

Maize Starch Based polymeric Surfactants for Liquid and Powder Detergents

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ABSTRACT

Maize starch sorbitol based polymers have been synthesized. Starch and sorbitol have been reacted with organic acids (Maleic, phthalic, citric and oxalic) to get polymers which can act as substitutes for conventional active materials linear Alkyl benzene sulphonate (LABS) and Alpha olefin sulphonates. The polymers were investigated for physicochemical and spectral properties and used successively in liquid and powder detergents compositions. Commercial production of these polymers can reduce the consumption of acid slurry and alpha olefin sulphonate which are totally based on crude petroleum.

Keywords: Maize starch, sorbitol, polymeric Surfactant, esterification, organic acids.

1. INTRODUCTION

Surfactants based on renewable resources have experienced increased attention in recent years. Maize starch and sorbitol based polymeric surfactant is our interest as an alternative for petroleum based surfactants¹. Commercially available detergents mostly contain acid slurry (LABSA) and alpha olefin sulphonate as major ingredient. These are less biodegradable chemicals². These are responsible for water pollution. Generally natural origin substances are biodegradable. If we synthesis polymeric surfactant from starch and sorbitol, it has more chances of showing biodegradable property. It is possible to convert starch and sorbitol into polymeric surfactants.

In a present work we synthesized starch and sorbitol based polymers by treating it with organic acids³. Organic acids used for this purpose are citric, oxalic, maleic and phthalic acids. The following reactions are possible in the process of polymerization.

Esterification of acids with OH groups of sorbitol. Etherification of OH groups to give ether linkage. Reaction of Maleic anhydride with sodium bisulphate to give sulphosuccinates. Reaction of OH groups with sodium bisulphate to give sulphonates^{4,5}.

We formulate some powder and liquid detergents based on starch sorbitol based polymeric surfactant and compares they with commercially available product. Our results are comparable and sometime better than commercial detergents. We are successful to replace acid slurry and alpha olefin sulphonate to the extent of 50 to 70% by our polymer.

2. Experimental

I. The Reactor

The reactor made up of glass. It consists of two parts. Lower part of reactor is a round bottom flask with very wide mouth. Upper part of reactor is its lid having four necks with standard joint. Out of these central one opening is for inserting mechanical stirrer, second is for charging of raw materials, third is connected to water condenser and four is to fit thermometer. An electric heating mantle having special arrangement for smooth control of the temperature (-/+ 2) has been used. Mechanical stirrer is provided with speed regulator.

II. METHOD OF SYNTHESIS

Initially stoichiometric quantity of sorbitol, maize starch, maleic anhydride, phthalic anhydride, citric acid, oxalic acid, sodium bisulphite, sodium bisulphate and sodium metabisulphite were added in the reactor. The temperature was raised slowly and steadily in about two hours to 130°C. The reaction was continued for three hours at this temperature. Then heating is stopped and reaction mixer cooled to room temperature. Product is filtered and then stored in glass bottles. The composition of three polymers is given in table 1.

Table 1: Ingredients for synthesis of Starch based polymers

S.No.	Ingredients	A ₂₆	A ₃₂	A ₃₆
1	Sorbitol (70%)	49.1	56.4	57
2	Starch (70%)	39.2	28.2	28.3
3	Maleic anhydride	4.9	4.7	2.0
4	Phthalic anhydride	2.4	1.9	-
5	Citric acid	2.4	1.4	1.5
6	Oxalic acid	-	1.4	1.5
7	Sodium bisulphate	1.5	3.0	2.0
8	Sodium bisulphite	0.5	3.0	-
9	Sodium metabisulphite	-	-	3

III. Preparation of Powder detergents

The raw materials were charged in a con type blender and mixed for 15 minutes.

IV. Preparation of Liquid detergents

A high speed homogenizer was used to mix all ingredients and stirring was continued for half an hour. Next day the product was filtered and stored carefully in glass bottles.

V. Measurement of % Detergency⁶

Stain removing characteristics of detergents. Concentration 1% solution of detergent in distilled water. Reflectance measured on clean cotton cloth $R_0 = 100$, Reflectance measured on soil stained cotton cloth, $R_s = 29$, Reflectance measured on Tea stained cotton cloth, $R_s = 53$, Reflectance measured on coffee stained cotton cloth, $R_s = 53$ and Reflectance measured on spinach stained cotton cloth, $R_s = 51$. The % detergency is found out by "Lamberts and Sanders" formula

$$\% \text{ Detergency} = \frac{R_w - R_s}{R_0 - R_s} \times 100$$

Where R_w , R_s , R_0 are the reflectance on washed cloth, stained cloth and clean cloth respectively.

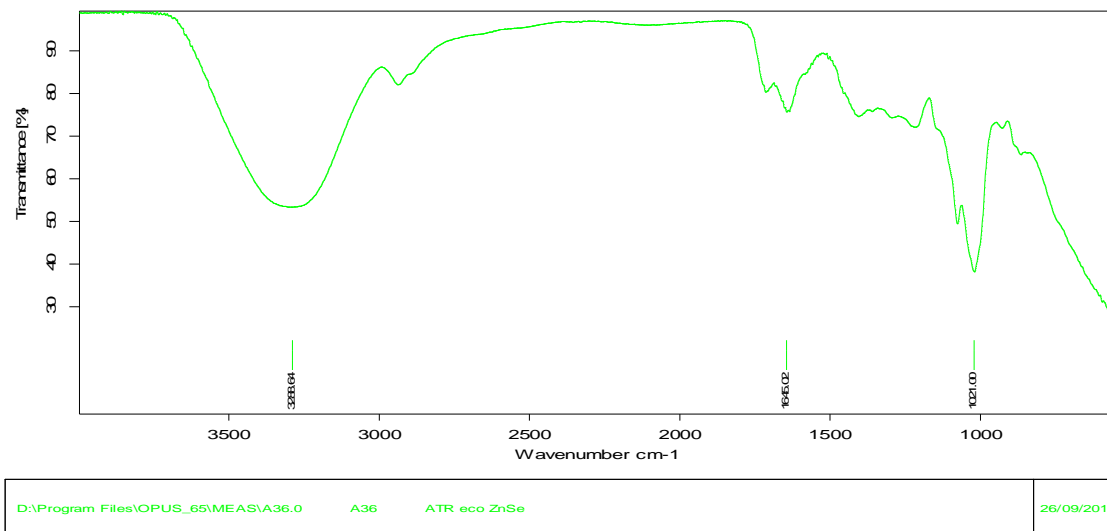
3. RESULTS AND DISCUSSION

The physicochemical characteristics of synthesized polymers are reported in table 2. The pH of samples is acidic. H.L.B. Value suggests the use of these polymers in powder and liquid detergent composition. The viscosity and percent solid make the sample workable for use in detergent compositions⁷⁻⁹.

Table 2: Physicochemical analysis of different starch based polymers

S.No.	Properties	A ₂₆	A ₃₂	A ₃₆
1	% Solid	77	74	74
2	pH	3	3.27	4.06
3	Acid Value	78	75	55
4	H.L.B. Ratio	15.34	15.64	15.96
5	Surface tension of neutralized samples (By stalagmometre in dyne/cm)	66.64	62	61.20
6	Colour	Colourless	Colourless	Yellow
7	Viscosity (by Ford Cup No.4) Seconds at 30°C	217	245	270

I.R. and ¹H NMR spectra of polymer sample A₃₆ is given in figure-1 and figure-2. The I.R. & NMR spectra confirm the presence of ester, ether, free acid and free-OH group¹⁰⁻¹¹.



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Fig. 1: Infra Red Spectra of A₃₆

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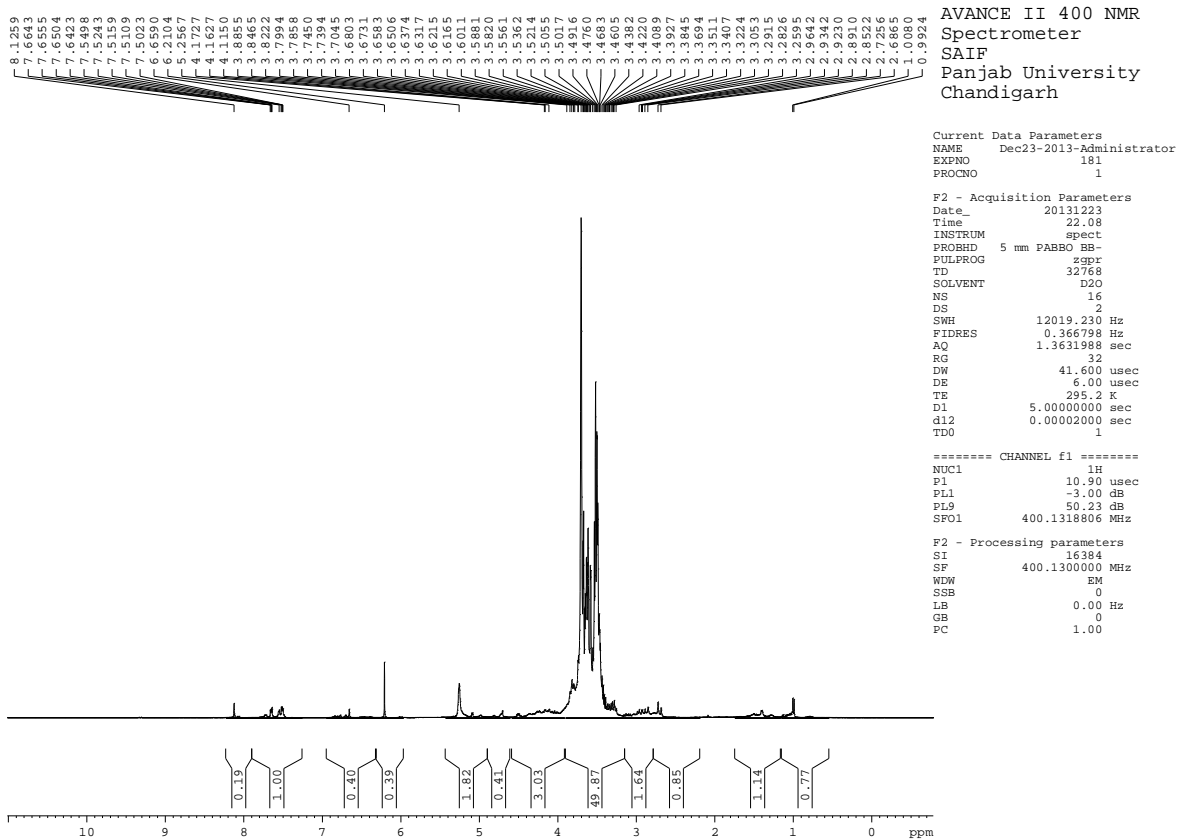


Fig. 2: ¹H NMR Spectra of A₃₆

Some liquid detergents of polymers

We prepared some liquid detergents based on polymers A₂₆, A₃₂ and A₃₆. Composition of liquid detergents is given in table-3.

Table 3: Composition of liquid detergents

Ingredients	LD-26	LD-27	LD-28
Acid Slurry(LABSA)	7.0	7.0	7.0
Sodium Lauryl Ether Sulphate (40%)	18.0	18.0	18.0
Sodium Lauryl sulphonate (30%)	2.0	2.0	2.0
Na ₂ CO ₃	2.5	2.5	2.5
Na ₂ SO ₄	1.0	1.0	1.0
Polymer	A ₂₆ = 8.0	A ₃₂ = 8.0	A ₃₆ = 8.0
fragrance	0.25	0.25	0.25
Water	61.25	61.25	61.25

We find out foaming characteristics, surface tension reduction, viscosity, pH and stain removing capacity of liquid detergents¹²⁻¹³. We get comparable result with commercial samples. Sometime we get better result than commercial one. Detail of analysis as shown in table-4 and table-5.

Table 4: Analysis of liquid Detergents

Sample	Foam volume(C.C.) by cylinder method	Surface Tension dyne/cm	Viscosity (30°C) S	pH
LD-26	1000	26.83	290	8
LD-27	1000	26.07	272	8
LD-28	1000	24.37	268	8
Commercial Liquid Detergent	350	27.32	360	9.0

Stain removing characteristics of detergents. Reflectance measured on clean cotton = 100, Concentration 1% solution of detergent in distilled water.

Table 5: Stain removing characteristics of liquid detergents

Sample	Soil stain	Tea stain	Coffee stain	Spinach stain
LD-26	92.3	92.8	93	96.1
LD-27	95.7	93.1	95.4	96.9
LD-28	97.2	94.3	96.8	97.3
Commercial Liquid Detergent	94.9	94.4	95.6	96

Composition Powder detergents

We prepared some powder detergents based on polymers A₂₆, A₃₂ and A₃₆. The composition of powder detergents as shown in table-6

Table 6: Composition of powder detergents

Ingredients	PD-26	PD-27	PD-28
Acid Slurry	05	05	05
SLS (100%)	01	01	01
Na ₂ CO ₃	30	30	30
Dolomite	29	29	29
Polymer	A ₂₆ = 05	A ₃₂ = 05	A ₃₆ = 05
Salt	30	30	30

We find out foaming characteristics, surface tension reduction, bulk density, pH and stain removing capacity of powder detergents. We get comparable result with commercial samples. Sometime we get better result than commercial one. Detail of analysis as shown in table-7 and table-8.

Table 7: Analysis of powder Detergents

Sample	Foam volume(C.C.) by cylinder method	Surface Tension dyne/cm	Bulk density g/cm ³	pH
PD-26	1000	27.27	0.92	8
PD-27	1000	26.81	0.90	8
PD-28	1000	24.77	0.88	8
Commercial Powder Detergent	1000	24.42	0.92	8

Table 8: Stain removing characteristics of powder detergents

Sample	Soil stain	Tea stain	Coffee stain	Spinach stain
PD-26	95.2	94.7	95.2	96
PD-27	96.9	95.1	95.9	96.3
PD-28	98.1	96.2	97.2	97.9
Commercial Powder Detergent	98.1	95.2	96.1	97.4

4. CONCLUSIONS

1. Starch and sorbitol based polymeric surfactants can successfully used to replace partially petroleum based acid slurry and alpha olefin sulphonates.
2. All polymers are useful for the production of eco-friendly powder and liquid detergents.
3. The polymer has a potential for use in making floor cleansers, hand washes, toilet cleaners, glass cleaners and shampoos.
4. The initial investment cost of plant is 10-15 lakhs and commercial trials are essential for study techno economic viability of polymers.

5. REFERENCES

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