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Synthesis and Characterization of Bio-based Polyester and Polyamide from Citric Acid and Mannitol

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ABSTRACT

The present work is synthesis of biobased polyesters from citric acid and mannitol while polyamide from citric acid and diethylene triamine (DETA). Both reactions are carried by melt condensation polymerization technique. The products are characterized by FTIR for functional group conversion. The acid value also determined. The thermal properties are characterized by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC).

Keywords: Biobased polymer, polyester, polyamide, FTIR, TGA, DSC.

INTRODUCTION

Recently the biobased polymers are attract the attention of scientist due to their biodegradability and biocompatibility. There are many biobased monomers which can be used for polymer preparation. Generally biobased monomers are easily available in abundance quantity and are economically cheap. Biobased compounds such as vegetable oil, citric acid, carbohydrates etc cane used for polymer synthesis. Beside the use of carbohydrate in food, biomass and raw materials they are modified with chemical reaction in applicable polymers. Many researcher are interested in carbohydrate polymer because it offering large hydroxyl functionality. Carbohydrates based polymers are being used in biomedicine, tissue engineering, polymeric detergents, macromolecular drugs, drug carrier and release systems, hydrogels, surface modifiers.[1-11]

There is a field of research in United State Department of Agriculture which study on the use of citric acid and carbohydrates and others have

published reports of starch citrates, corn-fiber citrates, and cellulosic citrates. Citric acid was isolated from citrus fruits like lemon but recently fermentation method citric acid is produced commercially. Citric acid is easily available and economically cheap, in spite of increasing consumption in the food and beverage industries; also it is famous and used for its flavoring and buffering properties. It is also used in the petroleum industries as metal-chelating agent and cosmetics industries. Mannitol is natural sugar and has many industrial applications, medicinal uses as sugar it is often used as a sweetener in diabetic food as it is poorly absorbed from the intestines.[12,13]

The present work is synthesis of biobased polymeric material from the citric acid and mannitol giving the polyester while polyamide from the reaction with citric acid with di-ethylene triamine (DETA). They are characterized by FTIR and their thermal properties are studied by TGA and DSC.

EXPERIMENTAL

Raw materials:-

The following raw material was used in the synthesis; citric acid was obtained from s.d. fine India. The other chemicals mannitol, di-ethylene triamine and di-ethylene amine were purched loba chemie, India. The solvents ethanol and methanol were obtained from Rankem India. All the raw material used without purification.

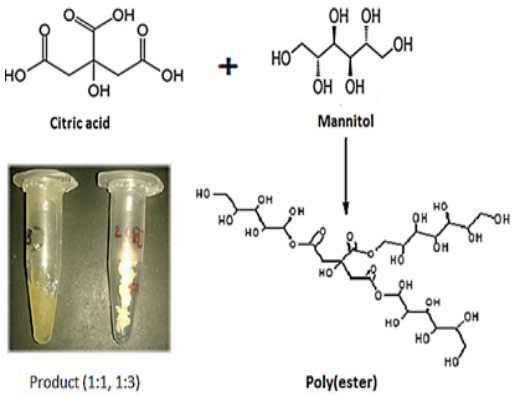

Fig. 1. Synthesis of polyester from citric acid and mannitol

Synthesis of polyester from citric acid and mannitol:-

A measured amount of mannitol (5.465 g) was weighted in 500 ml glass beake .Then desired amount of citric acid (1.921g) was added into it. The molar ratio is citric acid : mannitol is 1:3 maintained. The reaction mixture were placed inside the oven and polymerization is run at 150 to 170 ˚C.There was no string during reaction, except that produced by bubbling (the release of water).Reaction completed after five hours remove the product for analysis.

Reaction Scheme 1:

Synthesis of polyamide from citric acid and di-ethylene triamine (DETA) using solvent:

Procedure:-

The desired amount of citric acid (3.842 g, 0.02 moles) in 500 ml glass beaker which is dissolved in minimum quantity of ethanol. Then measure di-ethylene triamine (3.095 g, 0.03 moles). which added into the beaker drop wise manner with constant stirring. Reaction is carried out at room

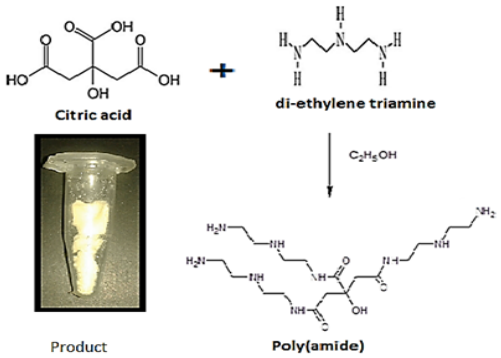

Fig. 2. Synthesis of polyamide from citric acid and di-ethylene triamine (DETA) using solvent

Table. 1: Formulation for Citric acid based polyester and polyamide

Sr.No	Citric Acid	Mannitol	Diethylene triamine (DETA)	Molar ratio
1.	1.921 g	1.8217 g	—	1:1
2.	1.921 g	5.465 g	—	1:3
3.	3.842 g	—	3.095 g	2:3

temperature and polymerization is done with condensation. Then remove the product washes with solvent and dries it for characterizations.

Reaction scheme-2

Characterization

Determination of acid value of polyester:-

Procedure:-

The weight 2 to 4 g of sample dissolved in 50 ml of neutral methyl ethyl ketone (or any other water miscible suitable solvent) at room temperature. Then 2-3 drops of phenolphthalein indicator was added to the solution. Titratation of the solution against the standard alcoholic KOH solution until pale pink color appears permanently was done. Record volume of alkali consumed as an "A" ml. If the solvent is not neutral, carry out a blank titration and record the volume of alkali consumed as "B" ml.. Take at least 3 reading and then calculate the acid number. Acid value can be determined by using following formula.

$$\text{Acid Value} = \frac{56.1 \times \text{ml of KOH consumed } (A-B) \times \text{exact normality of KOH solution}}{\text{Weight of sampl e in gram}}$$

Table. 2 : Acid values of polyester during reaction

Sr. No.	Time	Acid value (mg of KOH/ g of sample)
1	10	106.59
2	70	98.175
3	130	86.95
4	190	75.735
5	220	58.905

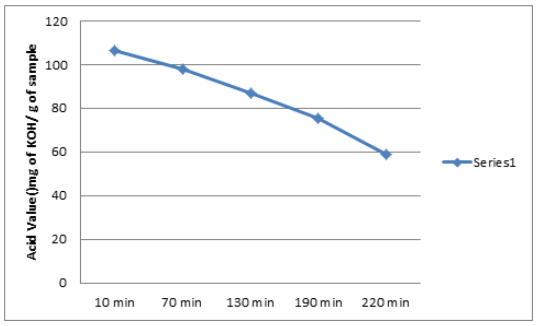

Fig. 3. Graphical presentation of Acid value Vs time

IR spectroscopy

IR of polyester and polyamide was determined on Perkin Elmer spectrum one FTIR spectrophotometer by pallet method using nujole oil.

TGA and DSC Results

Thermal analysis of polyester and polyamide was determined on Perkin Elmer TGA and DSC.

RESULTS

From the above results it can be concluded that the acid value decreases with time. Prepared polyester was characterized in the laboratory by analysis

Acid values for solvent used polyamide:-

In the initial state of reaction acid value is 173.91 and at the end of reaction acid value is decreases 56.1 mg of KOH/g of sample.

IR of polyester and polyamide

IR for poly (ester)

FTIR of the above polymer was taken using FTIR and data is analyzed as given below. FTIR spectra of our sample showed the important bands for presence of –OH group, -$CONH_2$- group and esters groups also. Presence of other groups like –CH_2- was also seen in the FTIR of the sample.

As FTIR contains frequencies for amide, ester and hydroxyl groups the products was polyester and polyamides it was as per the desire.

Thermal Gravimetric Analysis (TGA)

TG of poly (ester)

This TGA data is showing the thermal stability of polymer. It shows two step degradation. First degradation occurs between 90° to 305 °C,

Table. 3 : IR frequencies of the polyester and amides

Sr. No.	Frequency	Functional group
1	2962	C-H stretching
2	1746	Ester
3	1746.94	Ester stretching
4	1638.33	Amide
5	1284	CH_2-CH_2 stretching

during that 40.936% of polymer is degraded. Second degradation start from 305° to 570 °C and during this temperature 48.689% polymer degraded.

TG of poly (amide)

This TGA data is showing the thermal stability of polymer. It shows two step degradation. First degradation occurs between 120° to 280 °C, during that 43.762% of polymer is degraded. Second degradation start from 280° to 490°C and during this temperature 32.728% polymer degraded.

Deferential Scanning calorimeter

DSC of polyester

This DSC data showing thermal stability. Polyester shoes glass transition temperature (Tg) is 22.95° C and melting temperature is 133.83° C.

DSC of polyamide

This DSC data shows thermal stability. Polyamide shoes glass transition temperature (Tg) is 5.36° C and melting temperature is 218.34° C. it indicates thermal this polymer is very

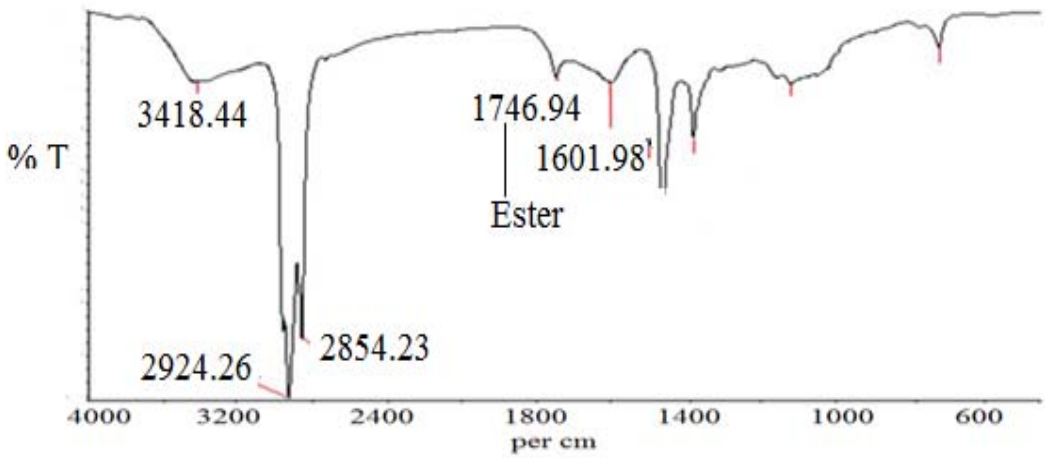

Fig. 4. IR of polyester of citric acid and mannitol

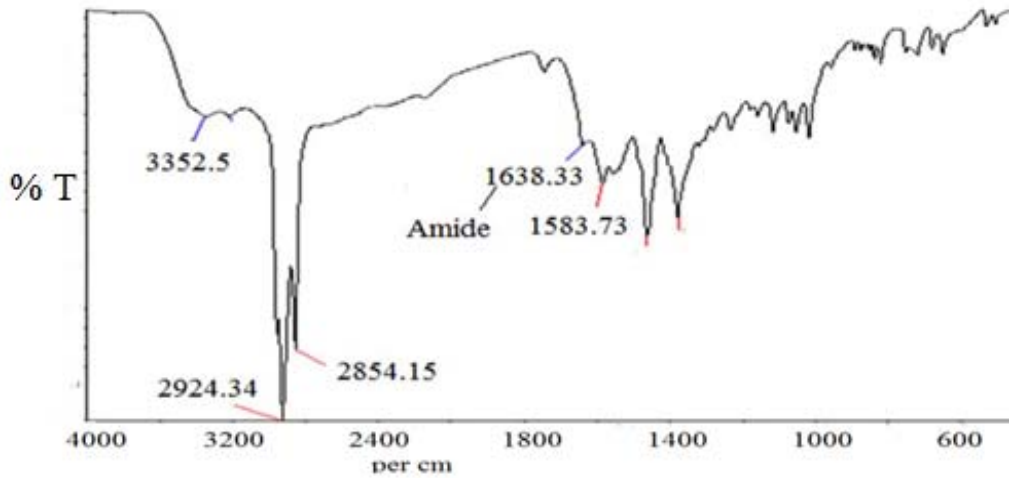

Fig. 5. IR of polyamide from citric acid and DETA

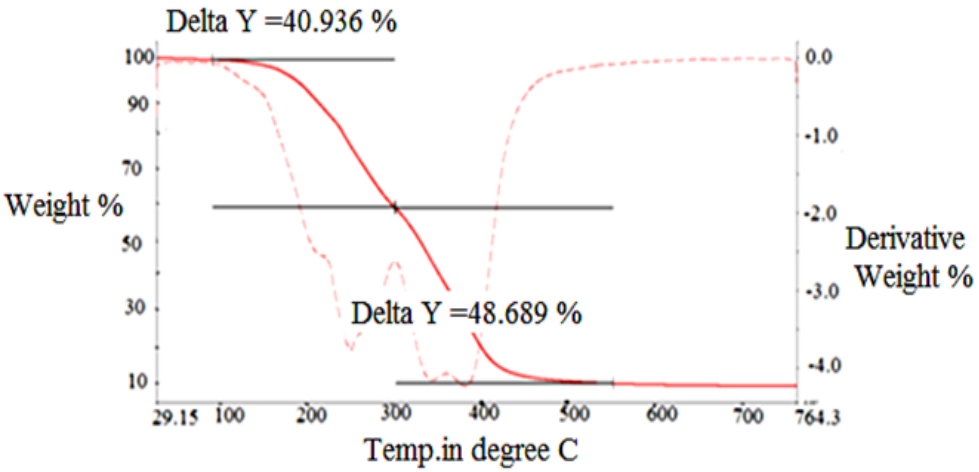

Fig. 6. TGA of polyester from citric acid and DETA

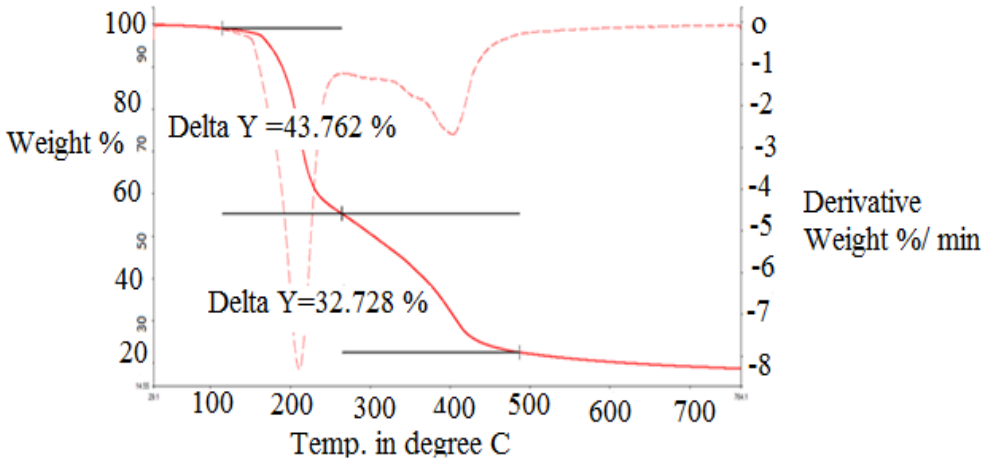

Fig. 7. TGA of polyamide from citric acid and DETA

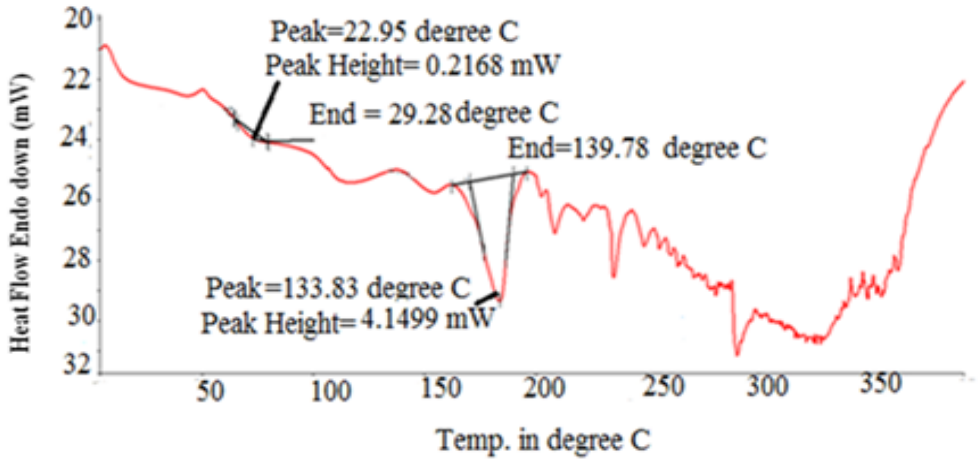

Fig. 8. DSC of polyester of citric acid and DETA

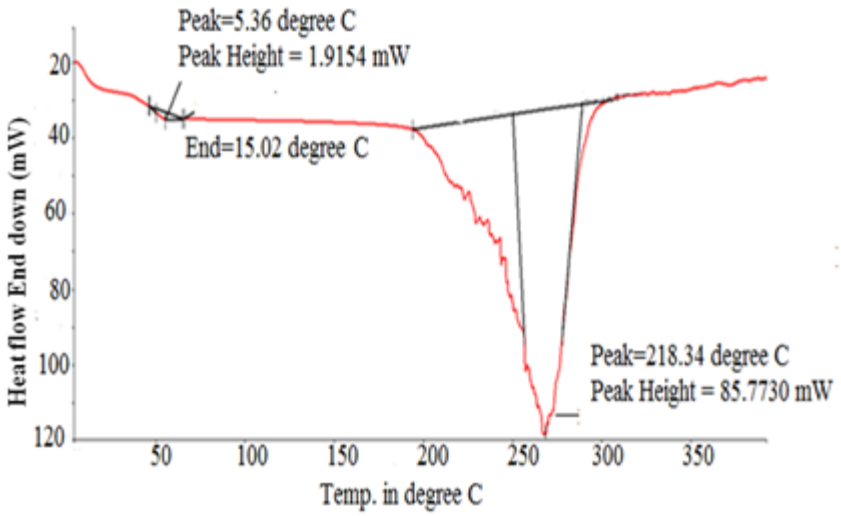

Fig. 9. DSC of polyamide from citric acid and DETA

CONCLUSIONS

We synthesized polyester using citric acid and mannitol with solvent free condensation polymerization method. The synthesis reaction occurs at both 150 and 170° C, but it is significantly faster at the higher temperature. The molar ratio of the reactants is major factor in the material properties like solubility. The polyamide also synthesis with solvent and by solvent-free condensation polymerization method, using monomer citric acid and di-ethylene triamine. The synthesis reaction of solvent used polyamide occurs at room temperature and solvent free at 100 and 110° C. These two polymers are novel and water soluble. Overall, this work has contributed to the understanding of the condensation polymerization of citric acid and mannitol bio-based monomers and should help us shift towards the use of agricultural products in the bio-based economy of the future.

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