

BIODEGRADATION STUDIES OF NOVEL POLYMER BASED ON CARBOHYDRATE ORIGIN

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ABSTRACT

A novel polymer based mainly on 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: Biodegradation, HLB ratio, esterification, BOD/COD ratio.

INTRODUCTION

A large number of household and industrial products are mainly based on crude petroleum. India as, a country is imparting 2/3rd of our requirement by way of import from other countries Soft Acid slurry and Alpha olefin sulphionate are the active ingredients for powder, liquid & cake detergents. These actives are also used in toiletries, cleansers, cosmetics and many industrial products. Our laboratory is working since a decade on replacing acid slurry with polymeric surfactants based on, starch,^[1] sorbitol,^[2] vegetable oil.^[3]

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. 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.^[5] 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 contain hydrolysable groups along the polymer main chains. Only a few high molecular weight carbon chains containing polymers are biodegradable. Polysaccharides react with small carboxylic acids to produce derivatives that are biodegradable.

In the present research work, we have used polyethylene glycol (400), sorbitol 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,^[7] saponification value,^[7] viscosity, foaming, oxirane oxygen,^[8] surface tension and biodegradability using BOD and COD method.^[9-11] Our attempt is to get excellent properties and formulations which are technically and economically viable propositions.

MATERIALS AND METHODS

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 $\pm 30^\circ\text{C}$ 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 130°C 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 $50-60^\circ\text{C}$, filtered, weighed and stored in air tight bottles. The molecular weight of polymer is calculated from mass spectra of polymer.

Table 1: Composition of polymer containing polyethylene glycol (400) and sorbitol as main ingredients (% by weight).

Ingredients	%
Polyethylene glycol (400)	10
Sorbitol (70% solids)	65
Maleic Anhydride	-
Citric acid	18
Oxalic acid	-
Phthalic Anhydride	-
Benzoic acid	-
Sodium bisulphate (NaHSO_4)	3.5
Sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$)	3.5

Analysis of novel polymer

Table 2: Physicochemical analysis polymers containing polyethylene glycol (400) and sorbitol as main ingredients.

Sr. No.	Polymer Property	Observation
1	Acid value of the polymer	83.48
2	pH of 1% solution	4
3	% Solids	89.00
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)	15.9
6	Viscosity by Ford cup No. 4 at 30°C in seconds.	272
7	Foam height (Cm^3) by cylinder method (For combination of 90% polymer + 10% Acid slurry)	1000
8	Surface tension (dyne/cm) (By stalagnometer)	27.07
9	% oxirane oxygen (By HBr method)	4.2

1. IR spectra of polymer

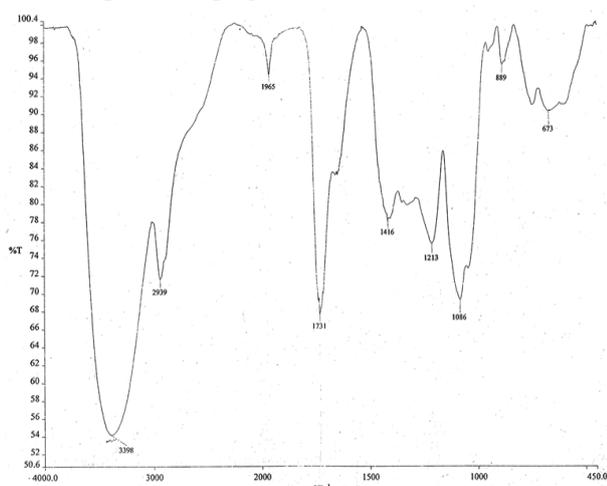


Table 3: The prominent Peaks of the IR spectra of Novel polymer-P1.

Wave No. (cm^{-1})	Functional group	Literature value (cm^{-1})
3398	-OH stretching	3450-3200
2939	-COOH stretching	2500-3000
1731	-COO stretching	1740-1710
1086	C-O-C stretching	1050-1250
1213	C-O stretching	1200-1400
889	= C-H bending	700-1000

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

The peak at 3398cm^{-1} is due to O-H stretching. This shows broad intermolecular hydrogen bonding of O-H group. The peak at 3398 shows the presence of OH groups in the polymer molecule.

The peak at 2939cm^{-1} is due to $=\text{C-H}$ stretching. We have two peaks at 1731cm^{-1} and 1213cm^{-1} which are characteristic peaks for ester group. These two peaks i.e. confirm the presence of $-\text{C}=\text{O}$ group in the polymer. The peak at 1086cm^{-1} shows symmetric C-O-C stretching mode and 1213 is for asymmetric C-O-C stretching vibration confirms the presence of ether group in the molecule.

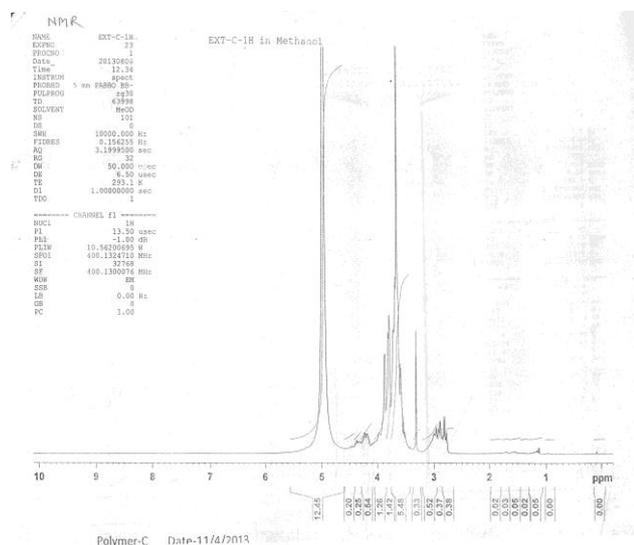


Fig 2: NMR spectra of polymer-P1.

Table 4: The prominent Peaks of the NMR spectra of Novel polymer.

Range δ (ppm)	Type of proton	Literature value(ppm)
3.37-4.04	H-C-O-R(ether)	3.3-4.0
1-4	R-OH(Hydroxyl)	1-5.5
2-2.9	H-COO(ester)	2-2.2

The various peaks of NMR spectra observed for polymer P1 are given in Table-4 The value 2-2.9ppm shows the presence of H-COO proton. The NMR peak in the range 3.37-4.04 ppm shows the presence of H-C-OR proton.

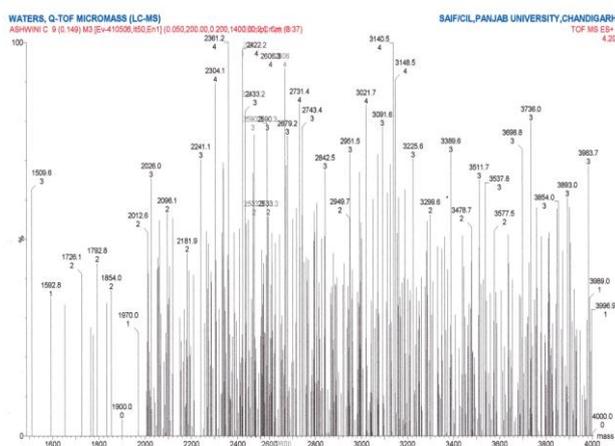


Fig 3: Mass spectra of polymer.

Table 5: Number average molecular weight of polymers.

Sr. no	Polymer	Number average molecular weight
1	P1	2768

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.

Standard 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 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. Dilution of Sample and Incubation.

The sample was neutralized to pH 7.0 using alkali.

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. The 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 stoppers 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 a BOD incubator maintained at 20°C(±0.1°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.

4. Determination of Dissolved Oxygen^[12]

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 shaken 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.

Calculations

BOD Analysis of polymer P1 (polyethylene glycol, sorbitol, citric acid)

Table 6: 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
PolymerP1		125	0	5.3	5.3	5.3
Blank	2 nd day	125	0	6.1	6.1	6.1
PolymerP1		125	0	3.0	3.0	3.0
Blank	4 th day	125	0	6.1	6.1	6.1
PolymerP1		125	0	2.3	2.3	2.3
Blank	6 th day	125	0	6.0	6.0	6.0
PolymerP1		125	0	1.5	1.5	1.5
Blank	8 th day	125	0	6.0	6.0	6.0
PolymerP1		125	0	1.4	1.4	1.4
Blank	10 th day	125	0	6.0	6.0	6.0
PolymerP1		125	0	0.7	0.7	0.7

Calculations for BOD

Initial DO of the diluted sample, D0 = 5.3 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

$$\text{BOD (PolymerP1 2nd day)} = \frac{(5.3-3.0) - (6.2-6.1) \times 125}{2}$$

$$= 137.5 \text{ mg/l}$$

5. Formula for calculate the BOD

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

Where

D₀ = Dissolved oxygen in sample on 0 day

D₁ = Dissolved oxygen in sample on 1st/2nd/---- 10th day

B = (C₀ - C₁)

C₀ = Dissolved oxygen in blank on 0 day

C₁ = Dissolved oxygen in blank on 1st/2nd/---- 10th day

Standard Procedure of COD Analysis^[9]

Procedure

In the reflux flask, 0.4 g of HgSO₄, 20 ml of diluted sample were added and mixed well. Subsequently 10 ml of 0.25 N K₂Cr₂O₇ and 30 ml H₂SO₄-Ag₂SO₄ 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.

Calculation

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

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)

$$\text{BOD (PolymerP1 4th day)} = \frac{(5.3-2.3) - (6.2-6.1) \times 125}{2}$$

$$= 181.25 \text{ mg/l}$$

$$\text{BOD (PolymerP1 6th day)} = \frac{(5.3-1.5) - (6.2-6.0) \times 125}{2}$$

$$= 225 \text{ mg/l}$$

$$\text{BOD (Polymer P1 8}^{\text{th}} \text{ day)} = \frac{(5.3-1.4) - (6.2-6.0) \times 125}{2}$$

$$= 231.25 \text{ mg/l}$$

$$\text{BOD (Polymer P1 10}^{\text{th}} \text{ day)} = \frac{(5.3-0.7) - (6.2-6.0) \times 125}{2}$$

Polymer P1

2ml. polymer sample was taken, Normally of Ferrous Ammonium Sulphate = 0.101N.

Calculation for COD

Volume required for blank = 6.7 ml

Volume required for Sample = 5.6 ml

$$\text{COD of Polymer Sample} = \frac{(B - S) \text{ ml} \times \text{Normality} \times 800}{\text{ML of sample}}$$

$$= \frac{(6.7-5.6) \times 0.1 \times 8000}{2}$$

$$= 440 \text{ mg/l}$$

Table 7: Result of ultimate BOD and COD analysis.

Sr. No.	Particulars	Concentration (mg/g)		
		BOD AT 27°C	COD	BOD: COD
1	After 2nd day	137.5	440	0.3125
2	After 4th Day	143.75		0.4119
3	After 6thDay	225		0.5113
4	After 8th Day	231.25		0.5255
5	After 10thDay	275		0.625

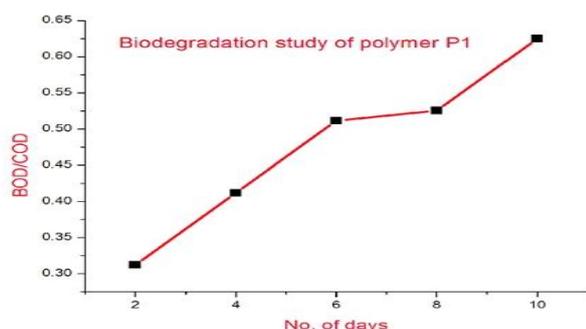
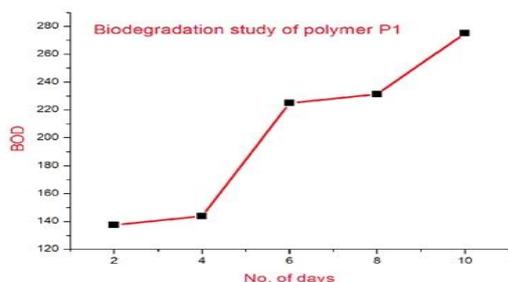
RESULT AND DISCUSSION

Table-1 gives composition of Novel polymer based on sorbitol & polyethylene glycol. About 10% polyethylene glycol 400 has been used in formulations. 18% of citric acid has been used in compositions. In about 3 hours of heating at 130°C we get desired viscosity, acid value.. The physicochemical analysis of Novel polymer is given in Table-2.

The acid value of sample is 83.48. The sample has a reasonable viscosity of 272 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) Sample P1 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 c in liquid laundry detergent composition.

The BOD to COD ratio for Polymer P1 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 and small quantities of acids like, citric can be prepared. The polymer after selection of proper 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 polymerP5 has ratio 0.6107. Therefore these samples can be considered as biodegradable.

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

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