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Microwave Induced Reaction for Synthesis of Novel Polymer Based on Fumaric Acid and Glycerol

Suhas Shinde[1], K. V. Koranne[2], V.Y.Karadbhajne[3]*, B.B. Gogte[4]

[1,2]Department of Chemical Engineering and 3,4, Department of Oil Technology, Laxminarayan Institute of Technology, R.T.M Nagpur University, Nagpur (Maharashtra) - India.

***Corres.Author: drvijaylit@gmail.com, vijaykb1@rediffmail.com (M) 09822367657.**

Abstract: Glycerol is a byproduct of various oil and fat industries like Biodiesel manufacture. In coming decades a huge amount of glycerol will be available as a byproduct. In the present research work Novel polymer based on glycerol and fumaric acid has been synthesized by novel microwave technique. Various parameters like wattage, reaction time and temperature have been studied. These samples are analyzed for physicochemical characteristics. IR spectroscopy for selected polymer has been used to understand the chemical linkages in the polymer. This investigation positively confirms the presence of ester and ether groups' polymer. The acidity of the polymer has been neutralized by 30% Potassium hydroxide solution.
The same exercise was also carried out by conventional heating system and the results have been compared. Microwave synthesized resin has been used in liquid detergent compositions as an active ingredient. A parallel sample of liquid detergent based on conventional heating system polymer was also prepared. The results of liquid detergents based on both type of polymers (microwave and conventional polymer) have been compared with commercial liquid detergents. Novel Polymer based samples are on par with commercial products.
Key Words: Glycerol, Microwave, Conventional, Novel Polymer.

Introduction

Microwave Synthesis[1]:

Microwave synthesis represents a major break through in synthetic polymer chemistry because of following reasons:-

1. Conventional heating is known to be less efficient and time consuming. Many polymers require three to eighteen hours or more to get desired molecular weight, viscosity, and physico-chemical characteristics this limits the scientific creativity, development of new process and efficient technology. Instead of spending hours or even days the same reactions can be conducted in minutes.

2. Microwave reactions system can be effectively applied to any reaction scheme creating faster reactions improving yield and clear chemistries.

3. Microwaves can transfer energy directly to the reactive species so called molecular heating they can promote transformations that are not currently possible using conventional heat this is creating a new realm in synthetic organic chemistry.

4. Microwaves also provide chemists with the option to perform "cool reactions". Energy is applied directly to the reactants however bulk heating is minimized by use of simultaneous cooling this allows heat sensitive molecules (e.g. proteins) as the temperature are low enough to eliminate thermal degradation.

The present research work is aimed at synthesizing novel polymers based on glycerol and fumaric acid, glycerol is a byproduct for Biodisel manufacture. If we wish to promote green fuel we must take care of using byproducts in novel applications. In past we have synthesized novel polymers based on sorbitol[2], white dextrin[3], starch[4] and vegetable oils[5] and used successfully these polymeric surfactants as ingredients to detergent compositions. In the present work we synthesize glycerol fumaric acid polymer with microwave technique as well as conventional heating, this will help as to directly compare the performance, economics and technical viability of microwave synthesis with conventional mode of heating. It will also be interesting to find out how microwave synthesize affect the colour, viscosity and molecular weight distribution of polymer[12].

The effect of microwave technique on performance characteristics of polymers when used in detergents is also a curiosity and matter of research. Therefore liquid detergents have been formulated using these novel synthesized polymers. The same composition was also tried using polymer based on conventional heating and the results are compared to know the competence of microwave heating.

Experimental

Microwave Heating system used in the present study[1]:-

The CEM focused microwave synthesis system model discover is used in the synthesis (see figure 1) (CEM corporation U.S.A).

Discover System - Front View

Figure No. 1

The system facilities either homogeneous or heterogeneous solution phase chemistry, solution phase chemistry solid phase chemistry or chemistry conducted on solid supports. It accommodates vessels ranging in volume from 5 ml to 125 ml for reactions performed at elevated temperature and pressures. The discover system consist of a continuous microwave power delivery system with operator selectable power output 0-300 watts. An infrared temperature control system direct pressure control system, stirring and cooling operation is also provided in the equipment.

Conventional Heating System[11]:

The preparation of polymer was carried out in a glass reactor. The reactor consists of two parts lower part of the reactor consists of a round bottom vessel with very wide mouth the capacity of the flask is about two

liters. The upper part of the reactor is its lid having four necks with standard Joints. A motor driven stirrer is inserted in the reactor through the central neck, while another neck was used for the thermometer. A condenser was fitted with the reactor through the third neck. The remaining neck was closed, controlled heating in a range of ± 20C was provided through an accurate temperature regulator.

Table 1:- Microwave Synthesis of Novel Polymer

Name of novel polymer	Mole Ratio of fumaric to glycerol	Weight of fumaric in grams	Weight of glycerol in grams	Reaction temperature in ^{0}C	Microwave power in watt	Reaction time minutes
NP1	0.45:1	3.8	5.9	150	100	5
NP2	0.45:1	3.8	5.9	200	125	5
NP3	0.45:1	3.8	5.9	225	140	5
NP4	0.45:1	3.8	5.9	250	160	5
NP5	0.05:1	0.39	5.22	250	160	5
NP6	0.09:1	0.78	5.8	250	160	5
NP7	0.19:1	1.17	4.06	250	160	5
NP8	0.11:1	0.78	4.64	250	160	5
NP9	0.2:1	1.16	3.9	250	160	8

Table 2:- Conventional Synthesis of Novel Polymer

Name of novel polymer	Mole Ratio of fumaric to glycerol	Weight of fumaric in grams	Weight of glycerol in grams	Reaction temperature in ^{0}C	Reaction time hours
NP10	0.2:1	116	390	225	4

Formulation NP9 was also prepared by conventional method as described in table no2.

Table 3:- Physico Chemical Analysis of Microwave Synthesized Polymer and Conventional heating Method Polymer

Sr. No	**Physical Property**	**Polymer NP9 (Micro)**	**Polymer NP10(Conv)**
1	Acid value of resin	34.45	22.77
2	pH value (1% sol^n)	2.08	2.44
3	Solubility of Resin 1) In water 2) In Xylene 3) In I.P.A	 Soluble Insoluble Soluble	 Soluble Insoluble Soluble
4	% Solid	84.99	88.84
5	Refractive index 30^0C by Abbes Refractometer	1.45	1.47

Table 4:- Analysis of Polymer Neutralized with KOH

Sr. No	**Property**	**Polymer NP9 (Micro)**	**Polymer NP10 (Conv)**
1	% Solid	82.34	85.98
2	pH value (1% sol^n)	6.48	6.52
3	Colour (Lovibond tintometer) 1/4" cell (Y+R units)	1.3	90

FTIR Spectroscopic Data[13,14]:-

Spectroscopic investigation of Novel Resin (NP9)

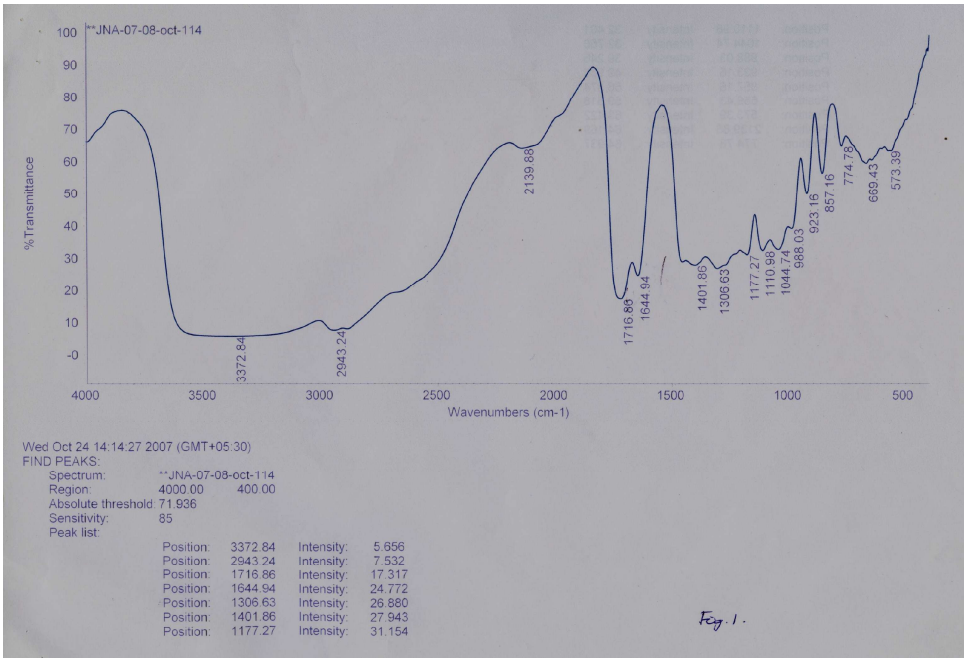

Figure 2 – Infra-Red spectral study of microwave synthesized Polymer or Resin

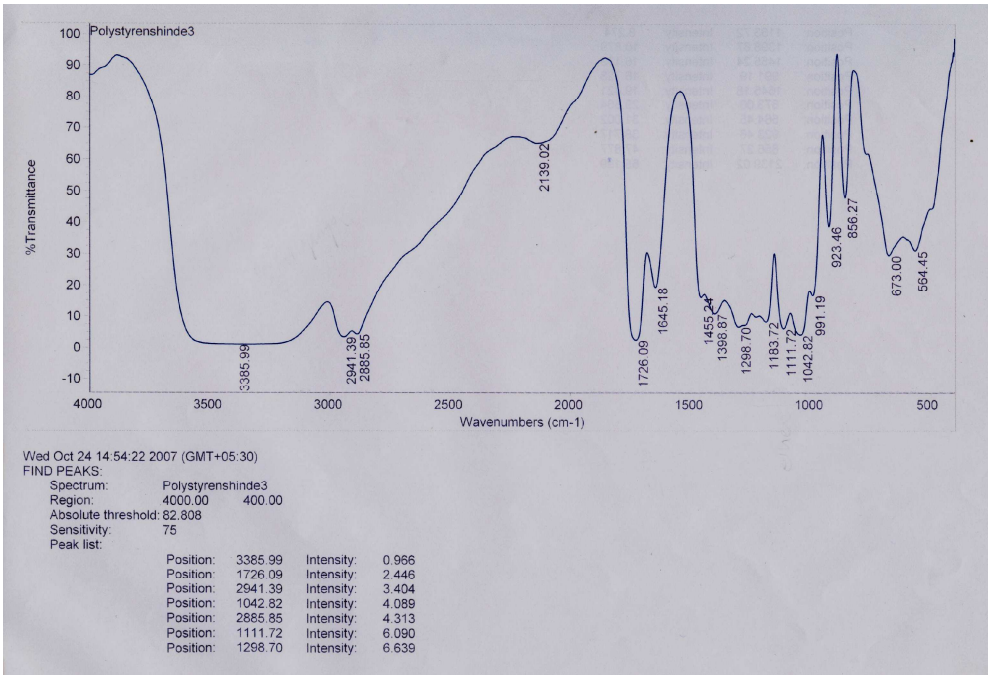

Figure 3 - Infra-Red spectral study of conventional method Polymer or Resin

The pick observed at 1177.27 cm^{-1} in figure 2 and at 1183.72 cm^{-1} in figure 3 is due to C-O stretching which is characteristic absorption due to acid present in the chemical reaction. Absorption in region 1070-1150 cm^{-1} is most characteristic of ether that is C-O starching in C-O-C group. This confirms the presence of free acid groups and ether groups in resin composition. The free acid group pick in figure 2 is 2943.24 and 2885.85, 2941.39 in figure 3.

The pick 3372.84 cm^{-1} in figure 2 and 3385.99 cm^{-1} in figure 3 is due to O-H stretching this shows intermolecular hydrogen bonding –OH group (polymeric association) this indicates positively the presence of free –OH group in resin structure[6].

Table 5:- Composition of Liquid Detergent

Detergent based on novel polymer sample NP9

Ingredients	**Wt% of sample**
Sodium lauryl Sulphate	1.50
Sodium lauryl ether Sulphate (100% solid)	5.25
Alfa Olefin Sulphonate (100% solid)	7.00
Neutralized Novel Polymer (100% solid)	8.80
Urea	2.50
Glycerol	2.50
Ethyl cellulose	1.00
Polyvinyl alcohol (10% solid)	0.5
Water	70.95

Note: - Sodium lauryl ether Sulphate was used as 35% solution in water, Alfa Olefin Sulphonate was used as 67% solution in water, Novel polymer was used as 82.34 (Microwave polymer sample) and 85.98 (Conventional heating sample)

Sample ND9 was based on microwave synthesized polymer while sample ND10 has similar compositions with only difference of using conventional synthesis polymer.

Table No. 6:- Analysis of Liquid Detergent Based on Novel Polymers:-

Name of novel polymer	Concentration % by weight	Foam Height (cm^3)				Density (gm/cm^3)	Surface Tension (Dynes/cm)
		Time in minute					
		0	5	10	15		
ND9	0.1% 0.25% 0.5% 1%	190 290 550 670	170 290 540 650	170 280 530 640	160 270 530 640	0.981 0.983 0.99 0.998	28.299 25.179 20.286 16.02
ND10	0.1% 0.25% 0.5% 1%	145 260 320 650	140 250 310 630	130 245 300 620	120 245 295 610	0.977 0.978 0.978 0.98	25.24 20.04 19.90 19.67
Commercial sample	0.1% 0.25% 0.5% 1%	160 350 660 1000	150 300 600 700	140 250 490 450	130 230 300 350	0.993 0.998 0.999 1.00	21.85 21.64 21.35 20.35

Table 7: Detergency Evaluation of liquid detergents (Brightness Test):-
(Soil, Tea and Coffee stain on terricot and cotton cloth samples)

Stain	%Concentration	Sample ND9 (Micro)		Sample ND10 (Conventional)		Commercial	
		%Detergency		%Detergency		%Detergency	
		Cotton	Tericot	Cotton	Tericot	Cotton	Tericot
Soil Stain	0.5	90.97	86.69	78.81	79.08	78.81	90.49
	1.0	99.65	86.69	87.50	92.39	89.00	92.40
Tea Stain	0.5	83.11	75.60	70.12	90.85	79.87	81.70
	1.0	99.35	78.65	86.36	93.90	96.10	84.75
Coffee Stain	0.5	95.55	68.72	93.90	56.87	91.49	49.76
	1.0	97.57	73.46	97.57	66.35	95.55	82.5

Note:- Ro = Reflectance measured on clean tericot cloth = 75.0
Ro = Reflectance measured on clean cotton cloth = 82.2
Rs = Reflectance measured on Soil stained tericot cloth = 22.4
Rs = Reflectance measured on Soil stained cotton cloth = 24.6
Rt = Reflectance measured on Tea stained tericot cloth = 42.2
Rt = Reflectance measured on Tea stained cotton cloth = 51.4
Rc = Reflectance measured on Coffee stained tericot cloth = 40.0
Rc = Reflectance measured on Coffee stained cotton cloth = 32.8

Analysis of Liquid Detergent:

- **Surface tension[7]:**

Surface tension may be defined as the force in dynes acting at right angle to the surface of a liquid along one centimeter length of the surface. It is generally represented by the symbol "**Y**" and expressed in dynes/cm.

The stalgamometer method was used for calculating the surface tension of sample. If knowing the surface tension of the one liquid, we can calculate the surface tension of other liquid easily by using following formula

$\Psi_1 = (n_2 \rho_1 / n_1 \rho_2)^{\Psi 2}$

Where Ψ_1= surface tension of the sample
Ψ_2= surface tension of water (i.e.71.18 dyne/cm)
ρ_1=density of sample
ρ_2=density of water
n_1=no. of drops of sample
n_2=no. of drops of water

- **Foam height[7,10]:**

Manual manipulation of closed container method was used for calculating the foam height.

Procedure:-

Foam characteristics are measured in terms of volume. The following are carried out for it

1. Take 1000 ml cylinder provided with stopper. Add to it, 100 ml solution of particular concentration whose foam characteristic is to be measured.
2. Give it 30 up-down rotation within time period of 30 seconds.
3. Keep that cylinder on table and observe the foam above liquid level and note down reading at zero minute.
4. The readings were measured after 5, 10, 15 minutes respectively.
5. Same procedure is carried out for the solution of different concentration like 0.1 %, 0.25 %, 0.5 % and 1%.

From above experiment we can easily find out the foam stability and change in foam characteristics with time.

- **Percentage detergency[7,8,9]**

The samples, which are washed dried and ironed, are used for percentage detergency. The % detergency is finding out by using Lambert and slandered formula

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

Where, Rw = Reflectance measured on washed cloth.
Rs = Reflectance measured on soiled cloth.
Ro = Reflectance measured on clean cloth.

The reflectance of the cloth samples were measured by using "reflectance meter" manufactured by Universal Engg. Corporation, Ambala road, Saharanpur (UP). This is digital instrument. Once this is adjusted, then samples were kept on the instrument and the reading was noted down on digital instrument.

Results and Discussion

Table no. 1 gives various parameters for synthesis of novel polymer based on glycol and fumaric acid. The optimization of microwave synthesis conditions has been achieved by studying variables like mole ratio of reactants, reaction temperatures, microwave power wattage and reaction time. The objective is to develop a polymer of desired acid value, viscosity, lighter color, excellent clarity, homogeneity and stability. Various mole ratios from 0.05:1.00 to 0.45:1.00 (fumaric acid: glycol) have been studied. The stirring was achieved by magnetic stirring using stir bars supplied by CEM Corporation. The reaction was carried out in Bench mate type microwave reactor supplied by CEM Corporation, USA (see figure 1). At first 5 ml sample was prepared and analyzed. Polymer NP9 was selected as it had highest viscosity, desired acid value, clarity and stability; therefore a bulk sample was prepared in a 125 ml open flask in microwave reactor and used in liquid detergent composition. The same composition of polymer (NP9) was also prepared by conventional heating system using a glass reactor and heating mantle. The comparative analysis of the two polymer prepared by microwave and conventional synthesis are given in table no.3. The conventional heating systems give a polymer with slightly lower acid value. The two polymers have excellent solubility in water and isopropyl alcohol. The two polymers were neutralized by 30% KOH solution and the characteristics of neutralized polymers are given in table no.4.

A comparison of microwave technique with conventional technique shows that there is a tremendous saving of time. By using microwave technique the same reaction can be carried out in just 8 minutes instead of four hours. The reaction is at least 24 times faster than conventional method. There is definite saving of time, energy and manpower. The space required is also less.

Liquid detergents formulations have been prepared both by using microwave synthesized polymer and conventional heating system polymer. The speciality of liquid detergent prepared by as freedom from petroleum based acid slurry and sodium tripolyphosphate. We used only vegetable based actives so certainly both are ecofriendly compositions. The sample have been tested for foaming characteristics, surface tension, detergency on soiled cloth and stain removing by standard techniques. The samples prepared by both the types of polymers (microwave and conventional) have good foaming at very low concentration of 0.1% this is comparable to commercial products. The foam stability is also reasonable. At higher concentration of 0.25 to 1.0 % the foam is slightly less than commercial product. However the foaming and the foam stability characteristics are reasonably good for both polymers. The foaming characteristics of sample based on microwave polymer are better than conventional polymer. The reduction in surface tension is good in both the samples and comparable to commercial samples (table 6).

The detergency characteristics as measured by brightness tester are shown in table no.7. The soil stain removal by both the samples on terricot and cotton clothes is good and results are comparable with commercial samples. Microwave based samples give excellent detergency as compared to commercial and conventional samples.

The samples based on microwave synthesized polymer give excellent and better tea and coffee stain removing characteristics. They are better than commercial samples.

Thus we can say that liquid detergent based on microwave synthesized polymer is better than sample based on conventional method polymer and commercial sample.

Conclusion

1) Glycerol is the byproduct in manufacturing of biodisel and it will be available in commercial quantities in coming years. There is need to develop novel industrial product based on glycerin. In this research work novel polymers based on glycerol and fumaric acid have been synthesized. The polymer has been prepared by novel microwave synthesis technique in special equipment model discover supplied by CEM Corporation USA.
2) The polymer has also been synthesized by conventional batch reactor technique.

3) Various parameters for microwave synthesis like time, temperature, and wattage and mole ratio have been studied. The parameters which have been standardized are as follows,

   Mole ratio- fumaric acid: Glycerol = 0.2:1

   Wattage- 160 Watt

   Temperature- 250^0C

   Reaction time- 8 minutes

4) The same temperature and mole ratio has been tried on glass reactor in conventional system using heating mental with accurate temperature control. The reaction time for conventional batch reactor was

5) A comparison of the product obtain by microwave synthesis and conventional method show that, we get superior product, shorter reaction time and there is certainly saving of manpower, energy and space.

6) The IR Spectra shows picks which are indicated in figure 2 and 3. The picks observed show the presence of the ether, carboxylic and free alcoholic groups.

7) Novel liquid ecofriendly detergents have been prepared based on both types of polymers.

8) Novel resins have been used to the extent of 8.8 in these formulations. The other ingredients are conventional but basically they are of vegetable origin.

9) Petroleum based acid slurry and sodium triphosphate has not been used. This will certainly promote green chemistry. The physicochemical characteristics of liquid detergent based on microwave and conventional polymer have been compared with commercial liquid detergent sample (see table no 6). The results of foam height, surface tension and detergency are quite comparable to commercial product. In some instances the formulations based on microwave synthesis polymer is superior to conventional polymer product.

10) The raw material price of our composition is around Rs. 40 per Kg. This is certainly attractive preparation.

11) Pilot plant studies should be undertaken so that production we can.

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