checked by soil burial test in laboratory for 200 days observation period.

Keywords: Lactic acid, Polylactic acid, FT-IR, DSC thermogram, PLA film, Soil Burial test.

1. INTRODUCTION

To minimize the rate of pollution is by manufacturing article from biodegradable material. Biodegradable material are those which can be degraded in the presence of environmental condition like soil, moisture, microorganism, light, heat, etc. and end products of this is not harmful to environment.[1]

Lactic acid has received attention for use if a wide range of applications mostly as it acts as a monomer for the production of biodegradable poly (lactic acid) or polylactide (PLA).PLA can be produced chemically and biotechnologically but biotechnological routes are mostly favored because of environmental concerns and limited nature of petrochemical feedbacks. Worldwide efforts have been made for the production of lactic acid and PLA with good yield and low cost management.[2]

For the pilot scale production of lactic acid though biotechnological route[3,4], there have been various requirement for high productivity i.e. cheap raw material, lactic acid producing microorganism, fermentation approach, type of bioreactor and finally purification of optically pure lactic acid for production of highly crystalline lactic acid.[1]

So that production of PLA can be divided into two step i.e. production of lactic acid and its polymerization to PLA.[1]

2. MATERIAL AND METHODS

2.1 Polylactic Acid from Lactic Acid:

80 g of the product of distillation lactic acid, 1% stannous octoate (Sn $(Oct)_2$) catalyst and 200ml m-xylene (Sovlent) were added into 500 ml glass reactor equipped with mechanical stirrer and the reaction mixture was heated. The water was azeotropically distilled off by using Dean and Stark assembly. The reaction was continued at 160ºC for 12-48 hrs under the flow of nitrogen gas. Then, the catalyst was filtered off, and the resulting polymer was dissolved in chloroform, and then was precipitated twice in excess of methanol. The product was dried in a vacuum oven at 60ºC until constant weight was attained.[5]

2.2 Structural Analysis:

2.2.1 Structure analysis of LA monomer and PLA polymer by FT-IR and DSC are described here. [5, 6]

A Perkin Elmer FT-IR spectrometer model spectrum BX was used to obtain the IR of lactic acid and polymer PLA. Thermal analysis was carried out with a differential scanning calorimeter. For DSC the measurements were run from 20 to 200ºC at the heating rate 10ºC/ min.

2.2.1.1 Fourier Transform Infrared (FT-IR) Spectral Studies

FT-IR spectral data of lactic acid and polylactic acid were taken using FTIR spectrophotometer instrument (OPUS software). FTIR spectra were recorded by a potassium bromide (KBr) disc method and scanned at the resolution of 4.0 cm^{-1} by keeping dried sample on Zinc selenide crystal and the wave number region between 4000–650 cm^{-1}.

2.2.1.2 Differential Scanning Calorimetry (DSC) Study

Thermal behavior polylactic acid was carried out using DSC analysis. The inert atmosphere was maintained by purging nitrogen gas throughout the experiment at the rate of 40 ml/min. The samples (1-2mg) were carefully transferred and heated in a crimped aluminum pan for accurate results. The samples were heated from 20°C-200°C at the rate of 10°C/min.

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2.3 Procedure for Preparation of PLA Film [7]

After completion of preliminary trials, amount of film forming agent and plasticizer were decided to obtain good flexible film.

The Film was prepared in the laboratory using PLA by solvent casting method is shown in Fig 1. 400 mg of PLA was dissolved in beaker containing 10 ml of Distilled water and stirred well As soon as the solution becomes clear, 120 mg of PEG was added in that solution. Solution was stirred until it becomes clear and homogenize properly. The solution was casted in glass petri dish of uniform size 10X10 cm^2 and dried at room temperature. The film was carefully removed from the petri dish with the help of spatula.

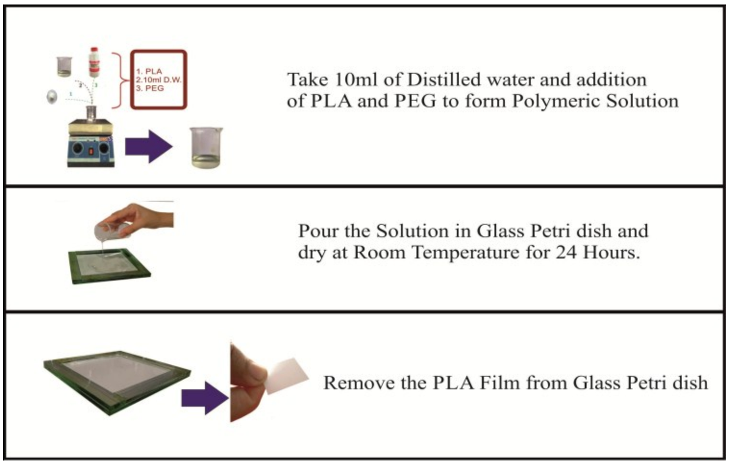

Figure 1: Procedure for PLA Film Preparation

2.4 Soil Burial Test

To examine the biodegradability of the PLA Film, soil burial test was carried out on a laboratory scale. Moist soil was placed into containers with tiny holes was perorated at the bottom and on the body of the container to increase air, and water circulation. The PLA film was buried in the soil at a depth of 10 cm from the surface and thus subjected to the action of microorganisms in which soil is their major habitant. The test was carried outside the room for 200 days time period.

3. RESULTS AND DISCUSSION

3.1 Polylactic Acid Polymer from Lactic Acid Monomer

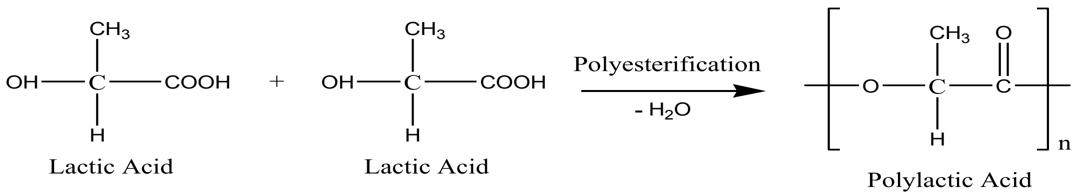

Figure 2: Polylactic Acid from 2 LA Monomer

Synthesis of polylactic acid from 2 monomer of lactic acid by polyesterification process is shown in Fig 2.

3.2 FT-IR spectra for Lactic Acid and Poly Lactic Acid:

The FTIR study of LA and PLA were carried out. The presence and absence of characteristics peaks associated with specific structural characteristics of LA and PLA were noted. The wave numbers (cm^{-1}) of bands observed in the infrared spectrum of LA and PLA is described in Tab 1.

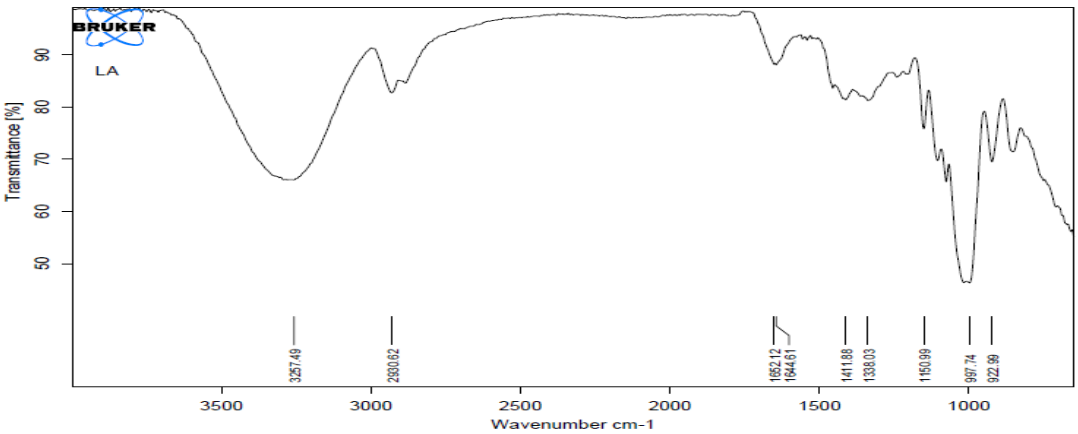

Figure 3: FT-IR spectra of (LA) Lactic Acid

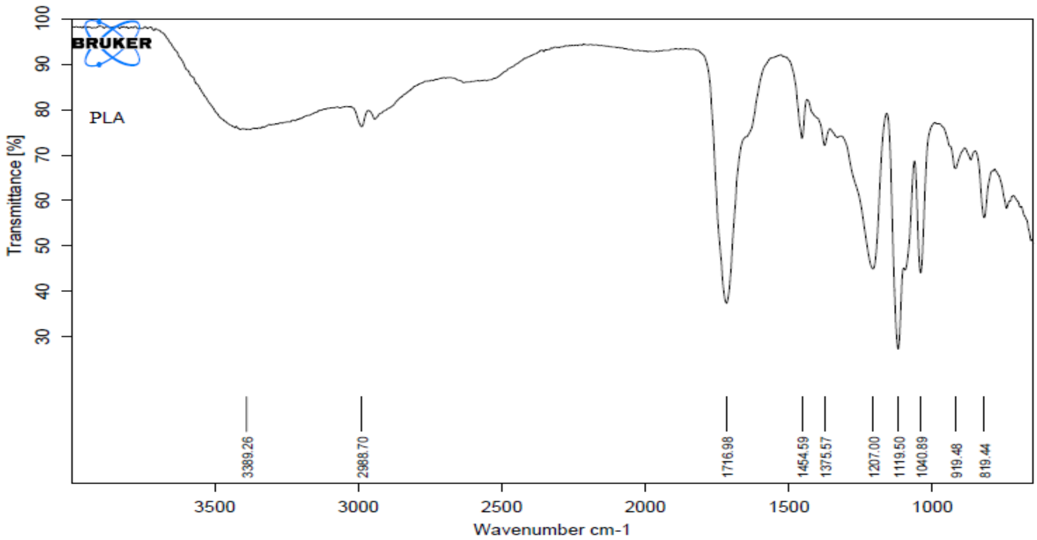

Figure 4: FT-IR spectra of (PLA) Lactic Acid

FT-IR spectra of lactic acid and poly lactic acid synthesized at 160°C for 48hrs which is shown in Fig 3 and Fig 4. IR spectra of PLA revealed characteristic absorption peaks of ester (1716.98 and 1119.50 cm-1 for –COO- and –CO-, respectively) and –CH_3 (Stretching) group (2988.70 cm-1). As lactic acid was polymerized, the hydroxyl group will react with carboxylic group. The sharp absorption peak in case of LA was observed at 3257.49 cm^{-1} with greater intensity which in case of PLA was almost disappeared due to reaction polyestrification that consumes the OH groups when they react with the acid groups to form the ester bond indicating that the number of –COOH and –OH were reduced and sharper absorption peak of C=O stretching (1716.98 cm^{-1}) was observed.

Table 1: Conformations of Lactic Acid and Polylactic Acid

Sr. No.	Functional Group	Standard Frequency (cm^{-1})	Lactic Acid (cm^{-1})	Polylactic Acid (cm^{-1})	Conclusion
1	-OH (COOH)	2400-3400	3257.49	3389.26	Pass
2	-CH_3(S)	2850-3000	2930.62	2988.70	Pass
3	-C=O	1650-1750	1652.12	1716.98	Pass
4	-C-O (COOH) -OH	1000-1300	1150.99 997.74	1119.50 1040.89 1207	Pass
5	-CH_3(B)	1375-1475	1411.88	1454.59	Pass

The FT-IR spectrums of the LA monomer and the poly (lactic acid) were obtained from reaction of 2 monomer of LA of reaction, which is shown in Fig 3 and Fig 4 respectively. The spectra show the bands at 2930.62cm^{-1} (LA) and 2988.70 cm^{-1} (PLA) from symmetric and asymmetric valence vibrations of C-H from CH_3, respectively.

It is possible to observe a band shift related to the C=O stretch in the monomer in 1652.12 to 1716.98 cm^{-1} in the polymer. These bands show that shifts of monomer to polymer also show a difference in the peak intensity which suggests the arrangement of molecules in the polymer chain. Bands corresponding to bending vibrations of CH_3 were found in 1454.59 cm^{-1} in the polymer spectrum as greater intensity peaks compared with those from monomer found in 1411.88 cm^{-1}. In PLA, 1119.50 cm^{-1} is detected the C-O-O stretching vibration.

3.3 DSC Analysis of Polylactic Acid

Thermal behavior of PLA was carried out using DSC analysis. The inert atmosphere was maintained by purging nitrogen gas throughout the experiment at the rate of 50 ml/min. The sample (1-2mg) was carefully transferred and heated in a crimped aluminum pan for accurate results. The sample was heated from 20°C-200°C at the rate of 10°C/min. (DSC-60, Shimadzu, Japan).

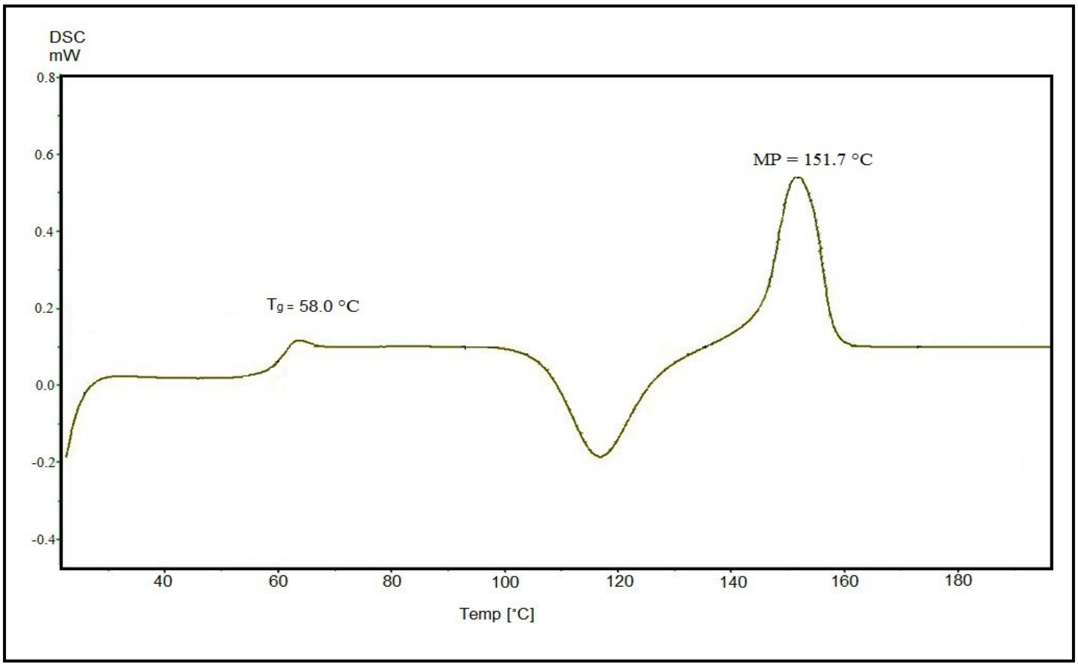

Figure 5: DSC of Polylactic Acid

The result of DSC of PLA was shown in Fig 5. DSC thermogram of PLA showed Glass Transition temperature (T_g) at 58.0˚C and endothermic peak at 119.4°C in Fig 5.37 which indicate removal of water and Sharp exothermic peak at 151.7°C, which is the melting point of PLA.

3.4 PLA Film Preparing

PLA film was prepared using three different plasticizer and two different amounts. Among all three plasticizers film made with PEG was found flexible and got separate from glass surface than glycerine and propylene glycol. The PLA Film was prepared in the laboratory using PLA by solvent casting method is shown in Fig 6.

Figure 6: PLA Film

For Further characteristics of PLA Film was checked (Uniformity of Thickness, Folding Endurance, Tensile Strength Measurement, % Elasticity). The 2x2 mm of PLA film of same concentration i.e. 400mg was added with 10 ml D.W and PEG. PEG was selected with different concentration i.e. 80mg, 100mg, 120 mg respectively which label as Film1 (F1), Film 2 (F2) and Film 3 (F3). Tensile strength and Elasticity of PLA film was found good in F3 batch with compare to F1 and F2 Batches, and (N/mm2)Tensile strength and % Elasticity was found in F3batch i.e. 13.75 and 2.08% respectively.

3.5 Soil Burial Test of PLA Film

The biodegradability of the PLA Film was checked by soil burial test. Test was carried out on a laboratory scale for 200 days observation period. The PLA film was buried in the soil at a depth of 10 cm from the surface and checked after 50 days duration cycle. First 50 days there was not major change in film but after 100 days film was braked out in 3 Pisces while after 150 days most of the part degraded in soil particles. PLA film was 98% degraded after 200 days under soil burial container.

Figure 7: Biodegradation Cycle Observation of PLA film

4. CONCLUSION

Synthesis of biodegradable polymer polylactic acid was carried out by using lactic acid. FT-IR technique was used for confirmation of LA and PLA. DSC thermogram of PLA showed Glass Transition temperature (T_g) at 58.0˚C, endothermic peak at 119.4°C and Sharp exothermic peak at 151.7°C, which is the melting point of PLA.PLA film was prepared by using solvent casting method. Good mechanical strength and flexibility was found when PEG was used as plasticizer in PLA film formation. From the result it was concluded PEG has potential to modify disintegration rate and mechanical property. Thickness, Folding endurance and % elasticity of PLA film was found good in F3 batch as compared to F1 and F2 Batches. In F3 batch, thickness, folding endurance and % elasticity were found maximum i.e.0.06mm, 101 times and 2.08% respectively. PLA Film was degraded 98% after

200 days observation time period by using soil burial test. It shows that PLA Film is eco-friendly and biodegradable.

5. RECOMMENDATION

Dairy Industry waste is a good source for isolation of lactic acid bacteria. Food wastes used as substrate which reduces the waste and it will be used for lactic acid production. Lactic acid can be utilized as raw material in pharmaceutical, food preservative, polymer synthesis. Lactic acid produced from combination of dairy waste and food waste can be best solution for waste reduction and utilized for PLA production.

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