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Synthesis and characterization of biodegradable polymer from mixed carbohydrate and maleic anhydride as precursor

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Abstract

The synthesis of polymer from carbohydrates sorbitol and white dextrin with maleic anhydride using HCl as catalyst is carried out. The polymer obtained has an average molar mass of 1850 g/mol; this and other physico chemical properties of this polymer are presented. The polymer is analysed by IR and NMR spectral studies to possess the ester group. The polymer is found to be useful in detergent formulation.

Keywords: Synthesis; Polymer; Carbohydrate

1. Introduction

The advent of polymers represents one of the important industrial revolutions of the 21st century. Polymers based on carbohydrates have re-emerged as exciting topics of polymer research, due to worldwide focus on sustainable materials. Research activities throughout the world are concentrated to find an alternative to non-biodegradable polymer. Considering the importance of an environmental protection and conservation the scientific community is exploring the various possibilities of finding environment friendly product/ biodegradable product.

In the recent years, biodegradable polymers have been widely investigated, especially for biomedical field. (Varma, Kennedy, & Galgali, 2004). There has been a worldwide realization that nature derived monosachharides, disachharides, oligosachharides and polysachharides can provide us a raw material needed for the production of numerous industrial consumer goods (Kunz, 1993; Pacitti, 2003; Varma, 2003). Functionalization of polymers has emerged as another important area of polymer science and technology.

The esters of carbohydrates are completely soluble in water and found to be suitable in the detergent formulation. The detergents made out of an acid slurry cause harm to aquatic flora and fauna. Acid slurry has a petroleum origin. The detergents of petroleum origin are responsible for river foaming and eutrophication. By using biodegradable polymers in detergent formulation the above-mentioned problems of water pollution can be minimized to a greater extent.

The polymers containing carbohydrates are potentially processable and biodegradable (Carneiro, Fernandes, Figneiredo, Fortes, & Frietas, 2001) and biocompatible (Chen, Dordick, & Rethwisch, 1995; Patil, Dordick, & Rethwisch, 1991a; Patil, Rethwisch, Dordick, 1991b) polymers. The present work encompasses the polymer synthesis from carbohydrates sorbitol and white dextrin and maleic anhydride using water as a solvent and concentrated HCl as a catalyst in order to formulate the biodegradable detergents. The applications of this polymer will be presented elsewhere.

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 sorbitol, white dextrin 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

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Table 1
Stoichiometric proportion of components in polymer synthesis

Serial No.	Raw material	Concentration (%)
1	Sorbitol	53.84
2	White dextrin	30.76
3	Maleic anhydride	15.38
4	Water as solvent	700 ml (Total)

Table 2
Physico-chemical properties of polymer

Serial No.	Polymer property	Observation
1	Acid value of the polymer	115.40
2	pH value (by pH paper)	2.00
3	Saponification (Sap) value	156.24
4	Solid (%)	62.00
5	Yield of the polymer (%)	53.84
6	Acid value of white dextrin	0.90
7	Acid value of maleic anhydride	1144.00
8	Solubility of polymer (g/mol)	
	(i) In water	Soluble
	(ii) In Xylene	In soluble
	(iii) In alcohol + water	Partially soluble
	(iv) In NaOH solution	Soluble
9	HLB of polymer	11.89
10	MW of the polymer	1850

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 field of the product was measured. The molecular weight of the polymer was determined by viscosity average method. This method depends upon the principle that the limiting viscosity number is proportional to the molecular weight. The molecular weight is related to the limiting viscosity number (η), specific viscosity (η_{sp}) and ratio of amount of non-volatile to the amount of volatile (C) component according to equations.

$$\frac{\eta_{sp}}{C} = \eta + K'[\eta]^2\eta_{sp} \quad \text{[Schulz–Blachkeel equation]}$$

$$\eta = K_s M \quad \text{[schulz equation]}$$

where K_s is proportionality constant, which depends on polymer.(non-volatile), solvent and temperature. M is the molecular weight of the non-volatile compound. Thus it is clear from the above equations that knowledge of K_s is required for calculating for molecular weight of polymer. This can be done by calculating K_s from the known molecular polymer (reference polymer). The reference used in our work was polyethylene glycol. The operation was carried out in Redwood viscometer.

The acid value (Bacher, 1960a) and the sap value (Bacher, 1960b) and other physical constants were determined.

The polymer synthesized from white dextrin, sorbitol and maleic anhydride are found to be biodegradable. The resin/polymer formed is believed to be an ester of carbohydrate which has been corroborated by spectral studies.

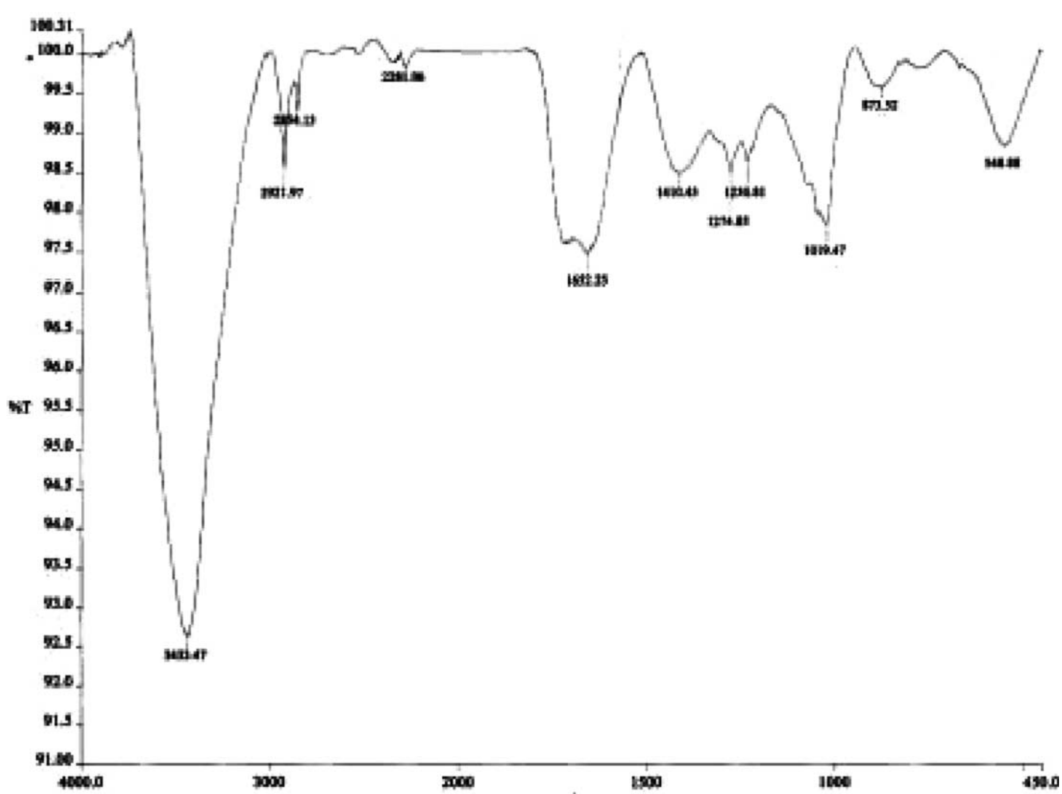

Fig. 1. IR spectra.

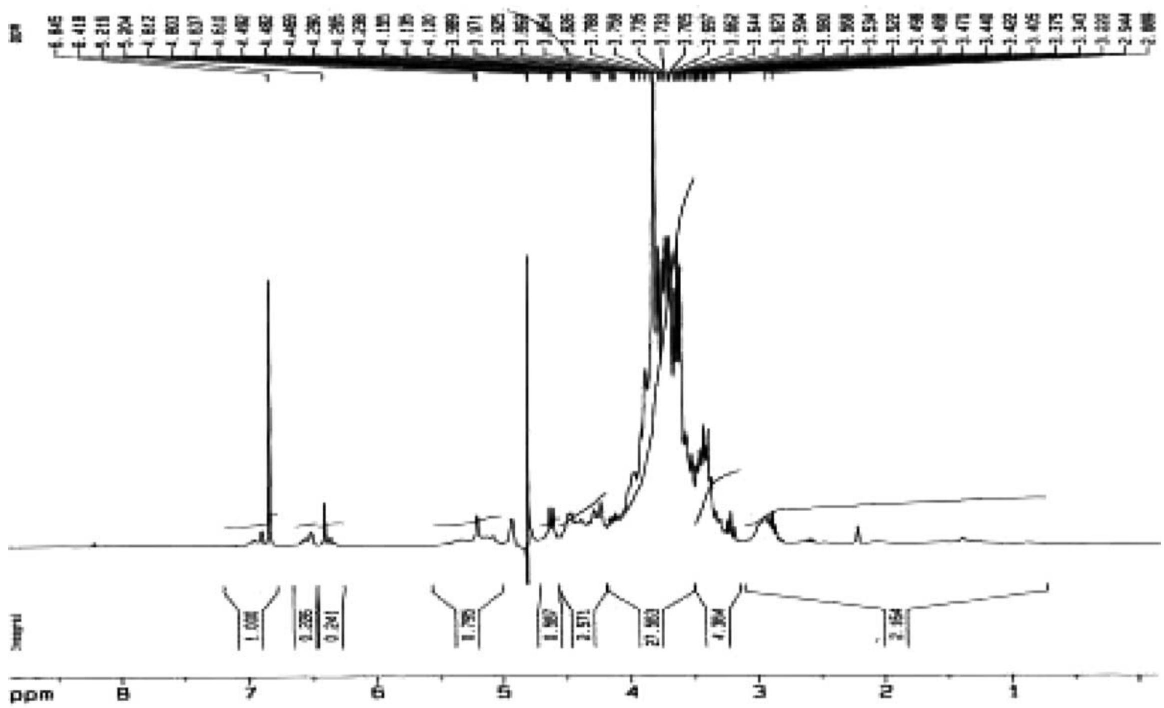

Fig. 2. NMR spectra.

The biodegradable evidence obtained through BOD and COD studies. The thermal analysis was done by DSC curve.

3. Results and discussion

The synthesis of the polymer from sorbitol, white dextrin and maleic anhydride was performed in presence of HCl as a catalyst at 120 °C. The physicochemical properties of the synthesized polymer are shown in Table 2.

Figs. 1 and 2 show the IR and NMR spectra, respectively, of the synthesized polymer. The IR spectra, shows a doublet near wavenumber 1700 cm^{-1}, (1718.51 cm^{-1}, 1652.25 cm^{-1}) which is an indication of C=O stretching in the compound. The peak at 1230 cm^{-1} is due to C–O stretch. The two peaks collectively verify the presence of ester group in the synthesized polymer. The formation of ester is also confirmed by NMR study. The various peaks between the region 3.705–3.826 indicate the esteric proton (R–COOCH) while peak at

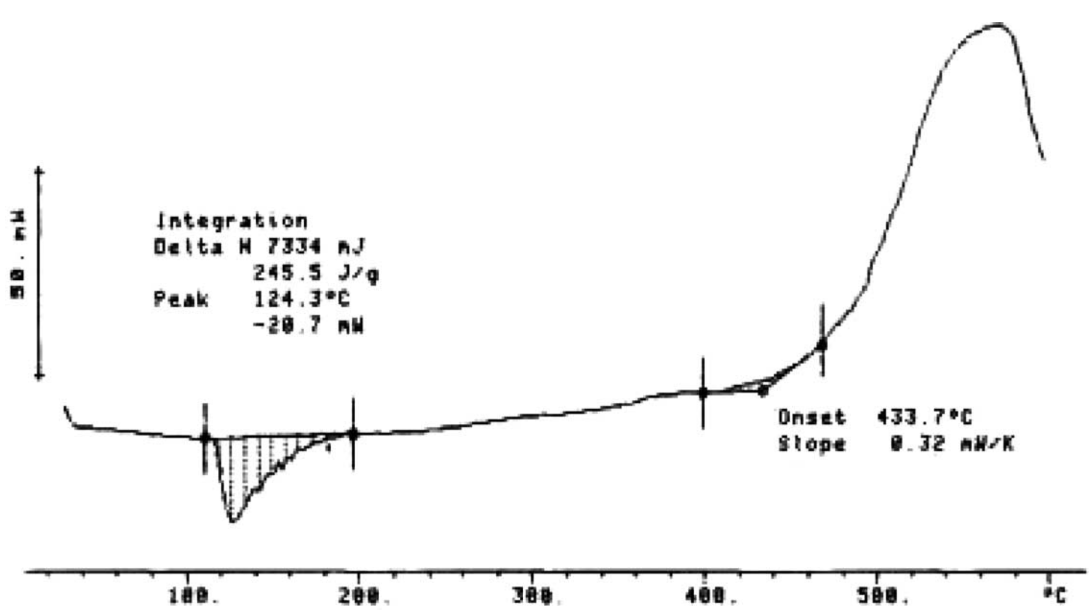

Fig. 3. DSC curve.

4.803 indicate presence of vinylic proton (C=C–H) which is due to the maleic anhydride structure in the compound. This collectively reveals the presence of $\text{-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}\underset{\underset{\text{-CH}}{\|}}{\text{CH}}$ group in the polymer. The strong peak in IR spectra at 3433.47 cm^{-1} may be due to the unreacted –OH group in the carbohydrate component.

The carbohydrate polymer formed out of white dextrin, sorbitol, maleic anhydride is found to be bio-degradable. The biodegradability is verified by the BOD to COD ratio which comes out to be 0.936 in the synthesized polymer. This value exceeds 0.6 validating the biodegradability of synthesized polymer.

The application of the synthesized polymer/resin with respect to detergent formulation is checked by HLB value which is calculated as

$$\text{HLB} = 1 - \frac{\text{Sap value of the polymer}}{\text{Acid value of the raw materials}}$$

The HLB value of 11.89 (almost equal to 12) is indicative of the use of the synthesized polymer in detergent formulation and in some cases for paints, inks and emulsions, etc. Regarding solubility the polymer is soluble in water and NaOH and insoluble in the organic solvent xylene.

The DSC curve (Fig. 3) of the synthesized polymer indicates mp 124.3 °C which is an indication of stability at normal temperature. This will make the polymer useful for various applications described earlier. The exothermic reaction starts at 433.7 °C which may be due to the oxidation of carbon. No glass transition found in the curve.

4. Conclusion

The polymer with MW 1850 g/mol of was synthesized by direct condensation using HCl as catalyst. The polymer is an ester based on carbohydrates sorbitol, white dextrin with maleic anhydride. The polymer has good thermal stability and it can be used in detergent formulation, paint, inks, emulsions, etc. The polymer is soluble in water and NaOH.

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