

Sugar Based Polymeric Surfactants FOR Powder AND Liquid Detergents

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Abstract

There is a worldwide mission to replace petroleum originating substances like Acid Slurry and Alfa Olefin Sulphonate. In the present piece of work, we have developed a novel polymer based on Sugar. We analyzed conditions of mole ratio, heating period and catalyst to get a polymer of desired molecular weight, H.L.B. ratio and cleaning properties. The polymer has been used to the extent of 50-100% as a replacement to Acid slurry in liquid and powder detergents. The performance characteristics of our product match with commercial products in respect of foam height, surface tension and stain removal. The cost of the polymer and finished detergent products are reasonable and are technically economical and fusible.

Keywords : Sugar, Maleic anhydride, polymeric surfactant, Powder detergents, Liquid detergents.

1. Introduction :

Petroleum is one of the largest single sources of energy consumed all over the world. If we take a panoramic view of various industrial and household products like liquid, powder and cake detergents, paints, printing inks, lubricants, cosmetics; large number of the products based mainly on petroleum. However, due to shrinking supply and global industrial expansion, the prices of petroleum products will continue to increase, affecting all aspects of the global economy. Furthermore, use of petroleum based raw materials is a growing concern due to their unfavorable effects on the environment like global warming and residual toxication of the environment.

The recent trend and public awareness towards environment include products which are eco-friendly, readily biodegradable and at the same time they are renewable. In India, a very vast created opportunities to researchers to use natural and agro-based products in lubricant, coating and surfactant. Natural products are compatible to human health¹. These products can be substitutes for hazardous petroleum products. The petroleum-based products are now being replaced by non-conventional natural products. Polymer including natural products like starch, sorbitol, glucose, polyethylene glycol, sugar, vegetable oil and their applied products are being increasingly explored as biocompatible and bio-renewable materials. In our earlier experiment, we have synthesized polymeric surfactant based on natural products of vegetable origin like sorbitol² and maize starch² along with organic acid and anhydride. These surfactants were successfully used in preparing powdered and liquid detergents. In present work, we have prepared polymeric surfactant³ using sugar with maleic anhydride and sodium metabisulphite.

2. Experimental :

The Reactor for Synthesis

The synthesis of polymeric surfactant is carried out in the glass reactor. Reactor includes two sections. Upper section is a round bottom flask while upper section is having lid with four opening necks along with standard joints. Out of these four, center one is for stirrer through which a motor driven stirrer is introduced into the reactor. Second one is used to connect water condenser. Third one is for thermometer and last one is for adding the raw material to the reactor. The reaction mixture is heated with the help of heating mantle. Stirrer with speed regulator is used to stir the reaction mixture homogeneously. The reaction vessel and its lids used to tie together with the help of clamps.

Synthesis of polymeric surfactants

Accurate and required amount of sugar, maleic anhydride and sodium metabisulphite were taken in the reaction flask. This reaction mixture was heated slowly to attain a temperature of 80°C with continuous stirring. Heating was continued till it reaches to 130°C. At a constant temperature 130°C, further heating was continued for three hours. After heating, the reaction mixture is cooled to room temperature. Then, it was filtered and stored in an amber colored air tight bottle.

In these polymers, sugar is the main ingredient. It was heated with different proportions of organic acids and anhydrides at 130°C for three hours. Different polymers have been prepared. Compositions of polymers are shown in table 1.

Table 1: % Composition by weight of Sugar polymers

Ingredients	A ₃₈	A ₄₂
Sugar (60%)	90	83.8
Maleic anhydride	02	11.4
Sodium metabisulphide	08	4.8

Preparation of powder detergents:

Ingredients in the powdered form are weighted and mixed thoroughly in a tray. To this, pre-weighted liquid ingredients like acid slurry, sodium lauryl sulphate (S.L.S.), sodium lauryl ether sulphate (SLES) and polymerA₃₈ was added. Whole mass is then transfer to homogenizer pot. It is then mixed thoroughly. After mixing, this homogeneous mass was dried in an open tray. Then it was stored in a plastic bag. Some formulation of powder detergents are given in a table 2.

Table 2: Powder detergents based on Polymer A₃₈

Ingredient	PD-26	PD-27	PD-28	PD-29	PD-30
Acid Slurry	05	08	06	03	00
SLS (100%)	01	01	01	01	2
SLES (40%)	-	02	02	03	7
Sodium Carbonate	30	35	33	30	35
Dolomite	29	-	22	27	20
PolymerA ₃₈	05	05	06	06	06

Salt	30	30	30	30	30
Sodium sulphate	-	19	-	-	-

Preparation of liquid detergents:

All the ingredients present in formulation with precise weight was taken in a large beaker. It was mixed thoroughly to form a slurry. Then measured quantity of fragrance and distilled water was added in a slurry. After mixing, solution is kept steady for overnight. Now liquid detergent is ready, it is store in a plastic bottle.

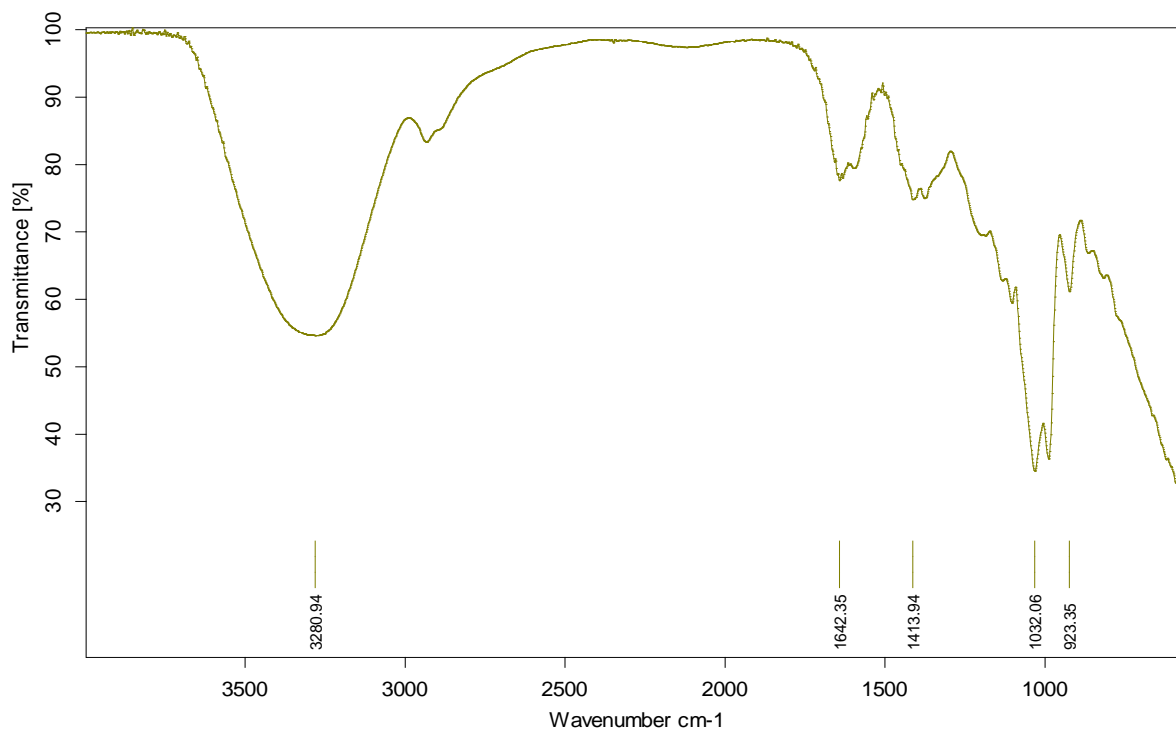
Table 3: Liquid detergents based on polymer A₃₈

Ingredients	LD-26	LD-27	LD-28	LD-29	LD-30
Acid Slurry	7.0	5.0	5.0	2.5	00
SLES (400%)	18.0	15	11	20	20
SLS (30%)	2.0	5.0	1.0	2.0	3
Sodium Carbonate	2.5	2.5	2.0	2.0	2.0
Sodium sulphate	1.0	1.0	1.0	1.0	1.0
PolymerA ₃₈	8.0	8.0	10	10	10
Fragrance	0.25	0.25	0.25	0.25	0.25
Distilled Water	61.25	63.25	69.75	62.25	63.75

Table 4: Physico-chemical Analysis of Sugar based Polymers

Polymer	% Solid	Viscosity (Sec.)	Colour	pH value	H.L.B. ratio	Oxirane Oxygen value	Surface Tension Dyne/cm	Acid Value
A ₃₈	77	145	Yellow	6	16.60	0.22	68	16.89
A ₄₂	79	152	Brown	3.70	16.11	0.33	64.49	109.32

Spectra 1: Infra-Red Spectra of novel polymer (A38)



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Table 5: FT-IR Spectroscopic analysis of Polymer A38

Sr. No	Functional groups	Literature Wave number cm ⁻¹	Observed Wave number cm ⁻¹
1	Hydroxyl group (OH stretch)	3200-3600	3280.94
2	Ether group (C-O stretching)	1260-1000	1032
3	C-O stretch (multiple bond)	1260-1000	923.35

Spectra 2: Mass spectra of Novel Polymer A42

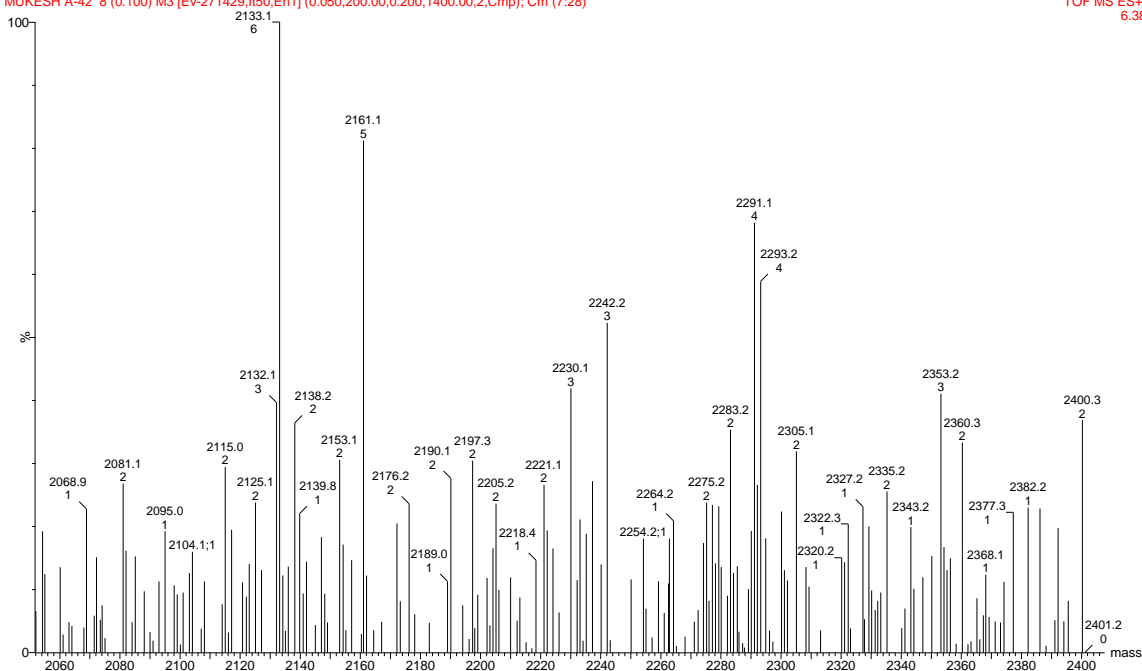


Table 6: Basic Analysis of Powder detergents based on Polymer A₃₈

Parameter	PD-26	PD-27	PD-28	PD-29	PD-30	CD-1	CD-2
Bulk density	0.83	0.81	0.86	0.91	0.99	0.88	0.94
pH(Digital pH meter)	9.4	8.9	9.1	9.9	10.6	9.3	9.6
Colour	White	White	White	White	White	White	White

Note: CD-1: Commercial powder detergent-1

CD-2: Commercial powder detergent-1

Table 7: Analysis of powder detergents based on polymer A₃₈ and commercial detergents

Concentration	Samples	Foam Volume in cm ³ (By glass cylinder method)				Surface tension Dyne/cm (Stalagmometer)
		0 min.	5 min.	10 min.	15 min.	
0.25%	PD-26	710	640	470	390	29.99
	PD-27	780	690	600	520	27.48
	PD-28	730	680	590	490	29.63
	PD-29	560	480	400	310	33.72

	PD-30	500	420	360	290	34.17
	CD-1	750	730	710	680	27.92
	CD-2	800	770	750	720	30.43
0.5%	PD-26	910	850	740	600	27.88
	PD-27	1000	880	790	680	25.96
	PD-28	960	820	750	630	27.43
	PD-29	700	630	570	490	30.41
	PD-30	610	540	450	360	31.82
	CD-1	900	870	850	820	25.27
	CD-2	1000	950	910	880	28.02
1%	PD-26	1000	900	830	760	23.20
	PD-27	1000	920	850	770	22.01
	PD-28	1000	920	840	760	24.78
	PD-29	900	810	720	650	26.31
	PD-30	800	700	610	530	27.66
	CD-1	1000	940	890	850	24.31
	CD-2	1000	940	880	830	26.56

Table 8: Removal of Soil Stain from cotton cloths at different concentration by powder detergent samples based on polymer A₃₈

R₀ = Reflectance measured on clean cloth = 100

R_s = Reflectance measured on stained cloth = 39

Sr. No.	Concentration	Sample	R _w (by reflectance meter)	% detergency
1	0.25%	PD-26	83	72.1
2		PD-27	84	73.7
3		PD-28	84	73.7
4		PD-29	82	70.4
5		PD-30	80	67.2
6		CD-1	84	73.7
7		CD-2	85	75.4
8	0.5%	PD-26	89	82.0

9		PD-27	90	83.6
10		PD-28	90	83.6
11		PD-29	88	80.3
12		PD-30	86	77.0
13		CD-1	90	83.6
14		CD-2	91	85.2
15		1.0%	PD-26	94
16	PD-27		95	91.8
17	PD-28		95	91.8
18	PD-29		93	88.5
19	PD-30		91	85.2
20	CD-1		95	91.8
21	CD-2		96	93.4

Table 9: Removal of Tea Stain from cotton cloths at different concentration by powder detergent samples based on polymer A₃₈

R₀ = Reflectance measured on clean cloth = 100

R_s = Reflectance measured on stained cloth = 41

Sr. No.	Concentration	Sample	R _w (by reflectance meter)	% detergency
1	0.25%	PD-26	84	72.9
2		PD-27	86	76.3
3		PD-28	85	74.6
4		PD-29	82	69.5
5		PD-30	81	67.8
6		CD-1	85	74.6
7		CD-2	86	76.7
8	0.5%	PD-26	89	81.3
9		PD-27	90	83.0
10		PD-28	90	83.0
11		PD-29	88	79.7
12		PD-30	87	78.0

13		CD-1	90	83.0
14		CD-2	91	84.7
15	1.0%	PD-26	94	89.8
16		PD-27	95	91.5
17		PD-28	94	89.8
18		PD-29	93	88.1
19		PD-30	91	89.8
20		CD-1	94	89.8
21		CD-2	96	93.2

Table 10: Removal of Coffee Stain from cotton cloths at different concentration by powder detergent samples based on polymer A₃₈

R₀ = Reflectance measured on clean cloth = 100

R_s = Reflectance measured on stained cloth = 42

Sr. No.	Concentration	Sample	R _w (by reflectance meter)	% detergency
1	0.25%	PD-26	85	74.1
2		PD-27	86	75.9
3		PD-28	85	74.1
4		PD-29	83	70.7
5		PD-30	82	69.0
6		CD-1	84	72.4
7		CD-2	86	75.9
8	0.5%	PD-26	89	81.0
9		PD-27	91	84.5
10		PD-28	90	82.7
11		PD-29	87	77.6
12		PD-30	86	75.9
13		CD-1	91	84.4
14		CD-2	92	86.2
15	1.0%	PD-26	94	89.6
16		PD-27	96	93.1
17		PD-28	95	91.4

18		PD-29	92	86.2
19		PD-30	91	84.5
20		CD-1	95	94.8
21		CD-2	96	96.5

Table 11: Removal of Spinach Stain from cotton cloths at different concentration by powder detergent samples based on polymer A₃₈

Ro = Reflectance measured on clean cloth = 100

Rs = Reflectance measured on stained cloth = 48

Sr. No.	Concentration	Sample	Rw (by reflectance meter)	% detergency
1	0.25%	PD-26	84	69.2
2		PD-27	87	75.0
3		PD-28	86	73.1
4		PD-29	83	67.3
5		PD-30	82	65.4
6		CD-1	86	73.1
7		CD-2	87	75.0
8	0.5%	PD-26	90	80.8
9		PD-27	92	84.6
10		PD-28	91	82.7
11		PD-29	90	80.8
12		PD-30	89	78.8
13		CD-1	92	84.6
14		CD-2	93	86.5
15	1.0%	PD-26	95	90.4
16		PD-27	96	92.3
17		PD-28	95	90.4
18		PD-29	95	90.4
19		PD-30	93	86.5
20		CD-1	96	92.3
21		CD-2	97	94.1

Table 12: Basic analysis of Liquid detergents based on polymer A₃₈

Parameter	LD-26	LD-27	LD-28	LD-29	LD-30	CLD-1	CLD-2
Viscosity(30°C) S	More than 300	More than 300	145	76	42	More than 300	More than 300
pH (Digital pH meter)	8.5	8.5	8.6	9.2	9.8	11	11
Colour	Yellow	Yellow	Yellow	Yellow	Yellow	Pale Yellow	Colorless

Note: CLD-1: Commercial Liquid detergent-1

CLD-2: Commercial Liquid detergent-2

Table 13: Analysis of Liquid detergents based on polymer A₃₈ & Commercial liquid detergents

Concentration	Samples	Foam Volume in cm ³ (By glass cylinder method)				Surface tension Dyne/cm (Stalagmometer)
		0 min.	5 min.	10 min.	15 min.	
0.25%	LD26	480	410	330	250	29.25
	LD27	480	400	320	250	28.31
	LD28	450	380	310	250	30.49
	LD29	370	310	250	210	33.01
	LD30	320	270	230	190	34.29
	CLD1	300	240	200	180	30.93
	CLD2	230	210	200	190	29.38
0.5%	LD26	600	520	460	400	26.84
	LD27	610	540	470	400	27.14
	LD28	600	520	480	410	26.28
	LD29	500	430	350	280	31.52
	LD30	450	380	300	240	33.99
	CLD1	490	400	320	250	29.43
	CLD2	260	230	200	190	28.53
1%	LD26	1000	900	790	600	25.67
	LD27	1000	910	800	600	26.84
	LD28	970	890	800	700	25.74
	LD29	800	690	600	520	29.65
	LD30	670	590	510	430	31.02
	CLD1	700	600	510	420	27.75
	CLD2	300	270	250	230	26.38

Table 14: Removal of Soil Stain from cotton cloths at different concentration by liquid detergent samples based on polymer A₃₈

Ro = Reflectance measured on clean cloth = 100

Rs = Reflectance measured on stained cloth = 39

Sr. No.	Concentration	Sample	Rw (by reflectance meter)	% detergency
1	0.25%	LD26	86	77.0
2		LD27	86	77.0
3		LD28	86	77.0
4		LD29	83	72.1
5		LD30	81	68.8
6		CLD1	86	77.0
7		CLD2	88	80.3
8	0.5%	LD26	90	83.6
9		LD27	90	83.6
10		LD28	90	83.6
11		LD29	87	78.7
12		LD30	83	72.1
13		CD1	90	83.6
14		CD2	92	86.9
15	1.0%	LD26	95	91.8
16		LD27	96	93.4
17		LD28	96	93.4
18		LD29	94	90.2
19		LD30	91	85.2
20		CLD1	96	93.4
21		CLD2	97	95.1

Table 15: Removal of Tea Stain from cotton cloths at different concentration by Liquid detergent samples based on polymer A₃₈

Ro = Reflectance measured on clean cloth = 100

Rs = Reflectance measured on stained cloth = 41

Sr. No.	Concentration	Sample	Rw (by reflectance meter)	% detergency
1	0.25%	LD26	87	78.0
2		LD27	87	78.0
3		LD28	87	78.0
4		LD29	84	72.9
5		LD30	81	67.8
6		CLD1	87	78.0
7		CLD2	88	79.7
8	0.5%	LD26	91	84.7
9		LD27	90	83.0
10		LD28	90	83.0
11		LD29	88	79.7
12		LD30	86	76.3
13		CLD1	91	84.7
14		CLD2	92	86.4
15	1.0%	LD26	95	91.5
16		LD27	95	91.5

17		LD28	95	91.5
18		LD29	93	88.1
19		LD30	90	83.0
20		CLD1	95	91.5
21		CLD2	96	93.2

Table 16: Removal of Coffee Stain from cotton cloths at different concentration by liquid detergent samples based on polymer A₃₈

Ro = Reflectance measured on clean cloth = 100

Rs = Reflectance measured on stained cloth = 42

Sr. No.	Concentration	Sample	Rw (by reflectance meter)	% detergency
1	0.25%	LD26	87	77.6
2		LD27	86	75.9
3		LD28	86	75.9
4		LD29	84	72.4
5		LD30	82	69.0
6		CLD1	87	77.6
7		CLD2	88	79.3
8	0.5%	LD26	90	82.7
9		LD27	90	82.7
10		LD28	90	82.7
11		LD29	88	79.3
12		LD30	85	74.1
13		CLD1	90	82.7
14		CLD2	91	84.5
15	1.0%	LD26	95	91.4
16		LD27	96	93.1
17		LD28	95	91.4
18		LD29	93	88.0
19		LD30	91	84.5
20		CLD1	96	93.1
21		CLD2	97	94.8

Table 17: Removal of Spinach Stain from cotton cloths at different concentration by powder detergent samples based on polymer A₃₈

Ro = Reflectance measured on clean cloth = 100

Rs = Reflectance measured on stained cloth = 48

Sr. No.	Concentration	Sample	Rw (by reflectance meter)	% detergency
1	0.25%	LD26	87	75.0
2		LD27	87	75.0
3		LD28	87	75.0
4		LD29	85	71.1

5		LD30	82	65.4
6		CLD1	87	75.0
7		CLD2	88	76.9
8	0.5%	LD26	91	82.7
9		LD27	90	80.8
10		LD28	90	80.8
11		LD29	88	76.9
12		LD30	86	73.1
13		CLD1	90	80.8
14		CLD2	92	84.6
15	1.0%	LD26	96	92.6
16		LD27	96	92.3
17		LD28	96	92.3
18		LD29	93	86.5
19		LD30	92	84.6
20		CLD1	96	92.3
21		CLD2	96	92.3

3. Result and Discussion:

Sugar molecule consist of glucose and fructose moieties, But, when it is heated under certain condition, it gives glucose and fructose. Glucose and fructose are the source of polyhydric alcohol groups. Sugar is commercially available in abundant quantity at reasonable prize. Present work includes polymers based on sugar. Several combinations were tried in which maximum % of sugar has been used with maleic anhydride as an acid part as in some formulations. In the present work, charring of sugar and dark color developments were major difficulty. We have attempted several mole ratios and different quantities of bisulphites. There were only two instances where charring does not occur (yellow or brown color polymers) as recorded in the table 1.

The physico-chemical analysis of sugar-based polymers is shown in a table 4. The HLB ratio⁴, viscosity⁵ and other parameter reveals its use in detergent composition. Neutralized samples were prepared for IR spectra⁶. Spectra-1 is an IR spectrum of Polymer A₃₈. It shows presence of hydroxyl and ether functional groups (table 5). Spectra-2 is Mass spectrum⁷ of polymer A₄₂. It clearly indicate that our polymer having the molecular weight in the range of 2000 - 2400. Table 2 shows the compositions of powder detergents based on polymer A₃₈. 5-8% polymer has been used in various combinations. In composition PD-30, acid slurry has been totally replaced. A higher proportion of salt up to 30% was used in all compositions. The bulk density and pH of polymer based composition are almost parallel to commercial compositions. The foaming characteristics⁸ are excellent at 1% concentration. Samples with nil acid slurry are slightly less foaming than other samples. The formulations having low foaming value can be recommended for washing machine detergents, as cleaning properties of the material are good. The surface tension reduction is good and comparable to commercial products which was simultaneously tested. Soil removal⁹ and stain removal of tea and coffee is good at 1% concentration and comparable to commercial products.

Several compositions of liquid laundry detergents have been formulated. They are containing 8 to 10% polymers. The other ingredients include routine commercial ingredients. An effort has been made to use least amount of acid slurry of petroleum origin. Liquid detergents based on A₃₈ polymer are recorded in table 3. Formulation LD-30 is free from acid slurry. SLES and SLS are common ingredients of detergent formulations for getting good foam. Table 4 shows viscosity and pH of various compositions. Highest viscosity is reported with 8% polymer and 18% SLES. The pH is in the range of 9-11. The foaming characteristics are given in table 13. Excellent foaming and surface tension reduction is observed at 1% concentration which is on par or some times better than commercial samples. Soil and stain removing properties are excellent as shown in table 14 to 17.

4. Conclusions :

- 1) Polymer can be synthesized based on vegetable products to get a partial or total replacement of petroleum-based acid slurry or Alpha olefin sulphonate in powder and liquid detergent compositions.
- 2) Etherification reaction between two internal hydroxyl groups in carbohydrate entity has been observed. The ether groups will make the polymer hydrophilic.
- 3) Infrared spectra of the polymer indicate that ether and hydroxyl groups are present in the molecule.
- 4) The mass spectra of polymer indicate that average molecular weights of polymers are in between 2000 to 2400.
- 5) The mole ratio of reactants, temperature and properties of catalyst can be optimized to get polymer of desired molecular weight and physicochemical properties like surface tension, acid value and cleaning properties.
- 6) All samples have 77 to 79 % solid and reasonably good viscosity. The HLB ratio, pH value and oxirane oxygen value suggest strongly their used in powder detergent.
- 7) Sugar is composite of glucose and fructose. This is potential source of hydroxyl group. Sugar is abundantly available and can be used to develop a polymeric surfactant having good cleaning properties. We have prepared 60% sugar solution and treated with maleic anhydride and sodium metabisulphite. The physico-chemical characteristics of these two polymers particularly HLB value, viscosity and color suggest their use in detergent compositions.
- 8) In powder detergent formulation (PD-30) and liquid detergent formulation (LD-30) we have successfully replaced acid slurry 100 % by our polymer A₃₈.
- 9) High foaming detergent powder PD-27 is recommended for hand washing of cloth while medium foaming detergent PD-30 is for washing machine application. Similarly liquid detergent LD-27 is suitable for hand washing of cloth and liquid detergent LD-30 is for Washing machine cleaning.

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