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BIODEGRADABILITY STUDY OF SYNTHESISED POLYMER BASED ON GLUCOSE AND SORBITOL

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ABSTRACT

In recent years, there has been a marked increase of interest in biodegradable materials for use in packaging, agriculture, medicine, and other areas. As a result, many researchers are investing time into modifying traditional materials to make them more environmental friendly, and into designing novel polymer composites out of naturally occurring materials. In order to overcome the environmental problems associated with natural and synthetic waste, biodegradation of materials holds good promise and a detailed and systematic study of the process are needed. Under ambient conditions, polymers are known to undergo deterioration in their properties characterized by change in their molecular weight and other physical properties. In this study biodegradable polymer based on natural products glucose and sorbitol were synthesized and were used in preparation of liquid and powder detergents, hand wash and dish washers. This investigation reveals that the polymers synthesized from raw materials of natural origin namely liquid glucose, glycerol, sorbitol etc. are susceptible to biodegradation.

KEYWORDS: Biodegradable polymer, Chemical and Biological Oxygen Demand.

INTRODUCTION

Biodegradable polymers[1] are a newly emerging field. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have been identified. In developing countries, environmental pollution caused mainly by synthetic polymers has assumed dangerous proportions. As a result, attempts have been made to solve these problems be introducing biodegradability into polymers through slight modifications of their structures. Biodegradation is a natural process, by which organic chemicals in the environment are converted into simpler compounds.

Since most of the polymers are resistant to degradation, research over the past couple of decades has focused on developing biodegradable polymers, which are degraded and catabolized ultimately to carbon dioxide and water by microorganism under natural environment. Another approach towards achieving biodegradability[2] has been through the addition of biodegradable groups into main chain during the preparation of industrial polymers by free radical copolymerization. Studies on the biodegradation of plastics have increased the information on degrading microbes, enzymes and their genes since the future lies in developing polymers that will degrade in the environment.

In the present investigation polymers based on natural products glucose and sorbitol were synthesized and were used in preparation of liquid and powder detergents, hand wash and dish washers[3-4]. These products were then evaluated for biodegradability. The details of the experimental work are explained below.

MATERIAL AND METHODS

Reaction programming and steps involved in synthesis of polymers

Polymers of various compositions were prepared in batch process. The mole ratios, reaction temperature and addition of ingredients are detailed below in four steps:-

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Step 1 - Liquid Glucose, Citric acid, Sorbitol, Sodium meta bisulphite were added in a definite proportion and converted into a homogenous dispersion by using electrical homogenizer. The dispersion prepared had flow and mobility and was introduced into the reactor (as given Table No. 1)

Step 2 - The reactor contents were slowly heated to 80 ^{0}C in about 15 minutes. The reaction temperature was subsequently raised to the desired temperature range of 120 -130 ^{0}C in about 20 minutes of controlled heating. The reactor contents were monitored every fifteen minutes for flow, homogeneity and viscosity. The heating was continued for predetermined time of 3 hours when the reaction was complete.

Step 3 - After attending the desired viscosity and clarity the heating was stopped and the mass was cooled to 80 ^{0}C.

Step 4 - The batch reactor contents were withdrawn, filtered through a strainer and stored in tightly closed bottles. The prepared polymer sample was then subjected to physiochemical analysis by standard laboratory methods.

Biodegradability analysis of selected polymers

Experimentally the biodegradability of polymer was evaluated by determined the COD[5] and BOD[6-7] of the prepared sample by standard methods. The ratio of biochemical Oxygen demand (BOD) and chemical oxygen demand (COD) was then calculated which gives the information of biodegradability of the sample.

Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) test measures the oxygen required to oxidize organic matter in water and wastewater samples by the action of strong oxidizing agents under acidic conditions. In the present work the COD value was determined as per the following procedure:

0.4g $HgSO_4$ was taken in an Erlenmayer flask and 20 ml solution of the sample of desired concentration prepared in distilled water was added to the flask. 20 ml of distilled was further added to the contents and mixed well, so that chlorides if any are converted into poorly ionized mercuric chloride and do not interfere with COD determination. 10 ml of standard $K_2Cr_20_7$ solution was then added to the flask followed by addition of 30 ml concentrated H_2SO_4 containing silver sulphate. These contents were then refluxed for 2 hours. Simultaneously, a blank sample i.e. without addition of 20 ml polymer sample was set up in another Erlenmayer flask and subject to refluxing. These flask contents were then cooled and the condenser was washed by about 50 to 60 ml distilled water and then the whole contents were titrated against standard ferrous ammonium sulphate solution using ferroin as indicator. The end point was determined by the sharp change in color from green blue to wine red and the COD value was determined using formula:

$$\text{COD in mg/L} = [(B - S) \times N \times 8000] / V$$

Where:

B = Ferrous ammonium sulphate used for blank (ml)
S = Ferrous ammonium sulphate used for sample (ml)
N = Normality of Ferrous ammonium sulphate
V = Volume of sample taken (ml)

Biochemical Oxygen demand (BOD)

The biochemical oxygen demand (BOD) test is based on mainly bio-assay procedure which measures the dissolved oxygen consumed by micro-organisms while assimilating and oxidizing the organic matter under aerobic conditions. The standard test condition includes incubating the sample in an air tight bottle, in dark at a specified temperature for specific time.

Procedure of BOD Analysis:

1. Preparation of Dilution Water:

The required volume of distilled water was aerated in a container by bubbling compressed air for 8 to 12 hours to attained dissolved oxygen saturation level. It was allowed to stabilize for about 4 hours at room temperature. At the time of use, 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and

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ferric chloride were added for each liter of dilution water. 5 ml of treated sewage per liter of dilution water was added for seeding purpose.

Dilution of polymer solution sample and incubation:

The sample was neutralized with the help of aqueous KOH solution and pH of solution was maintained to 7.0

Pre –treatment Methods:

- Sample solutions were thoroughly shaken just before dilutions were made. Series of dilutions of the sample were prepared to that at least three of the dilutions should depleted the initial oxygen concentration in the dilution water by 20 % to 90 %. The previously determined C.O.D. value was treated as guideline for the purpose of dilution.

- The diluted samples were then filled in standard BOD bottles which were then stoppered and placed in the incubator. In addition to the samples, standard dilution water was also taken into a BOD bottle and incubated as blank at 20 ^{0}C (± 0.1 ^{0}C) for 1, 2, 3..........days determination.

Determination of Dissolved Oxygen[8]:

After incubation for the desired period of time, 2 ml of manganese sulphate solution followed by 2 ml of alkaline iodide and sodium azide solution were added to the BOD bottles. The contents were mixed thoroughly by shaking the bottle several times by placing thumb over its mouth. The precipitate formed was allowed to settle at the bottom. The supernatant water was siphoned off and 2 ml of concentrated sulphuric acid was added to dissolve the precipitate and liberated iodine was titrated immediately against standard sodium thiosulphate solution using starch indicator. The dissolved oxygen concentration in mg/L was then calculated and used for BOD determination:

$$\text{BOD in mg/L} = \frac{[(D_0 - D_1) - (B)] \times \text{Volume of diluted sample (ml)}}{\text{Volume of Sample taken (ml)}}$$

Where,

D_o = Dissolved oxygen in sample on 0th day
D_1 = Dissolved oxygen in sample on 1st/2nd/---- 10th day
$B = (C_o - C_1)$
C_o = Dissolved oxygen in blank on 0th day
C_1 = Dissolved oxygen in blank on 1st/2nd/--- 10th day

Table No. 1: Composition of novel polymers

Sr. No.	Polymer (Ingredients in %)	B14	B33
1	Liquid Glucose	23.81	50
2	Polyethylene Glycol (400)	-	10
3	Sorbitol	52.39	17
4	Citric acid	4.76	10
5	Maleic Anhydride	9.52	10
6	Oxalic Acid	4.76	-
7	Sodium meta bisulphite	4.76	3

Table No. 2: Physico-chemical analysis of novel polymers

Sr. No.	Polymer Properties	B14	B33
1	% Solids	75.19	77.06
2	H.L.B Ratio	14.43	15.00
3	Viscosity In Seconds (Ford cup no. 4 at 30 ^{0}C)	255	235
4	Density (1% solution)	1.02	1.0092
5	Surface Tension (By Stalagmometer method)	45.29	59.74

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Table No. 3: Observation for dissolved oxygen for polymer sample B14

Day	Trial No.	Sample volume in ml	Volume of $Na_2S_2O_3$ used (ml)	Dissolved Oxygen (mg/L)
O Day	Blank	125	6.3	6.3
	Polymer B14	125	5.1	5.1
2nd Day	Blank	125	6.2	6.2
	Polymer B14	125	2.8	2.8
4th Day	Blank	125	6.1	6.1
	Polymer B14	125	2.1	2.1
6th Day	Blank	125	6.0	6.0
	Polymer B14	125	1.4	1.4
8th Day	Blank	125	6.0	6.0
	Polymer B14	125	1.1	1.1
10th Day	Blank	125	6.0	6.0
	Polymer B14	125	0.7	0.7

Table No. 4: Analysis of biodegradability of polymer B14

Sr. No.	Days	Biochemical Oxygen demand (BOD) mg/L	Chemical Oxygen Demand (COD) mg/L	BOD/COD Ratio
1	2nd Day	137.5		0.3131
2	4th Day	181.25		0.4127
3	6th Day	218.75	439.12 mg/L	0.4981
4	8th Day	237.5		0.5408
5	10th Day	262.5		0.5977

Fig. 1: Biodegradability of the polymer sample B14

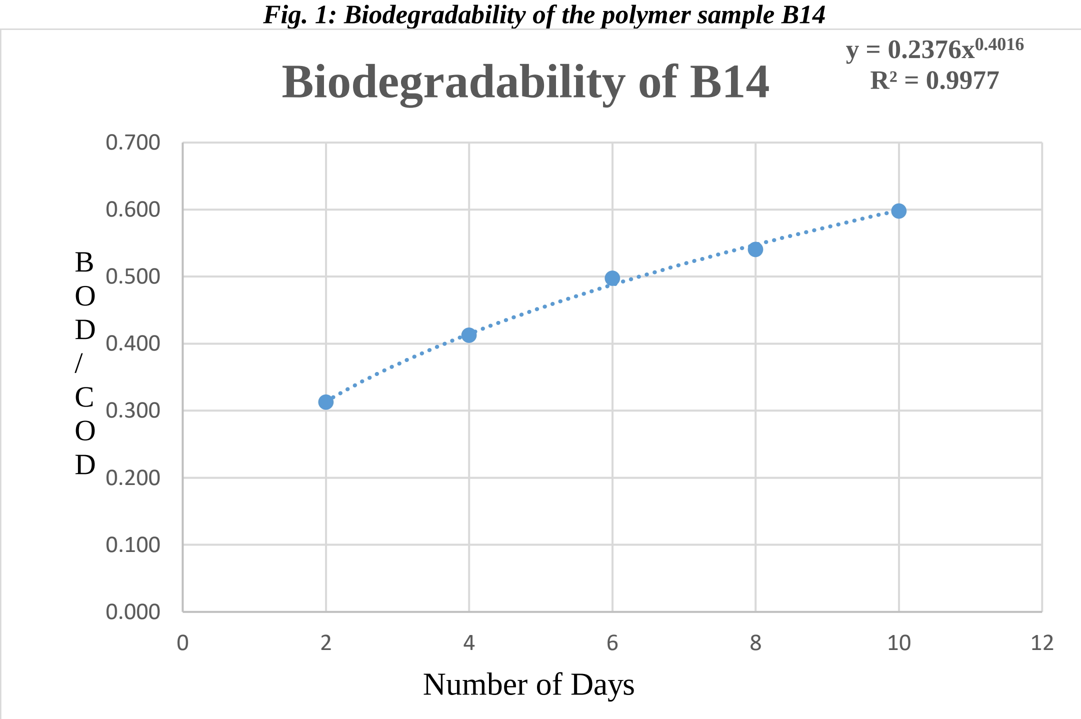

Table No. 5: Observation for dissolved oxygen for polymer B33

Day	Trial No.	Sample volume in ml	Volume of $Na_2S_2O_3$ used(ml)	Dissolved Oxygen (mg/L)
O Day	Blank	125	6.1	6.1
	Polymer B33	125	5.0	5.0

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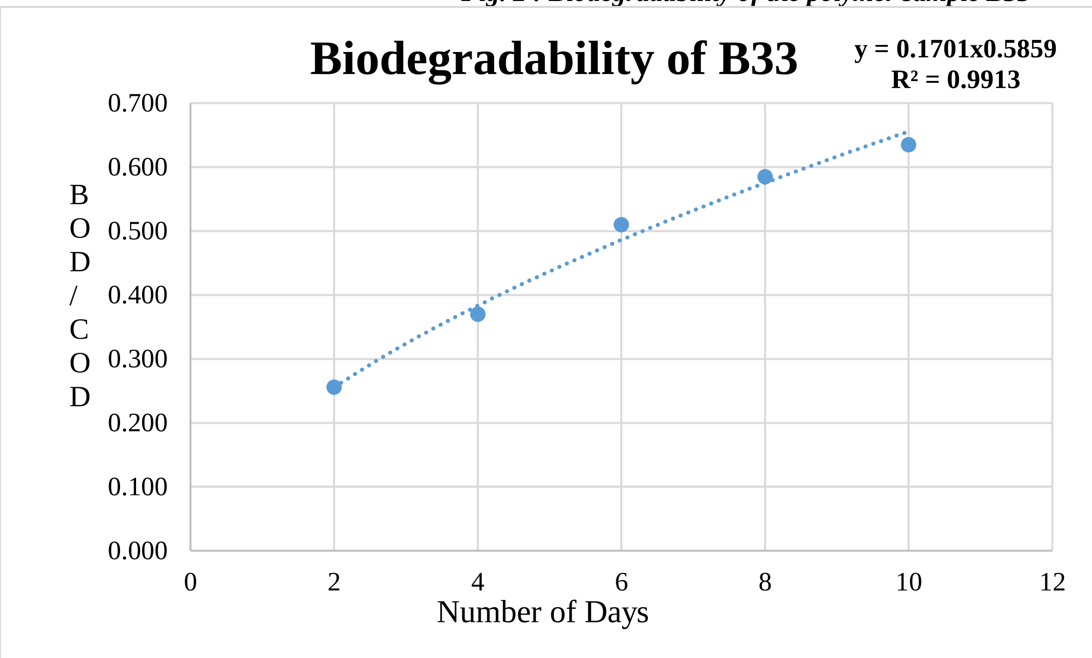
2nd Day	Blank	125	6.1	6.1
	Polymer B33	125	3.2	3.2
4th Day	Blank	125	6.0	6.0
	Polymer B33	125	2.3	2.3
6th Day	Blank	125	6.0	6.0
	Polymer B33	125	1.1	1.1
8th Day	Blank	125	6.0	6.0
	Polymer B33	125	0.8	0.8
10th Day	Blank	125	6.0	6.0
	Polymer B33	125	0.6	0.6

Table No. 6: Biodegradability of polymer sample B33

Sr. No.	Days	Biochemical Oxygen demand (BOD) mg/L	Chemical Oxygen Demand (COD) mg/L	BOD/COD Ratio
1	2nd Day	112.5	439.12 mg/L	0.2561
2	4th Day	162.50		0.3700
3	6th Day	237.5		0.5408
4	8th Day	256.75		0.5846
5	10th Day	268.75		0.6120

Fig. 2 : Biodegradability of the polymer sample B33



RESULTS AND DISCUSSION

1. Table 1 presents the chemical composition of various polymers prepared mainly from glucose and sorbitol. Polyols like glucose and sorbitol were reacted with citric acid, sodium bisulphate and sodium bisulphite to form polymer in the presence of sodium meta bisulphate which increases the rate of reaction.
2. The results of physicochemical analysis of prepared polymers are summarized in Table 2. These polymers samples were found to contain 75.19 % to 77.06 % solids and have excellent viscosity in the range 235 to 255 seconds. The H.L.B. ratio observed was between the values 14.43 to 15.
3. Chemical oxygen demand of diluted polymers B14 and B33 was observed to be 439.12 mg/L.
4. Biochemical oxygen demand analysis of the chosen samples are given in Table 4 and Table 6, and the plot of biochemical oxygen demands to chemical oxygen demand ratio against the number of days allowed for biodegradation id depicted in Figs. 1 and 2. The increasing BOD/COD ratio from about 0.2

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to 0.6 over the period of 10 days of observation indicates the biodegradable nature of the prepared polymer samples B14 and B33.

5. These polymer can be incorporated positively to the extend 12-15% without adversely affecting cost and technical properties of different composition tried.

CONCLUSION

Used of these biodegradable polymer can certainly replace 80 to 100% of acid slurry which is of petroleum origin. The synthesis of this polymer can be done in small kettle which is useful for small scale industries. In future our dependence on acid slurry can be reduced by 80-100%. Small scale manufacturer will be more self-sufficient on raw material front.

It promotes green environment and make our country self-sufficient by replacing a part of acid slurry with biodegradable polymer.

The experimental data is subjected to regression analysis; the BOD/COD ratio shows an increase with respect to the number of days, which can be expressed by the equation for B14 is
$\frac{BOD}{COD} = 0.2376(days)^{0.4017}$ and for B33 is $\frac{BOD}{COD} = 0.1701\ (days)^{0.5859}$.

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