Biodegradation studies of Novel polymer based on sugar

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Abstract

A novel polymer based mainly on sugar, polyethylene glycol (400) and sorbitol has been synthesized. Citric acid has been used for esterification. Temperature, time, ratio of ingredients requires for synthesis have been standardized to get desired HLB ratio, viscosity. The biodegradation study of polymer was carried out using BOD and COD method. The BOD/COD ratio for polymer was found to be favorable and well within the requisite data for biodegradation. The value of BOD/COD ratio for polymer was found to be 0.625.

Keywords: polymerization, HLB ratio, Oxirane oxygen, biodegradability, polymeric surfactants Mineralization.

1.Introduction

During the last decades, the demand of synthetic polymeric materials has been fairly increasing and presently they are one of the most attractive categories of material. This success is mainly related to their properties namely, low cost, aesthetic qualities, and resistance to physical ageing and biological attack. 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 CO_2, H_2O by bacteria, fungi under natural environment. During the degradation process they should not generate any harmful substances[5]

Increasing interest in plastic biodegradation is observed because of environmental pollution.

There is a world-wide research effort to develop biodegradable polymers as a waste management option for polymers in the environment[6]. Biodegradation (i.e. biotic degradation) is a chemical degradation of materials (i.e. Polymers) provoked by the action of microorganisms such as bacteria, fungi and algae. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions.

The nature of the chemical structure of the polymer determines the biodegradability. Whereas the physical properties of the polymer sample affect the rate of Biodegradation.

Biological systems degrade large natural Molecules[6] (Starch, Cellulose,

Proteins etc.) by hydrolysis followed by oxidation. It is therefore not surprising that by and large most of the known biodegradable polymers contact in hydrolysable groups along the polymer main chains. Only a few high molecular weight carbon chains containing polymers are biodegradable.

The biodegradation process can be divided into (1) aerobic and (2) anaerobic degradation

Polymer $+ O_2 -> CO_2 + H_2O +$ biomass + residue(s)
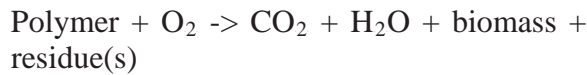
Fig. 1. Schema of polymer degradation under aerobic and anaerobic conditions[6]
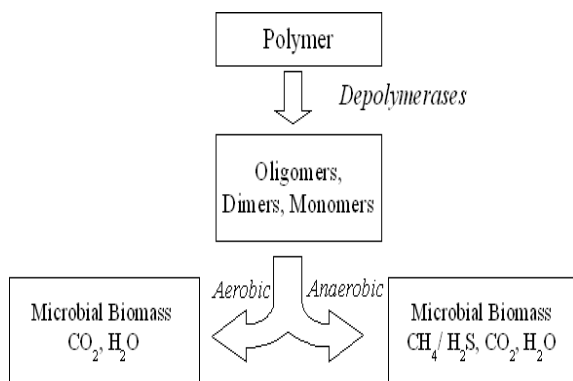
During degradation the PEG molecules are reduced by 1 glycol unit at a time after each oxidation cycles. Ester linkages are generally easy to hydrolyze and hence number synthetic polyesters are biodegradable. Flavobacterium species and pseudomonas species together associate and mineralize PEGs completely. We have incorporated sugar in our polymer as-

- Abundant availability of material at reasonable cost.
- Better chance of biodegradability.
- Produced in very large quantity in our country.
- Vegetable origin will be harmless to skin, cloths or various surfaces.
- At least 30-50% of petroleum based products can be replaced by sugar based polymer.
- Technically up to the mark in respect of foaming, detergency, stain removing capacity.
- Comparable to high standard commercial products.
- The market survey among customers is also encouraging.
- About 90% of customers have appreciated our product.
- The current price of sugar is around Rs. 35/Kg. valuable foreign exchange on crude petroleum.
- Enter into polymerization with acids, alcohols and other reactants.
- Sugar is a source of glucose and fructose which can enter into polymerization with acids, alcohols and other reactants

In the present research work,we have used polyethylene glycol (400), sorbitol, sugar and citric acid as novel ingredients for synthesis of polymeric surfactant Polyethylene glycol with high oxirane oxygen content and citric acid with three acidic groups can give surfactants with better cleaning ink and stain removing and foaming properties. And the synthesized polymers were analyzed for acid value[8], saponification value[8], viscosity, foaming, oxirane oxygen[9], surface tension and and biodegradability using BOD and COD method[10-12]. Our attempt is to get excellent properties and formulations which are

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Table-1.1   Composition of polymers containing polyethylene glycol (400) and sorbitol, sugar as main ingredients (% by weight)

Ingredients	P1
Polyethylene glycol (400)	10
Sorbitol (70% solids)	40
Maleic Anhydride	07
Sugar syrup	30
Citric acid	05
Oxalic acid	05
Phthalic Anhydride	03
Sodium bisulphate ($NaHSO_4$)	1.5
Sodium metabisulphite ($Na_2S_2O_{5)}$	1.5

2. EXPERIMENTAL

2.1 Synthesis of polymer-

In the experimental work novel polymer has been synthesized. The mole ratio, order of addition of ingredients, time of reaction and catalyst has been standardized to get desired HLB ratio, viscosity.

A two liter glass reactor fitted with stirrer, thermometer and condenser has been used.
The heating was affected by an electric heating mantle with temperature regulator. A
temperature control of ± 3oC can be achieved by regulator. Calculated quantity of

ingredients and catalysts are introduced step by step in the reactor. The temperature is raised
slowly and steadily to 130oC in about one hour. The heating is continued for 3-3.5 hrs. till the desired viscosity and characteristics are achieved.
At the end of heating period the sample is withdrawn at 50-60 ^{0}C, filtered, weighed and stored in air tight bottles. The molecular weight of polymer is calculated from mass spectra of Polymer.

2.2 Analysis of novel polymer-

Table –2.2.1 Physicochemical analysis polymers containing polyethylene glycol (400) and sorbitol, sugar as main ingredients

Sr. No.	Polymer Property	Observation
1	Acid value of the polymer	155
2	pH of 1% solution	3
3	% Solids	70.8
4	Solubility of polymer (i) in water (ii) in Xylene (iii) in 50% alcohol + 50% water (iv) in NaOH solution (60%)	Soluble Insoluble Partly soluble Soluble
5	Hydrophilic Lipophilic Balance Ratio of polymer (Based on saponification value)	18.1
6	Viscosity by Ford cup No. 4 at 30^0C in seconds.	203
7	Foam height (Cm^3) by cylinder method (For combination of 90% polymer + 10% Acid slurry)	800
8	Surface tension (dyne/cm) (By stalagnometer)	35.57
9	% oxirane oxygen (By HBr method)	3.49

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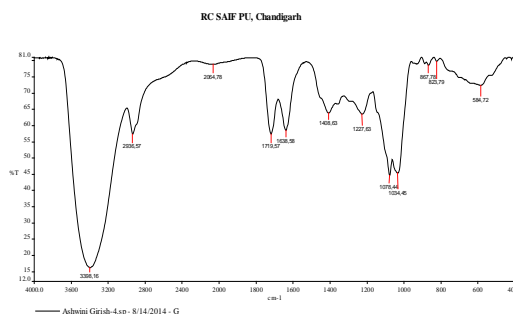
Fig. 1   IR spectra of polymer

Table-2.2.2   The prominent Peaks of the IR spectra of Novel polymer

Wave No.(cm⁻)	Functional group	Literature value(cm⁻)
3398.16	-OH stretching	3450-3200
2936.57	-COOH stretching	2500-3000
1719.57	-COO stretching	1740-1710
1078.44	C-O-C stretching	1050-1250
1227.63	C-O stretching	1201400

The various peaks of IR spectra observed for novel polymer are given in the Table-3

The peak at 3398.16cm^{-1} is due to O-H stretching. This shows broad intermolecular hydrogen bonding of O-H group. The peak at 3398.16 shows the presence of OH groups in the polymer molecule. The peak at 2936.57 cm^{-1} is due to =C-H stretching. We have two peaks at

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1719.57cm^{-1} and 1227.63cm^{-1} which are characteristics peaks for ester group. These two peaks i.e confirm the presence of –C=O group in the polymer. The peak at 1078.44 cm^{-1} shows symmetric C-O-C stretching mode and 1227.63 is for asymmetric C-O-C stretching vibration confirm the presence of ether group in the molecule.

Fig. 2   NMR spectra of polymer
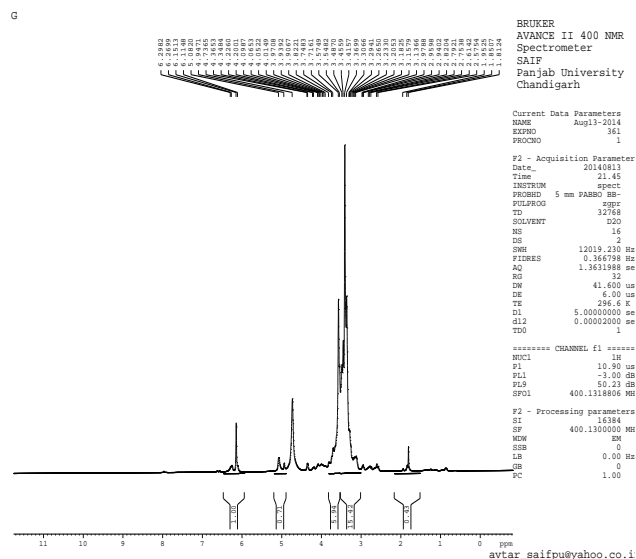
Table-2.2.3 The prominent Peaks of the The NMR spectra of Novel polymer

Range δ (ppm)	Type of proton	Literature valueδ (ppm)
3-4	H-C-O-R(ether)	3.3-4.0
1-2	R-OH(Hydroxyl)	1-5.5
2-2.9	H-COO(ester)	2-2.2

The various peaks of NMR spectra observed for polymer P5 are given in Table-   the value 2-2.9ppm shows the presence of H-COO proton. The NMR peak in the range 3-4 ppm shows the presence of H-C-OR proton.

2.3. BIODEGRADATION-

The term Biodegradation is often used to denote degradation occurring in biological environments. While this may seem to be a logical use, it is necessary to be more precise.

A better definition of biodegradation stipulates that it is the gradual breakdown of a material mediated by specific biological activity.

Biodegradation may also be defined as the decomposition of substances by biological systems. Microorganisms present in soil will try to utilize any substance encountered as a source of energy and carbon by breaking it down into simple chemicals that the organism can then digest.

Thus primary Biodegradation involves the conversion of the original substance into simple chemicals.

And ultimate Biodegradation involves complete "Mineralization" of the original substance into CO_2, water, new microbial mass and indigestible inorganic material if any.

2.4 Standard Procedure of BOD Analysis

2.4.1 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 4 hours at room temperature. At the time of use, 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and 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.

2.4.2. Dilution of Sample and Incubation.

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The sample was neutralized to pH 7.0 using alkali.

2.4.3. Pre –treatment Methods

Samples were thoroughly shaken just before dilutions were made. We made series of dilutions for a sample such that at least three of the dilutions should depleted 20 % to 90 % of initial dissolved oxygen.

2.4.4 Determination of Dissolved Oxygen

The sample was collected in 125 ml bottle; 2 ml of manganese sulphate solution followed by 2 ml of alkaline iodide and sodium azide solution were added. The contents were mixed thoroughly by shaking the bottle several times by placed thumb over it. The precipitate was allowed to settle at the bottom. After settling 2 ml of concentrated sulphuric acid was added to dissolve the precipitate. Again it is mixed and shaked to dissolve liberated iodine. This solution was taken and titrated immediately against standard sodium thiosulphate solution by adding 3-4 drops of starch indicator solution. The end point was pale blue to colorless. The dissolved oxygen in mg/L is equal to the volume in ml of the standard thiosulphate solution used for titration.

2.4.5 Formula for calculate the BOD

BOD mg/L =

$(D_0 - D_1) - (B)$ X $\underline{\text{Volume of the diluted sample}}$

$\qquad$ Volume of sample take

Where
D_0 = Dissolved oxygen in sample on 0 day
D_1 = Dissolved oxygen in sample on $1^{st}/2^{nd}/$ --- 10th day.

B= $(C_0$ - C_0= Dissolved oxygen in blank on 0 day
C_1= Dissolved oxygen in blank on $1^{st}/2^{nd}/$ -- - 10th day

2.5 Standard Procedure of COD Analysis Procedure:

In the reflux flask, 0.4 g of $HgSO_4$, 20 ml of diluted sample were added and mixed well. Subsequently 10 ml of 0.25 N $K_2Cr_2O_7$ and 30 ml H_2SO_4-Ag_2SO_4 solution were added with constant stirring and the contents were refluxed for 2 hours. After refluxing the contents were cooled, the reflux condenser was washed with about 60 ml of distilled water and the content was titrated against standard ferrous ammonium sulphate solution using ferroin indicator. The color change at the end point was green blue to wine red.

2.5.1 Calculation:

COD as mg /L = (B-S) $_X$ N $_X$ 8000 / V

B - Ferrous ammonium sulphate used for bla
S - Ferrous ammonium sulphate used for sample(ml)
N - Normality of Ferrous ammonium sulphate
V - Volume of sample taken (ml)
C.O.D. value was treated as guideline for the purpose of dilution.
Carefully transferred the prepared dilution water into one liter graduated cylinder until it was half full, without any air entrapment. Then added appropriate quantity of sample into the cylinder without producing any air bubbles. The volume was made up using dilution water. Mixed well with glass rod without any air entrapment. Filled the two BOD bottles carefully without any air bubbles inside it. Stopper the bottles and

prepared the other dilution of sample in similar manner.

Also the standard dilution water was taken into BOD bottle and stopper them after filling them completely.

Utilized one set of entire series of dilution prepared above for immediate determination of dissolved oxygen and kept the other set in aBOD incubator maintained at 20ºC($\pm$0.1^{0}C) for 1, 2, 3..........10 days or alternative days. After 1st day to 10th day we determined the

dissolved oxygen concentration of all the incubated sample of the set.

BOD Analysis of polymer (polyethylene(polyethylene glycol, sorbitol, Sugar).

Table – 2.3.1 Volume of sodium Thiosulphate required for dissolved oxygen Analysis.

Sample	Day	Volume of sample (ml)	Burette reading (ml)		Volume of titrant (ml)	Dissolved oxygen (mg/l)
			Initial	Final		
Blank	0 day	125	0	6.2	6.2	6.2
Polymer		125	0	5.2	5.2	5.2
Blank	2nd day	125	0	6.1	6.1	6.1
Polymer		125	0	3.0	3.0	3.0
Blank	4th day	125	0	6.1	6.1	6.1
Polymer		125	0	2.5	2.5	2.5
Blank	6th day	125	0	6.0	6.0	6.0
Polymer		125	0	1.8	1.8	1.8
Blank	8th day	125	0	6.0	6.0	6.0
Polymer		125	0	0.8	0.8	0.8
Blank	10th day	125	0	6.0	6.0	6.0
Polymer		125	0	0.7	0.7	0.7

For the calculation of initial DO, immediately after dilution the volume sample taken is 125 mL.

- For the blank titration the burette reading 6.2mL. The volume of titrant sodium thiosulphate is 6.2mL. The value of DO in mg/L is 6.2

- For the first titration the burette reading is 5.2mL. The volume of titrant is 5.2and the value of DO is 5.2 mg/L.

- For the second titration the burette reading is 3.0 ml. The volume of titrant is 3.0ml and the value of Do is 3.0 mg/L.

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- For the third titration the burette reading is 2.5ml. The volume of titrant is 2.5ml and the value of Do is 2.5 mg/L.
- For the fourth titration the burette reading is 1.8 ml. The volume of titrant is 1.8 ml and the value of Do is 1.8 mg/L.

Calculation:

Initial DO of the diluted sample, D0 = 5.2 mL

DO at the end of 1 day for the diluted sample, D1 = 3.0 mL

Blank correction =   C0 - C5, BC

Initial DO of the blank, C0

DO at the end of 1days for the blank, C1

Biochemical Oxygen Demand

BOD (Polymer 2nd day) =

$$\frac{(5.2-3.0)- (6.2-6.1) \times 125}{2}$$

= 131.25 (mg/L)

BOD (Polymer 4th day =
$$\frac{(5.2-2.5)- (6.2-6.1) \times 125}{2}$$

= 162.50 (mg/L)

BOD (Polymer 6th day) =

$$\frac{(5.2-1.8)-(6.2-6.1) \times 125}{2}$$
= 200 (mg/L)

BOD (Polymer 8th day) =

$$\frac{(5.2-0.8)- (6.2-6.1) \times 125}{2}$$

- For the fifth titration the burette reading is 0.8 ml. The volume of titrant is 0.0ml and the value of Do is 0.8 mg/L.
- For the sixth titration the burette reading is 0.7 ml. The volume of titrant is 0.7ml and the value of Do is 0.7 mg/L.

=   262.51 (mg/L)

BOD (Polymer 10th day)

$$= \frac{(5.2-0.7)- (6.2-6.1) \times 125}{2}$$
=   268.75mg/L

Observation Table

Polymer
2ml. polymer sample was taken
Normally of Ferrous Ammonium Sulphate = 0.101N.
Calculation
Volume required for blank   =   6.7 ml
Volume required for Sample =   5.6 ml

COD of Polymer Sample

$$= \frac{(B - S) \text{ ml x Normality x } 8000}{ML \text{ of sample}}$$

$$= \frac{(6.7-5.6) \times 0.1 \times 8000}{2}$$
=   440mg/l

Table- 2.3.2 Result of ultimate BOD & COD analysis Novel Polymer

International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-3, Issue-01 ,January 2017
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SR.NO	PARTICULARS	CONCENTRATION (mg/g)		
		BOD AT 27^{0}C	COD	BOD: COD
1	After 2nd day	131.25	440	0.2982
2	After 4th Day	162.5		0.3693
3	After 6thDay	200		0.4545
4	After 8thDay	262.51		0.5965
5	**After 10thDay**	**268.75**		**0.6107**

The BOD to COD ratio for PolymerP1 is found to be highest on 10th i.e. 0.625. That means highest biodegradation was observed on 10th day, which is evident from 10th day BOD of resin sample 275

The BOD to COD ratio for PolymerP5 is found to be highest on 10th i.e. that means highest biodegradation was observed on 10th day, which is evident from 10th day BOD of resin sample 268.75

RESULT & DISCUSSION:

Table-1 gives composition of Novel polymer based on sorbitol & polyethylene glycol and sugar about 10% polyethylene glycol 400 has been used in formulations. 5% of citric acid has been used in compositions. In about 3 hours of heating at 130^{0}C

We get desired viscosity, acid value.The physicochemical analysis of Novel polymer is given in Table-2

The acid value of sample is 155. The sample has a reasonable viscosity of 203 seconds by Ford cup No. 4. The HLB ratio suggests the use of these polymers in detergent compositions. The oxirane oxygen is quite high and comparable to 38% sodium lauryl ether sulphate.

The presence of oxirane oxygen will certainly add to foaming and other detergent characteristics.

The I.R. & N.M.R. spectra of polymer C confirmed the presence of ester, ether , free acid and free hydroxyl groups in the polymer(see I.R. and N.M.R. spectra-Fig.1, Fig-2. The molecular weight of polymer –C Obtained from mass spectra (see Fig.3). Polymer sample has been selected for formulations of liquid detergent based on physicochemical analysis of polymers. The higher H.L.B. ratio & % oxirane oxygen certainly suggest the use of polymer in liquid laundary detergent composition.

The BOD to COD ratio for Polymer is found to be highest on 10th i.e. 0.625. That means highest biodegradation was observed on 10th day, which is evident from 10th day BOD of resin sample 275

CONCLUSIONS:

1) The polymeric surfactants containing polyethylene glycol (400), sorbitol, sugar and small quantities of acids like, citric can be prepared. The polymer after selection of proper

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mole ratio, heating period and catalyst give final products which can be used as partial replacement of acid slurry in laundry detergent compositions.

2) The I.R. & N.M.R. spectra of the polymer show the presence of ester, ether, and free acid and free hydroxyl groups in the polymer.

3) The manufacturing cost of polymer is around 60Rs per Kg. Thus the use of this polymer is techno economically attractive.

4) The measure of biodegradability is the ratio of BOD: COD. Normally as a thumb rule if Ratio is 0.6 and above the polymer/Material is considered to be biodegradable. All the polymers give this ratio in 10 days. The studies conducted in the Laboratory indicate that PolymerP1 has ratio 0.625 and above and polymer has ratio 0.625.Therefore these samples can be considered as biodegradable.

5) Pilot plant & commercial products of the polymer must be started.
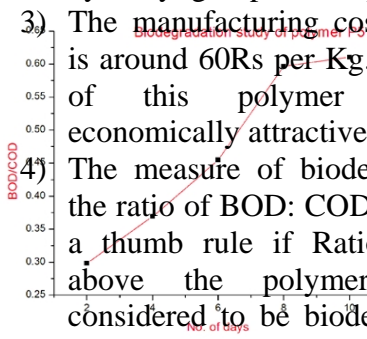
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