International Journal of Pharmacy
Journal Homepage: http://www.pharmascholars.com

Research Article **CODEN: IJPNL6**

MICROWAVE SYNTHESIS OF NOVEL CARBOHYDRATE POLYMER AND ITS USE IN PREPARATION OF LIQUID DETERGENTS

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ABSTRACT
During the last decades, a fast growing interest in natural, biodegradable and renewable materials has been noticed. As the current use of non-biodegradable surfactants is a drawback, there is a need to develop new families of 'green' surfactant molecules with starch, sorbitol, sugar maleic anhydride and phthalic anhydride. It can be used as a useful ingredient in preparing liquid detergent by conventional batch heating process and novel microwave synthesis technique. microwave synthesis is very fast gives clean polar and more homogeneous product the conditions of voltage temperature and time of heating have been standardize the product has been successfully used in formulation of liquid detergent.

Keywords: Microwave synthesis, Carbohydrate polymers, Sugar, Starch and Sorbitol

INTRODUCTION

In this present work we have suggested an alternative route for modification and synthesis of novel carbohydrate polymers with sugar, starch, sorbitol, phthalic anhydride maleic anhydride. This synthesized novel polymer can be used in manufacture of liquid detergent .the novel carbohydrate polymer has been prepared by conventional batch method as well as with novel microwave synthesis.

The microwave synthesis is a unique technique with tremendously the speed clarity and homogeneity of prepared polymer. Thus the polymer which required about 5 h in manufacture can be prepared in just in two to three min. thus in a small set of we can manufacture very large quantity of microwave synthesized novel polymers and the product based on microwave synthesis has been used for making liquid detergent.

EXPERIMENTAL

The synthesis of novel carbohydrate polymers has been carried out by conventional batch heating system and microwave synthesis system.

Conventional Batch Heating System: A four naked glass reactor (2 lit.) with outlet for thermometer, Teflon stirrer, condenser, and outlet for adding raw materials are used. As accurately temperature controlled (+/-2c) heating mental is used for heating. The ingredients are added in the reactor and heating is continued for desired period and finally the samples are with draw after cooling.

Microwave Heating System: The CEM focused microwave synthesis system model discover is used for this purpose .the discover system consist of following,

1. A continuous microwave power delivery system with operated table output from (0-300W) programmable in 1 W increment.
2. A self adjusting single mode microwave cavity i.e. manually assessed via multiple alternative parts the equipment shows in figure has infrared temperature controlled system, pressure control system, stirring option and cooling option.

Reaction Programming:

1. A mixture of starch, sugar, sorbitol, phthalic anhydride and maleic anhydride along with catalyst are well mixed to give a homogeneous mixture in a test tube and it is packed with scapta cap.
2. The test tube is introduce in to the microwave reactor then the temperature, microwave power and time are adjusted, after cooling the reaction mixture was taken out of the reactor 12 samples were studied at different temperature, microwave power and setting time of 3-15 min.
3. The analysis of novel carbohydrate polymer is given in table no.2. The experimental formulations which has been tried is also given in table no. 1
4. The variation in temperature, and reaction time and microwave power has been studied the analysis microwave synthesis of novel polymer is studied.
5. The final sample S1 was prepared under standard condition of temperature of 240° C time 10 min. and power of 140 W.
6. The sample S1 was specifically chosen because of the acid value higher H.L.B. ratio, clarity and homogeneity .the comparison of microwave batch and conventional batch is given in table no. 3 the sample prepared in microwave batch has slightly lower acid value but other parameters like consistency, HLB ratio and avg. molecular weight are quiet comparable thus the reaction of esterification which takes about 3-5 hrs. Can be completed in just three min. the product has cleaning, homogeneous and with good foaming characteristics.
7. The sample S1 has been chosen for formulation of liquid detergent as this has higher and desired HLB ratio and comparatively pink color clarity and mol. Weight compared to conventional batch.
8. The composition of liquid detergent based on S1 is given in table no.4 in initial formulation 6 % of acid slurry and Alpha Olefin Sulphonate has been used This has been Successively replaced by neutralized novel polymer S1 so that the final composition (LD5) only contains 0 % of acid slurry and AOS and maximum (15%) amount ofS1 has been used minor Sodium Laurel Sulphate (7.5%) and sodium sulphate (5%) has been used .the other important components are SLES,sorbitol and urea a small proportions which helps the detergent to function in hard water ,.the foaming characteristics and surface tension of samples at 0.5% and 1% quiet good as a substitute of (LABS and AOS) there is a significant foam control and we get a very low foaming product. The surface tension reduction is quiet appreciable and almost nearer to commercial detergent powder this will certainly helps for better wetting and cleaning of soil and other stains the stain removing characteristics are recorded in table no.5,6,7,and 8.the testing has been done at 0.5% and 1% conc. For all types of stain like soil tea spinach samples containing LD3 show excellent stain removing characteristics and they are on par and some time better than commercial products.

Conclusion: The following conclusion stand confirm in the light of about experimental work.

1. Novel carbohydrate polymer can be efficiently malenised to prepared product by conventional batch process heating and microwave heating.
2. The comparison of microwave product with batch process shows that microwave technique gives product which has similar and identical properties (see table no.3)
3. Microwave techniques give more transparent and homogeneous products. There is a tremendous time saving in microwave process thus the reaction which takes place 4-5 hrs. Just requires 2-3 min. in microwave synthesis. Although the initial investment in microwave heating is more but a small capacity plant can give the same output and product is certainly superior in homogeneity transparency and clarity.
4. The petroleum based product has been replaced in successive formulation with our novel carbohydrate polymer. About 20-80% replacement gives excellent result novel carbohydrate polymer have dual function of stain removing as well as good foaming characteristics .thus we get useful foaming

liquid detergent which can be used for washing machines and application like floor cleaning. The foaming and stain removing product saves water. Thus about two buckets of water can be saved from each house if these products are commercialized.

5. The detergent formulation contains Avery small proportion and they are also free from petroliumactive substances thus we can certainly promote ecofriendly products which are the requirement of future green pollution free world.
6. The space required for microwave reactor is very small thus the same reaction can be carried out in a small reactor in minutes with little manpower and risk.
7. Pilot scale studied should be carried for following sample LD3 and LD1 and novel carbohydrate polymer S1.

RESULTS AND DISCUSSION

In the microwave synthesis various carbohydrate polymers based on sugar, maize starch sorbitol and glycerin have been studied. The various parameters like Temperature, Time, and Microwave power have been kept constant. All carbohydrate novel polymers have been analyses for their physicochemical properties like Acid value, color, saponification value, HLB ratio, oxyrine oxygen content etc. The carbohydrate polymer (S1) sample has been chosen for preparation of powder and liquid detergent due to good % solids, consistency, color and HLB ratio.

To compare the microwave synthesis with conventional reactor synthesis, the sample which is prepared by conventional glass reactor was prepared by microwave reactor i.e. In the conventional method the reaction time was 5 hrs. And temp. 225ºc If we compare (table comparison between conventional and microwave results) the acid value is slightly higher the results are better than polymer prepared by conventional methods.

The carbohydrate polymer prepared by microwave was neutralized by 30%KOH as a conventional method. The polymer was used for the preparation of liquid detergent .The formulations were same as the formulations of liquid detergent prepared by using conventional method.

The analysis liquid detergent shows that the sample prepared by using microwave synthesis are on par and sometime better than conventional heating based polymers. The detergency is also compared with commercial products and the results are better than commercial products.

CONCLUSIONS

The presented result confirmed that the application of microwave heating substantially reduces the reaction time down to several min also in the case of the transesterification reaction and, in some cases, lower reaction temperatures can be used, when compared to the conditions of transesterification methods performed under classical heating.

The water – soluble polysaccharide esters with low degree of etherification were achieved under mild reaction conditions such as short reaction time, low amount of etherification agent, using appropriate reaction media. The following standard conditions can be recommended for synthesis of carbohydrate polymers. Carbohydrate polymers: Time 2 mins, Temp. 60ºc and wattage 60.

Comparison of conventional method of cooking with microwave synthesis has been undertaken. The microwave synthesis gives results which are on par or some times better than conventional methods. There is tremendous time saving in microwave synthesis, normally 2-3 hrs.are required for carbohydrate polymer preparation at 225ºc the time of reaction is 2 mins.

Thus the same reaction can be carried out in a small reactor with little man power and risk. The space required for microwave reactor is very small and man power required can be reduced continuously. The initial investment is higher but the recurring expences, energy expences, are lower in microwave reactor. Microwave reactor can be the desired route which if financially and technically viable option for future time. The reaction time can be reduced from hours to minutes. The presented microwave-assisted Trans esterification method might substitute the toxic, hazardous and time-consuming classical etherification processes in preparing polysaccharide based surfactants.

Table 1: Microwave Synthesis of Starch, Sugar, Sorbitol based carbohydrate polymers (Batch size =30 gms.)

Ingredients	B1	B3	S1	S4
Sorbitol (70%)	16.5	12	15.6	-
Maliec anhydride	1.5	1.5	1.5	-
Phthalic anhydride	1.5	1.5	0.6	1.5
Starch	7.5	12	3	-
Oxalic acid	1.5	1.5	1.5	1.5
Citric acid	1.5	1.5	1.5	
Sugar (80%)	-	-	6	15
Benzoic acid	--	-	0.3	-
Glycerol	-			12

Note: Sodium bisulphite, Sodium bisulphate, and Isopropanol are used as catalyst

Time for each batch 2 min. at 60□c pressure at 60 atm. Initial period to start batches are of 5 min. which is automatically set by microwave for starting and mixing of ingredients.

Table 2: Analysis of microwave synthesized novel polymers

Tests	B1	B3	S1	S4
% Solid	70.14	72.36	79.52	72.35
Acid value	19.15	23.28	21.52	31.14
Solubility	Water	Water	Water	Water
Color	Pink	Pinkish	Pinkish	Pinkish
H.L.B.	16.0	15.5	15.3	14.1
Mol.weight	4037.46	5417.56	5179.78	5182.26
Ester value	177.10	201.87	126.03	221.16
% Oxyrene oxygen value	14.12	14	14.24	14.3

Table 3: Comparison of Batch S1 (Prepared by conventional method and by microwave synthesis method)

Tests	S1(conventional method)	S1(microwave synthesis method)
% Solid	79.52	82.36
Acid value	21.52	20.28
Solubility	Water	Water
Color	pinkish	pinkish
H.L.B.	15.3	15.7
Mol.weight	5179.78	51234.56
Ester value	126.03	131.87
% Oxyrene oxygen value	14.24	15

Table 4: Liquid Detergent composition based on polymer S1 obtained by Microwave synthesis

INGREDIENTS	LD1	LD2	LD3	LD4	LD5
Acid slurry (70%)	6.0	4.5	3.0	1.5	00
AOS	6.0	4.5	3.0	1.5	00
SLS	7.5	7.5	7.5	7.5	7.5
SLES	10	10	10	10	10
Sodium sulphate	05	05	05	05	05
Urea	03	03	03	03	03
Sorbitol (70%)	10	10	10	10	10
Polymer (S1) (80.05)	3.0	6.0	9.0	12	15
Water	49.5	49.5	49.5	49.5	49.5

Table 5: Soil stain on Cotton, polyester and Terri cot cloth sample Based on carbohydrate polymers.

R_0= Reflectance measured on clean cotton cloth =100
R_0 =Reflectance measured on clean polyester cloth =100
R_0=Reflectance measured on clean Teri cot cloth =100
Rs=Reflectance measured on Soil Stained cotton cloth =33
Rs=Reflectance measured on Soil Stained polyester cloth =43
Rs=Reflectance measured on Soil Stained Teri cot cloth =39

Sr. no.	Sample	Conc.%	Cotton		Polyester		Tericot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	86	79.10	87	77.19	89	81.96
2		0.25	78	67.16	79	63.15	74	57.37
3		0.5	82	73.13	84	71.92	81	68.85
4		1.0	93	89.55	91	84.21	90	83.60
1	LD2	0.1	78	67.16	79	63.15	76	60.65
2		0.25	89	83.58	91	84.21	86	77.04
3		0.5	91	86.56	92	85.96	90	83.60
4		1.0	88	82.08	88	78.94	86	77.04
1	LD3	0.1	88	82.08	86	75.43	85	75.40
2		0.25	93	89.55	92	85.96	91	85.24
3		0.5	94	91.04	96	92.98	94	90.16
4		1.0	93	89.55	90	82.45	96	93.44
1	LD4	0.1	89	83.58	88	78.94	84	73.77
2		0.25	77	65.67	80	64.91	79	65.57
3		0.5	84	76.11	88	78.94	88	80.03
4		1.0	86	79.10	85	73.68	89	81.96
1	LD5	0.1	79	68.65	72	50.87	72	54.09
2		0.25	81	71.64	80	64.91	78	63.93
3		0.5	76	64.17	78	61.40	77	62.29
4		1.0	88	82.08	85	73.68	85	75.40
1	CLD1	0.1	86	75.43	88	80.32	86	79.10
2		0.25	89	80.70	91	85.24	89	83.58
3		0.5	91	84.21	93	88.52	91	86.56
4		1.0	94	89.47	96	93.44	93	89.55
1	CLD2	0.1	82	68.42	80	67.21	78	67.16
2		0.25	82	68.42	83	72.13	81	71.64
3		0.5	85	73.68	86	77.04	83	74.62
4		1.0	87	77.19	89	81.96	87	80.59

Table 6: Tea stain on Cotton, polyester and Terri cot cloth sample Based on carbohydrate polymers.

R_0= Reflectance measured on clean cotton cloth =100
R_0 =Reflectance measured on clean polyester cloth =100
R_0=Reflectance measured on clean Teri cot cloth =100
Rs=Reflectance measured on Tea cotton cloth =36
Rs=Reflectance measured on Tea polyester cloth =29
Rs=Reflectance measured on Tea Teri cot cloth =31

Sr. no.	Sample	Conc.%	Cotton		Polyester		Tericot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	79	67.18	84	77.46	86	79.71
2		0.25	81	70.31	85	78.87	88	82.60
3		0.5	85	76.56	89	84.50	90	85.50
4		1.0	89	82.81	92	88.73	93	89.85
1	LD2	0.1	83	73.43	87	81.69	87	81.15
2		0.25	86	78.12	89	84.50	90	85.50
3		0.5	88	81.25	92	88.73	92	88.40
4		1.0	91	85.93	94	91.54	95	92.75
1	LD3	0.1	84	75.00	81	73.23	80	71.01
2		0.25	86	78.12	84	77.46	83	75.36
3		0.5	90	84.37	87	81.69	87	81.15
4		1.0	94	90.62	92	88.73	90	85.50
1	LD4	0.1	89	82.81	85	78.87	88	82.60
2		0.25	91	85.93	87	81.69	90	85.50
3		0.5	93	89.06	91	87.32	93	89.85
4		1.0	96	93.75	94	91.54	95	92.75
1	LD5	0.1	82	71.87	85	78.87	85	78.26
2		0.25	84	75.00	87	81.69	87	81.15
3		0.5	87	79.68	90	85.91	89	84.05
4		1.0	90	84.37	92	88.73	91	86.95
1	CLD1	0.1	80	71.83	82	72.46	84	75.00
2		0.25	82	74.64	84	75.36	81	70.31
3		0.5	84	77.45	86	78.26	79	67.18
4		1.0	86	80.28	87	79.71	77	64.06
1	CLD2	0.1	77	67.65	79	68.11	81	70.31
2		0.25	79	70.42	81	71.01	79	67.18
3		0.5	81	73.23	83	73.91	77	64.06
4		1.0	83	76.05	85	76.81	75	60.93

Table 7: Coffee stain on Cotton, polyester and Terri cot cloth sample Based on carbohydrate polymers.

R_0= Reflectance measured on clean cotton cloth =100
R_0 =Reflectance measured on clean polyester cloth =100
R_0=Reflectance measured on clean Teri cot cloth =100
Rs=Reflectance measured on Coffee cotton cloth =31
Rs=Reflectance measured on Coffee polyester cloth =36
Rs=Reflectance measured on Coffee Teri cot cloth =30

Sr. no.	Sample	Conc.%	Cotton		Polyester		Tericot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	82	73.91	77	64.06	75	64.28
2		0.25	85	78.26	80	68.75	78	68.57
3		0.5	87	81.15	83	73.43	80	71.42
4		1.0	89	82.60	86	78.12	84	77.14
1	LD2	0.1	83	75.36	81	70.31	80	71.42
2		0.25	86	79.71	84	75.00	83	75.71
3		0.5	90	84.05	87	79.68	85	78.57
4		1.0	92	86.95	90	82.81	88	79.25
1	LD3	0.1	77	66.66	73	57.81	78	68.57
2		0.25	80	71.01	77	64.06	83	75.71
3		0.5	84	76.81	80	68.75	88	79.25
4		1.0	87	81.15	84	75.00	90	85.71
1	LD4	0.1	86	79.71	87	79.68	89	84.28
2		0.25	91	85.50	90	82.81	91	87.14
3		0.5	93	88.85	93	87.50	94	91.42
4		1.0	97	95.65	95	90.62	96	94.28
1	LD5	0.1	84	76.81	85	76.56	87	81.42
2		0.25	87	81.15	88	79.25	90	85.71
3		0.5	91	85.50	90	82.81	93	90.00
4		1.0	94	91.30	92	85.93	95	92.85
1	CLD1	0.1	89	82.81	91	87.14	87	79.71
2		0.25	87	79.68	93	90.00	89	82.60
3		0.5	85	76.56	95	92.85	91	85.80
4		1.0	82	71.84	97	95.14	95	92.75
1	CLD2	0.1	82	71.87	84	77.14	84	75.36
2		0.25	79	64.06	86	80.00	86	78.26
3		0.5	77	64.06	88	82.85	88	81.15
4		1.0	75	60.93	90	85.14	90	84.05

Table 8: Spinach stain on Cotton, polyester and Terri cot cloth sample Based on carbohydrate polymers.

R_0= Reflectance measured on clean cotton cloth =100
R_0 =Reflectance measured on clean polyester cloth =100
R_0=Reflectance measured on clean Teri cot cloth =100
Rs=Reflectance measured on Spinach cotton cloth =38
Rs=Reflectance measured on Spinach polyester cloth =32
Rs=Reflectance measured on Spinach Teri cot cloth =41

Sr. no.	Sample	Conc.%	Cotton		Polyester		Tericot	
			Rw	Detergency	Rw	Detergency	Rw	Detergency
1	LD1	0.1	82	70.96	86	79.41	85	74.57
2		0.25	88	80.64	91	86.76	89	81.35
3		0.5	91	85.48	94	91.17	91	84.74
4		1.0	94	90.32	96	94.11	93	88.13
1	LD2	0.1	87	79.03	85	77.94	86	76.27
2		0.25	91	85.48	88	82.35	90	83.05
3		0.5	93	88.70	90	85.29	93	88.13
4		1.0	95	91.93	94	91.17	95	91.52
1	LD3	0.1	84	74.19	83	75.00	80	66.10
2		0.25	87	79.03	85	77.94	83	71.18
3		0.5	90	83.87	88	82.35	86	76.27
4		1.0	93	88.70	90	85.29	89	81.35
1	LD4	0.1	80	67.74	81	72.05	83	71.18
2		0.25	84	74.19	85	77.94	86	76.27
3		0.5	86	77.41	87	80.88	91	84.74
4		1.0	89	82.25	91	86.76	94	89.83
1	LD5	0.1	85	75.80	86	79.41	86	76.27
2		0.25	88	80.64	89	83.82	89	81.35
3		0.5	90	83.87	92	88.23	91	84.74
4		1.0	92	87.09	95	92.64	93	88.13
1	CLD1	0.1	85	77.94	84	72.88	89	82.85
2		0.25	87	80.58	86	76.27	92	87.00
3		0.5	89	83.82	88	79.66	94	90.32
4		1.0	91	86.76	90	83.05	96	93.54
1	CLD2	0.1	81	72.05	79	64.40	84	74.19
2		0.25	83	75.00	81	67.79	86	77.41
3		0.5	84	76.47	83	71.18	88	80.64
4		1.0	86	79.41	85	74.57	90	83.87

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