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An esteric polymer synthesis and its characterization using starch, glycerol and maleic anhydride as precursor

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Abstract

The synthesis of polymer from starch, glycerol and maleic anhydride using HCl as catalyst is carried out. The polymer obtained has an average molar mass of 1875 g/mol. This and other physicochemical properties of this polymer are presented. The ester group in the polymer is analyzed by IR and NMR spectral studies. The COD and BOD study of polymer is done. The BOD shows first the increase and then decrease during the course of 10 days of analysis.

Keywords: Synthesis; Polymer; Carbohydrate; BOD

1. Introduction

In the recent years, biodegradable polymer systems have been widely investigated. In medicinal fields, it is being studied with great attention especially for the controlled drug delivery, vaccines, proteins and peptides (Cohen, Yoshioka, Lucarelli, Hwang, & Langer, 1991; Hora et al., 1990).

Polyesters are mostly studied biodegradable polymers. The study of synthesis and characterization of biodegradable low molecular weight aliphatic esters and their delivery in protein delivery systems is recently done (Zhou, Deng, Li, Jia, & Liu, 2004).

Polymers based on carbohydrates have emerged as an exciting topic of polymer research due to worldwide focus on sustainable materials. Almost all walks of life needs paradigmatic shift from petroleum and non-renewable source towards sustainable materials.

The polymers based on carbohydrates dates back to as early as the 1930s. Reppe (1930) was the first to synthesis vinyl saccharide monomer. He synthesized ethers from glucose and fructose by alkali-catalyzed addition of protected sugars to acetylene.

Functionalization of polymers has emerged as another important area of research in polymer science and technology. The polymers containing carbohydrates are useful in various fields like pharmacological and biomedical applications (Kobayashi, Sumitoma, & Ina, 1985), in synthetic fibers like nylon type from 1,6-diaminosugars and dibasic acids (Bird, Black, Dewar, & Rutherford, 1960).

Very few workers have worked on polymers synthesized from maleic anhydride (Dontulwar, Borikar, & Gogte, in press; Vaidya & Bhattachrya, 1993). The esters of carbohydrates are completely soluble in water and found to be sustainable in detergent formulation (Dontulwar et al., in press). The detergent made out of an acid slurry causes harm to aquatic flora and fauna. Acid slurry has petroleum origin. The detergents of petroleum origin are responsible for foaming and eutrophication. By using biodegradable polymers in detergent formulation, the above said problem of water pollution can be minimized to a grater extent.

In our earlier work, we discussed the synthesis of biodegradable polymers from sorbitol, white dextrine and maleic anhydride (Dontulwar et al., 2005)

The present work encompasses the synthesis of polymer from carbohydrate starch, glycerol and maleic anhydride using water as solvent and HCl as catalyst in order to see its application in detergent formulation. The application of this polymer will be presented elsewhere.

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Table 1
Stoichiometric proportion of components in polymer synthesis

S. no.	Raw material	Concentration (%)
1	Starch (400 g)	30.76
2	Glycerol (700 g)	53.84
3	Maleic anhydride (200 g)	15.38
4	Water as solvent	1000 ml (total)

Table 2
Physico-chemical properties of polymer

S. no.	Polymer property	Observation
1	Acid value of the polymer	59.8
2	pH value of the polymer (by pH paper)	2.00
3	Saponification (sap) value	146
4	Solid (%)	64
5	Acid value of maleic anhydride	1144.00
	Acid value of glycerol	0.47
	Acid value of starch	6.0
6	Solubility	
	Starch	Soluble in hot water
	Glycerol	Water soluble
	Maleic anhydride	Soluble in hot water
7	Solubility of polymer (g/mol)	
	(i) in water	Soluble
	(ii) in xylene	Insoluble
	(iii) alcohol	Inoluble
	(iv) in alcohol + water (1:1)	Partially soluble
	(v) in NaOH solution	Soluble
8	HLB of polymer	12.39
9	MW of the polymer	1875 g/mol

2. Experimental

A glass reactor fitted with stirrer, heating mantle and condenser has been used in the synthesis of novel polymers. The temperature control of 2 °C can be achieved by using an efficient temperature regulator. A constant water supply through a condenser helps to control reactor temperature. Initially stoichiometric quantity (Table 1) of starch, glycerol and maleic anhydride was added in the reactor. Hydrochloric acid was used as a catalyst. Now about 200 ml of water was added so that a free flowing homogenous paste was formed. The temperature was raised slowly and steadily in about 0.5 h to 120 °C. The reaction was continued for 3.5 h till the desired molecular weight was achieved. The consistency of the paste was maintained by adding additional water after 0.5 h. At the end of this period, the reaction was terminated and the prepared polymer was collected in a glass-stoppered bottle with least air gap. The final yield of the product was measured. The molecular weight of the polymer was determined by viscosity average method using Redwood viscometer. The acid value and the sap value (Bacher, 1960a,b) and other physical constants were determined by standard methods.

The polymer formed is believed to be an ester of carbohydrate, which has been corroborated by spectral studies. The biodegradable evidence is obtained through BOD and COD studies. The COD of the synthesized polymer was found to be 970,305.67 mg/g of the polymer. For BOD study, the bacteriological seed was brought from bacteriological reactor of food industry and preserved at 37 °C in laboratory. The seed was activated by adding the nutrients as phosphate buffer, dextrose and ammonium chloride in sufficient quantity. The seed was then aerated for 48 h and multiplied. This activated seed was inoculated or added to dilute polymer sample (0.241 g in 500 ml water) for analysis and subsequent BOD of the dissolved resin was estimated for 10 days. The results are described in Table 3.

3. Results and discussion

The synthesis of polymer from starch, glycerol and maleic anhydride was performed in the presence of HCl as catalyst at 120 °C. The physiochemical properties are shown in Table 2.

Figs. 1 and 2 show the IR and NMR spectra, respectively, of the synthesized polymer. The IR

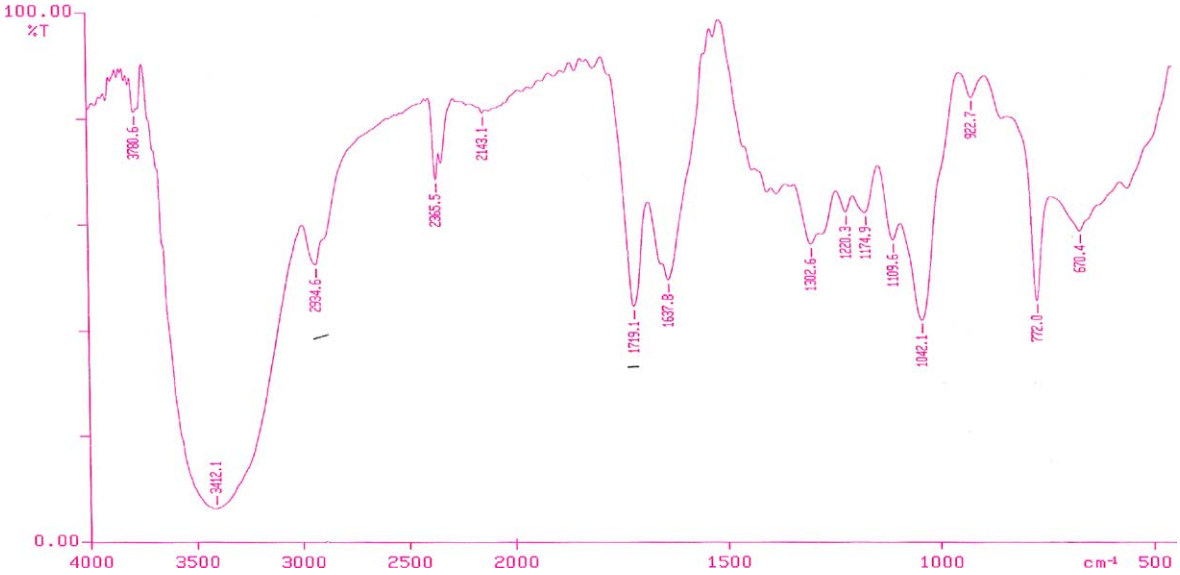


Fig. 1. IR spectra.

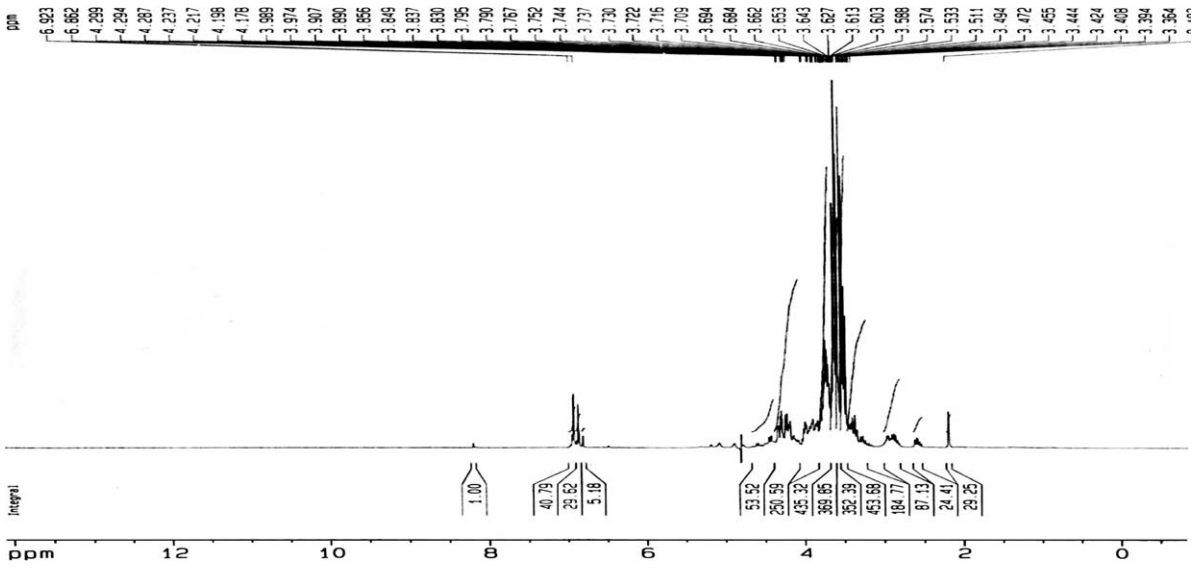
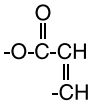


Fig. 2. NMR spectra.

spectra show a doublet near 1700 cm^{-1} (1719.1 and 1652.25 cm^{-1}), which is an indication of C=O stretching in the synthesized polymer. The peak at 1220.3 cm^{-1} shows C–O stretching. The IR spectra also show the various peaks between 1300 and 1050 cm^{-1}, which are due to maleic anhydride C–O stretch. This shows that all the molecules of maleic anhydride are not participating in the reaction from the same side. The peaks at 1719.1, 1652.25 and 1220 cm^{-1} collectively verify the presence of esteric group in the synthesized polymer. This is further verified by the NMR spectra showing peak at 3.709 ppm. The unreacted alcoholic groups are shown by a peak at 3412.1 cm^{-1} in the IR region, which can be also verified by NMR by the peaks between 3.4 and 4 ppm. The peak in NMR is specifically strong at 3.627 ppm, which is an indication that not all the –OH groups of starch and sorbitol are reacted. The reaction is specific with the reactive alcoholic groups in the glycerol and starch with maleic anhydride. The peak in the region of 4.299 ppm in NMR is an indication of the vinylic form (C=C–H) which is due to the maleic anhydride structure in the compound. Thus the spectral study is revealing the presence of



group in the synthesized polymer.

The carbohydrate polymer formed out of starch, glycerol and maleic anhydride is studied in order to see the its biodegradable nature. The results (Table 3) show 11% reduction of BOD on first day, which increases to 61% on the seventh day. The results also show the drastic reduction of BOD, which was compared with normal BOD estimation of 5 days of BOD (Fig. 3).

The application of the synthesized polymer/resin with respect to detergent formulation is checked by HLB value. The HLB value of 12.39 is indicative of the use of synthesized polymer in detergent formulation and in some cases for paints, inks and emulsions, etc. The polymer is soluble in water and NaOH and insoluble in organic solvent xylene and alcohol and is partially soluble in alcohol-water (1:1) mixture.

Table 3
Table3 COD and BOD study of the synthesized polymer

S. no.	Time	Parameters		BOD:COD
		BOD at 20 °C	COD	
1	After 24 h (1st day)	104,803.49	970,305.67	0.1080
2	After 48 h (2nd day)	209,606.98		0.2173
3	After 72 h (3rd day)	393,013.10		0.4015
4	After 96 h (4th day)	445,414.84		0.4590
5	After 120 h (5th day)	563,318.77		0.5806
6	After 144 h (6th day)	576,419.21		0.5941
7	After 168 h (7th day)	589,519.65		0.6076
8	After 192 h (8th day)	550,218.34		0.5670
9	After 216 h (9th day)	524,017.46		0.5401
10	After 240 h (10th day)	235,807.86		0.2430

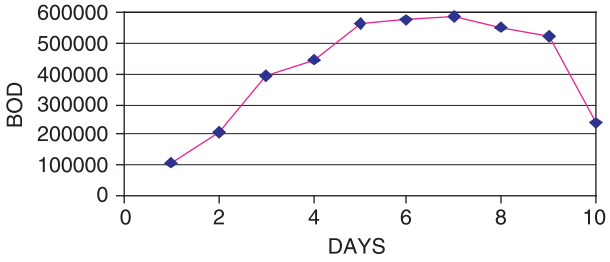


Fig. 3. Trend of BOD with time.

4. Conclusion

The polymer with MW 1875 g/mol was synthesized by direct condensation using HCl as catalyst. The polymer is as ester based on starch, glycerol with maleic anhydride. The polymer is biodegradable in nature. The polymer can be used in the detergent formulation, paints, inks, emulsions, etc. The polymer is soluble in water and NaOH.

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