International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.4, pp 1975-1979, Oct-Dec 2010

Ecofriendly Green Polymers based on Maize Starch and Sorbitol for Powder Detergent

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Abstract: Novel polymers based on maize starch, sorbitol and maleic anhydride have been synthesized. The variation in mole ratios, reaction temperature, type of catalyst and the time of heating has been studied. Two polymers after analysis have been selected & used as ingredients in powder detergent formulations. As a curiosity to know the individual effect of various ingredients on foam height and surface tension, individual components are tested for foam height, surface tension & % detergency. Powder detergent free from acid slurry & containing sodium lauryl sulphate and polymer as active ingredients have been formulated. The special feature of powder detergent is freedom from petroleum products and use of very small amount of Sodium tripolyphosphate . They are eco friendly products promoting green chemistry.

Key words: Ecofriendly Green Polymers ,Maize Starch,Sorbitol, Powder Detergent.

Introduction:

In the Era of 1960-1990, a large number of industrial products like detergents, lubricants, paints and cosmetics were based on petroleum products. As we know the price and availability of petroleum products is souring every year, we must think of alternative vegetable products. In our laboratory we have prepared novel polymeric surfactants based on vegetable products like vegetable oils[1], rosin[2], starch[3] and sorbitol[3].

In the present work, an effort has been made to develope polymeric surfactants which will substitute conventional petroleum based actives. The composition of two selected polymers was found to be useful for detergents (given in table no.1).Sorbitol is a major ingredient in these formulations i.e. 70 to 80%, Maize starch 10 to 12% and 10 to 20% maleic anhydride are minor ingredients.The possible chemical reactions are as follows:

1. Esterification reaction between acid groups of maleic anhydride and OH-group of sorbitol and starch.
2. Etherification reaction- between two OH-groups of starch and sorbitol to produce exthoxy groups .

Both these reaction are expected to give good surfactants properties. The physicochemical analysis of these polymers is given in table no.2. The samples have low acid value of 17 to18. They have very thick consistency & have distinct solubility in water, alcohol and alkali. The reduction in surface tension is also remarkable and quite comparable to commercial active materials. To have better control on final characteristics of detergents, each individual component of detergent formulation has been tested for foam height, surface tension and cleaning. Surprising sorbitol gives foam height 300mm at 1%

conc. The surface tension reduction by use of novel polymer is good yet not equivalent to commercial active materials. The composition of powder detergents based on novel polymer (P-1) & (P-2) and individual performance test is given in table no.3. No petroleum active has been used in composition. Sodium lauryl sulphate has been used to extent of 5 to 7%, sodium carbonate has been used to extent of 30 to 40%. About 5 to 15% of novel polymer has been used in different compositions. The foam height and surface tension characteristics at 1% solution are reported in table no.4. All samples show excellent foam height & surface tension reduction characteristics which are comparable to commercial sample CD-1 & CD-2. The sample PD-3 is unique & it does not use sodium lauryl sulphate but only 15% polymer has been used as active ingredient.

Experimental:

Preparation of novel synthetic Polymer:- the reaction was carried out in four-neck wide mouth glass reactor of 2 liter capacity. The temperature control of $\pm 2^0$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 of sorbitol, maize starch & maleic anhydride[5] were added in the reactor .Sodium bisulphate & sodium bisulphate were used as a catalyst .The temperature was raised slowly & steadily in about one hour to 150^0C.The reaction was continued for five hours at this temperature ,till the desired molecular weight was achieved. The consistency of the paste was maintained by adding 2% isopropanol as a solvent .At the end of this period of the reaction was terminated & the prepared polymers[4] were collected in a glass-stoppered bottle with least air gap. The final yield of the product was measured.

TABLE NO 1.: COMPOSITION OF NOVEL POLYMER (INGREDIENTS % BY WEIGHT)

Ingredient	Polymer 1 (P-1)	Polymer 2 (P-2)
Maize starch	12.5	10
Sorbitol (70%)	75	80
Maleic anhydride	12.5	10
% yield	87.50	89.70

Note:

- Sorbitol was used as 70% solid, sodium bisulphate (1.5) and sodium bisulphate (0.5) were used as catalyst in both batches.
- Isopropanol (2%) was used as solvent.
- Heating Schedule: 5 hours at 150^0c

TABLE NO.2: PHYSICO-CHEMICAL PROPERTIES OF NOVEL POLYMER

Sr.No.	Physical Property Observations	Observations of Polymer 1	Observations of Polymer 2
1	Acid Value	17.83	18.22
2	Color	Cream	Cream
3	Consistency	thick	thick
4	Solubility		
	1) hot water	soluble	soluble
	2)alcohol	soluble	soluble
	3)NaOH	soluble	soluble
5	% Solid	76.25	70.15
6	Surface Tension(dyne/cc)	41.72	42.70
7	pH	1.21	1.31
8	HLB	13.77	12.44
9	Viscosity by ford cup no. 4 at 30°c	120	122

Preparation of Powder Detergents:

The different compositions of powder detergents have been prepared based mainly on neutralized novel polymer, sodium carbonate, salt, STPP(sodium tripoly phosphate) and Dolomite etc. STPP has been maintained at 5%. In this method the neutralized novel polymer, sodium carbonate, sodium lauryl sulphates[7], dolomite etc according to compositions was taken in a blender. All the contents were mixed together for 30minutes in a powder blender. After ensuring the intimate contact of all the contents in a mixture the detergents were taken out. Then powder detergents were dried to get required moisture. After getting dry, free flowing property the sample were packed into air tight polyethylene bags.
Analysis and testing of Powder Detergents

Surface Tension[10]: The surface tension of powder detergents was measured using stalagnometer.

Foam volume[8]: foam is a cause of dispersion of gas relatively in a small amount of liquid. This was measured by using mechanical agitation in a closed vessel method. Foam chacteristics were measured in terms of volume by Bubble Cylinder Method.

Detergency Test: This includes the following steps:
Preparation of Soil Medium[11]: The soil medium was prepared with following composition. The mixture of carbon black (28.4%) and lauric acid (17.9%) along with mineral oil (17.9%) was taken in a pestle mortal for 1-2hrs to get fine grinding and smooth filling. About 2gm of above paste was mixed well with 500ml of carbon tetrachloride and for soiling of fabrics.

Fabrics Washing: The solutions of 1% concentration of powder detergents in tap water were prepared. These solutions were heated to 60^0C and stained fabrics were dipped in it for five minutes. Ten to and fro hand washes in tap water were given with equal strokes. After washing, the test materials were rinsed in running tap water, dried and ironed. It was also tried with commercial powder detergent. After, the %detergency was found out by using Lambert and Sanders formula.

$$\% \text{ Detergency} = \frac{(Rw - Rs) \times 100}{(Ro - Rs)}$$

Where Rw, Rs and Ro are the reflectance measured on washed fabrics, stained fabrics (before washing) and clean fabrics respectively. The reflectance was measured with an elrepho reflectance photometer with filter R-46 against an MgO-standard.

TABLE NO. 03: INDIVIDUAL RESPONSE OF INGREDIENTS FOR FOAM HELGHT, SURFACE TENSION AND DETERGENCY
(ALL TESTING IS DONE AS 1% SOLUTION IN DISTILLED WATER)

Sr.No.	Ingredients	Foam Volume In CM^3(time in min)	Density(gm\cc)	Surface Tension(dyne/cm)	%Detergency on cotton fabrics
1	Acid Slurry	1000	1.0154	31.49	85
2	SLS	1000	1.0772	42.37	81.66
3	AOS	1000	1.0238	38.44	83.33
4	SLES	900	1.0172	37.92	85
5	Acid Slurry (neutralized)	700	1.0238	49.48	80
6	Sodium carbonate	120	1.0788	53.58	58.33
7	Sodium per borate	110	1.0208	51.28	65
8	Sodium chloride	100	1.027	46.05	50
9	Sodium sulphate	110	1.0174	52.71	45
10	Sorbitol	300	1.0218	51.23	35
11	Polymer-1	200	1.214	50.11	68.33
12	Polymer-2	200	1.212	45.22	66.66C

Reflectance on clean cotton cloth,Ro=100
Reflectance on soil cloth ,Rs=40

TABLE No.4: COMPOSITION OF POWDER DETERGENT BASED ON NOVEL POLYMER (P1) & (P2)

Ingredients	PD 1	PD2	PD3	PD4	PD5	PD6
SLS	5	5	-	7	7	7
Sodium carbonate	30	30	30	40	40	40
SLES	10	-	-	10	-	5
Sodium sulphate	10	10	10	10	10	10
STPP	5	5	5	-	-	-
Salt	15	15	15	12	12	12
Dolomite	24	24	24	20	20	20
Sodium per borate	01	01	01	01	01	01
optical whitener *	0.5	0.5	0.5	1	1	1
Polymer (P1)	-	10	15	-	-	-
Polymer (P2)	-	-	-	-	10	5

Note:-*Titanium dioxide and sorbitol are mixed with each other in the ratio 1:1.

TABLE NO.5: FOAM HEIGHT, SURFACE TENSIN AND % DETERGENCY OF POWDER AND COMMERICAL DETERGENT AT 1% CONC.

Sample	Foam volume in cm^3 (time in min)				Density (gm/cc)	Surface Tension	% Detergency
	0	***5***	***10***	***15***			
PD1	600	550	500	500	1.019	32.083	86.66
PD2	500	450	400	350	0.988	45.882	84.66
PD3	400	350	350	300	0.997	42.09	86.66
PD4	600	550	500	450	0.996	42.09	80.00
PD5	500	450	450	400	1.011	42.01	84.65
PD6	600	550	500	500	1.121	40.88	83.33
CD1	700	650	600	600	0.996	42.61	87.77
CD2	650	600	550	500	0.9964	40.48	85.00

Reflectance on clean cotton cloth, Ro=100
Reflectance on soil cloth, Rs=40

Result and Discussion

1. Table no.1 gives composition of selected novel polymers with desired properties. The major ingredient of polymer is sorbitol while minor ingredients are maize starch and maleic anhydride. The catalysts used are sodium bisulphite and sodium bisulphate. Isopropanol has been used as a solvent.isopropanol will control the rheology of polymer and its flow chacteristics.The time of heating is 5hr at 150°C.
2. The physiochemical properties of these polymers are given in table no.2. The acid value indicates the acid group of maleic anhydride react with –OH group of sorbitol and starch to form esters. The color and consistency of the polymer is acceptable for commercial use. The polymers are soluble in water, alcohol and NaOH. The surface tension data indicates significant lowering of surface tension by novel polymers The HLB value[9] of products indicates it utility as ingredient in detergent compositions.
3. Table no.3 shows individual response of various ingredients towards foam height, surface tension[1] and detergency. In all the samples testing has been done at 1% solution in distilled water. The foam chacteristics of the entire conventional actives are excellent, the other ingredients shows poor foaming chacteristics except sorbitol.The prepared polymer have lower tendency of foaming. There is a significant change in surface tension of various individual ingredients; the polymers have also show significant reduction in surface tension but not equivalent to conventional actives.
4. The detergency evaluations[11] test shows that conventional actives like alpha olephine sulphonate, linear alkyl benzene sulphonate, sodium lauryl sulphate have same range of detergency 80 to 85. Sodium carbonate and sodium perborate have also play vital role in soil removing. Polymer-1 and 2 also give soil removing chacteristics. The soil removing characteristics of novel-polymer are 75 to 80% of

conventional actives like linear alkyl benzene sulphonate.

5. The compositions of powder detergents are shown in table no.4. The polymer P-1 and P-2 have been used in powder detergent compositions PD-2, PD3, PD-5 and PD-6.All the compositions containing 5 to 7% Sodium lauryl sulphate, and 5to 15% of polymer show excellent detergency chacteristics.
6. The samples have foaming characteristics[8] equivalent to commercial sample the reduction in surface tension is also appreciable and comparable to commercial samples the special features of formulation are freedom from petroleum based actives, very small amount of Sodium tripolyphosphate, and use of special optical brightener.

Conclusions:

1. Novel polymer based on maize starch, sorbitol and maleic anhydride can be prepared which are useful ingredients in powder detergent formulations.
2. Any petroleum based ingredients is not being included in recipe. The amount of STPP has been restricted to 5% level. Both these fact make the composition eco-friendly.
3. We can incorporate polymers without using any conventional petroleum based surfactant. Different proportion of polymer can be used to get the desired properties by suitable adjustments of SLS, SLES and polymer.
4. The foam height of various compositions is equivalent or better than the commercial sample. The foam stability is also good there is a considerable reduction in surface tension by using novel polymers to the entire sample. All these ecofriendly samples have excellent detergency characteristics comparable to commercial samples.
5. We can be recommended the sample PD2 & PD3 containing 10 to 15% of polymer for pilot plant studies The cooking of polymer is easy and controllable & it does not used any hazardous chemical like H_2SO_4
6. The process is easy, controllable and safe compared to production of acid slurry. Thus polymeric surfactant can be produced by small scale entrepreneurs in-house with a small investment. The cost of polymeric surfactant comes out to 75 per kg. which is comparable or even less than price of acid slurry.

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