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Experimental Design of High Yield Polypyrrole by Taguchi Method

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ABSTRACT
Taguchi method was successfully implemented in the robust design and development of Polypyrrole synthesis employing inverted emulsion polymerization technique using methanesulfonic acid as a novel dopant along with Potassium persulfate as an oxidant. Polypyrrole salt was obtained in a very high percent yield (83.77 %) with respect to the amount of pyrrole used and the reaction time was considerably reduced (1 hour and 10 minutes) as compared to previously reported synthesis methods. The settings of the process parameters were determined by using Taguchi's experimental design method. Orthogonal arrays of Taguchi, the signal-to-noise (S/N) ratio, the analysis of one way variance (ANOVA), and regression analyses are employed to find the optimal process parameter levels and to analyze the effect of these parameters on percent yield of Polypyrrole salt.
Keywords: Taguchi optimization method; inverted emulsion polymerization; ANOVA; organic semiconductors; Polypyrrole; Percent Yield.

I. Introduction

Five membered fused heterocyclic ring systems have been extensively studied since their discovery, Shirakawa et al. (1977). These natural terthienyl compounds display exceptional ability as organic semiconductors and possess the inherent property of photodynamically destroying tumor cells, Kanatzidis (1990). Several fused five membered heterocyclic rings have a tendency to behave as organic semiconductors when doped and conduct electricity, Shirakawa et al (1977). Substituted Polythiophenes and Polypyrroles are the most extensively studied conducting polymers due to their unique properties (tractability, air stability and having a low band gap), Heeger (1986). Some of the first examples of polypyrroles were reported in 1963 by Weiss and coworkers. These workers described the pyrolysis of tetraiodopyrrole to produce highly conductive materials. Most commonly polypyrrole is prepared by oxidation of pyrrole, which can be achieved using ferric chloride in methanol:

$$n\ C_4H_4NH + 2\ FeCl_3 \rightarrow (C_4H_2NH)_n + 2\ FeCl_2 + 2\ HCl$$

Polymerization is thought to occur via the formation of the pi- radical cation $C_4H_4NH^+$. This electrophile attacks the C-2 carbon of an unoxidized molecule of pyrrole to give a dimeric radical $(C_4H_4NH)_2]^+$. The process repeats itself many times.

Conductive forms of polypyrrole are prepared by oxidation ("p-doping") of the polymer:

$$(C_4H_2NH)_n + x\ FeCl_3 \rightarrow (C_4H_2NH)_nCl_x + x\ FeCl_2$$

The polymerization and p-doping can also be affected electrochemically. The resulting conductive polymer is peeled off of the anode.

An innovative experimental robust design methodology based on Taguchi method is employed to synthesize high yield polypyrrole salt through inverted emulsion polymerization technique. The Taguchi method is immensely helpful in data analysis and sampling when more than five experimental parameters are to be varied, Apte et al. (2012). This technique is based upon a set of "orthogonal array" experiments with "optimum settings" of each experimental parameter. The experimental parameters in turn are classified as "Signal-to-Noise" ratios which are log functions of desired output serving as object functions for process optimization. "Signal" factors (experimental control factors) define the course of an experiment whereas "Noise" factors impart variability in an experiment. The purpose of Taguchi analysis is to reduce this variability thereby helping to set "optimum control/experimental parameters", using larger-the-better Signal-to-noise ratio (S/N) approach i.e. optimum "signal" and lowest "noise" by treating the optimization problem through the dynamic system of Taguchi Method, Apte et.al.(2012). Dr. Genichi Taguchi who developed this method divided it into seven steps to avoid the loss functions and improve the mean outcome of an experimental process.

Polypyrrole salt is synthesized in a very high percent yield (83.77 %) with respect to the amount of pyrrole. Integrating an innovative method called inverted emulsion polymerization technique, the reaction time was significantly reduced (1h 10 min.) as compared to the previously reported synthesis methods, Saravanan et.al. (2006), Helmers (1973), and Karambelkar et.al. (2011), by following the seven steps of the Taguchi method.

II. Experimental Section: Plan of Experiment

Sampling of polypyrrole salt according to the Taguchi Method: The seven steps.

Identification of Main Function, Side Effects, Failure Modes and control parameters/Signal-to-Noise ratios:

While designing an experiment the first step is to prioritize the primary objective, its possible side effects, different failure modes and the main control/experimental parameters which decide the course of an experiment along with the factors which give an error/variation in the experiment (also called as Noise factors). Hence, in the synthesis of polypyrrole salt, we identify (i) Main function: Synthesis of Polypyrrole, (ii) Side Effects: Low yields, Difficult impurities, (iii) Failure Modes: Long steps, Hazardous chemicals, and (iv) Control Factors: Concentrations of Surfactant, Oxidant, Dopant, Monomer, Variation in Temperatures and Stirring times.

Identification of Noise factors, Testing conditions and Quality Characteristics:

Noise factors lead to “variability” in yield. There is no control on these parameters in the manufacturing environment. The experiment was performed at low stirring (low rpm)(100 rpm),medium stirring (medium rpm) (200 rpm) and high stirring (high rpm) (300 rpm). Hence, in the synthesis of polypyrrole salt, variation in stirring time was identified as a noise parameter, since different stirring times gave variability in percent yield of polypyrrole salt. We can control the rpm but the variability in percent yield of the polypyrrole salt classifies it as a “Noise” parameter. The synthesis of polypyrrole salt was carried out using a standard Schlenk apparatus. Pyrrole monomer (Acros) 99.9% extra pure, organic reagents like chloroform (Fischer Scientific) (99.9% extra pure), acetone (Fischer Scientific) (Analar grade, 99% pure), dopant methanesulfonic acid and surfactant sodium lauryl sulfate (National Chemicals, India) along with oxidant potassium persulfate (Qualigens Fine Chemicals, India) were used as received.

Identification of the objective function to be optimized:

Control factors, i.e Concentrations of Surfactant, Oxidant, Dopant, Monomer and Variation in temperatures were identified as the main objective function to be optimized, since these parameters can alter the course of an experiment. Upon varying these parameters the “response factor” i.e. percent yield of the polymer can be increased thereby helping to “set” the control (experimental) parameters while designing an experiment.

Identification of the control factors and assigning their levels:

Control factors or process parameters i.e Concentrations of Surfactant, Oxidant, Dopant, Monomer and Variation in temperatures were identified and assigned levels. (Figure:1) and (Table:1)

Parameter	**Code**	**Levels**		
Monomer Concentration (ml)	A	1 2	2 4	3 5
Surfactant Concentration (g)	B	1	2	3
Oxidant Concentration (g)	C	2	4	6
Dopant Concentration (ml)	D	4	6	8
Temperature (^{0}C)	E	20	30	40
Stirring Time (hrs)	F	1	3	4

Table:1 Inverted Emulsion Polymerization Process Parameters

CONTROL FACTORS/LEVELS	1	2	3
Monomer	M1	M2	M3
Surfactant	S1	S2	S3
Oxidant	O1	O2	O3
Dopant	D1	D2	D3
Temperature	T1	T2	T3
Stirring Times	ST1	ST2	ST3

Figure: 1 Control Factors and their levels

Selection of the orthogonal array matrix experiment:

Since ther'e are six control factors which can alter the course of the experiment, L18 orthogonal array (OA) was selected for polypyrrole sampling as per Taguchi method. The degrees of freedom for six parameters in each of the three levels were calculated as follows (Table:2)

Degree of Freedom (DOF) = number of levels-1
For each factor, DOF equal to:
For (A); DOF = 3-1 = 2
For (B); DOF = 3-1 = 2
For (C); DOF = 3-1 = 2
For (D); DOF = 3-1 = 2
For (E); DOF = 3-1 = 2
For (F); DOF = 3-1 = 2

L18 OA has 18 rows corresponding to the number of tests, with three columns at six levels. L18 OA has seventeen DOF, in which 12 were assigned to six factors (each one 2 DOF) and 2 DOF was assigned to the error.

Expt No.	A	B	C	D	E	F	G	H	Yield of Polypyrrole salt (%)
1	1	1	1	1	1	1	1	1	10.64
2	1	1	2	2	2	2	2	2	19.04
3	1	1	3	3	3	3	3	3	21.14
4	1	2	1	1	2	2	3	3	24.06
5	1	2	2	2	3	3	1	1	33.73
6	1	2	3	3	1	1	2	2	40.28
7	1	3	1	2	1	3	2	3	52.20
8	1	3	2	3	2	1	3	1	53.41
9	1	3	3	1	3	2	1	2	68.0
10	2	1	1	3	3	2	2	1	70.01
11	2	1	2	1	1	3	3	2	74.40
12	2	1	3	2	2	1	1	3	74.76
13	2	2	1	2	3	1	3	2	79.73
14	2	2	2	3	1	2	1	3	83.57
15	2	2	3	1	2	3	2	1	83.63
16	2	3	1	3	2	3	1	2	83.69
17	2	3	2	1	3	1	2	3	83.72
18	2	3	3	2	1	2	3	1	83.77

Table: 2 Taguchi L18 OA for Percent Yield of Polypyrrole Salt

Conducting the matrix experiment:

Synthesis of high yield polypyrrole through inverted emulsion polymerization technique:

To a 250 ml Erlenmeyer flask was charged a mixture of methanesulfonic acid dopant (4 ml, 5.92 g, 61.5 mmol) and water (20 ml). Pyrrole monomer (1.2 ml, 1.16 g, 17.2 mmol) dispersed in water (30 ml) was added to the above mixture and constantly stirred at 20^0C. Sodium lauryl sulfate surfactant (1.0 g, 3.46 mmol) dispersed in water (20 ml) and Potassium persulfate initiator (3.0 g, 11 mmol) dispersed in Chloroform (30 ml) were added drop wise to the stirring reaction mixture. The reaction mixture was allowed to stir constantly for a 1 hour duration after which it was poured in acetone to precipitate the black colored polymer. The polymer was washed with water, dried in an oven at 100^0C, and weighed until a constant weight was maintained.

III. Results and Analysis of Experiments:

A. Regression Analysis

The concentrations of Monomer, Surfactant, Oxidant, Dopant, variations in Stirring times and Temperature were considered in the development of mathematical models for the percent yield of polypyrrole salt. The correlation between factors (Monomer, Surfactant, Oxidant, Dopant, Stirring Times and Temperature) and the percent yield of polypyrrole salt were obtained by multiple regressions.

The standard commercial statistical software package MINITAB was used to derive the models of the form:

Percent Yield (%) = 13.2 + 10.6 Monomer Concentration (ml)

$R^2 = 0.988$

In multiple regression analysis, R^2 is the regression coefficient ($R^2 > 0.90$) for the models, which indicate that the fit of the experimental data is satisfactory.

B. Analysis of the S/N Ratio

Taguchi method stresses the importance of studying the response variation using the signal-to-noise (S/N) ratio, resulting in minimization of quality characteristic variation due to uncontrollable parameter. The percent yield of polypyrrole salt was considered as the quality characteristic with the concept of "the larger-the-better". The S/N ratio used for this type response is given by:

The S/N ratio for the larger-the-better is :

S/N = -10 *log(mean square deviation) …………..(1)

$$S/N = -10\log_{10}\left(\frac{1}{n}\Sigma\frac{1}{y2}\right) \qquad \text{……………………..(2)}$$

Where n is the number of measurements in a trial/row, in this case, n = 1 and y is the measured value in a run/row. The S/N ratio values are calculated by taking into consideration equation (2). The percent yield values of the polypyrrole salt measured from the experiments and their corresponding S/N ratio values are listed in Table 3. The percent yield table for the concentrations of monomer, surfactant, oxidant and the variation in stirring times and temperatures was created in the integrated manner and the results are given in Table 4.

Exp. No.	Percent Yield (%)	S/N ratio (dB)
1	10.64	0.1994
2	19.04	0.1125
3	21.14	0.1015
4	24.06	0.0893
5	33.73	0.0639
6	40.28	0.0535
7	52.20	0.0414
8	53.41	0.0404
9	68.0	0.0318
10	70.01	0.0309
11	74.40	0.0290
12	74.76	0.0289
13	79.73	0.0271
14	83.57	0.0259
15	83.63	0.0258
16	83.69	0.0258
17	83.72	0.0258
18	83.77	0.0258

Table:3 Percent Yield and S/N ratio values for experiments

Level	Monomer Concentration	Surfactant Concentration	Oxidant Concentration	Dopant Concentration	Temperature Range	Stirring Time
1	-0.96	-3.0	-0.96	-0.26	-0.01	-3.01
2	-0.26	-0.96	-0.26	-0.11	-0.004	-0.45
3	-0.17	-0.45	-0.11	-0.06	-0.002	0.26

Table:4 S/N ratio values for percent yield by factor level

Regardless of the category of the performance characteristics, a greater S/N ratio value corresponds to a better performance. Hence, the optimal level of the percent yield is the level with the greatest S/N ratio value. Based on the analysis of S/N ratio, the optimal percent yield of 83.77% was obtained at Monomer concentration of 2 ml, Surfactant concentration of 1 ml, Oxidant concentration of 2 ml, Dopant concentration 4 ml, Temperature 20^{0}C, and Stirring Time 1 hour, (Level 1). Figure:2 shows the effect of process parameters on the percent yield values.

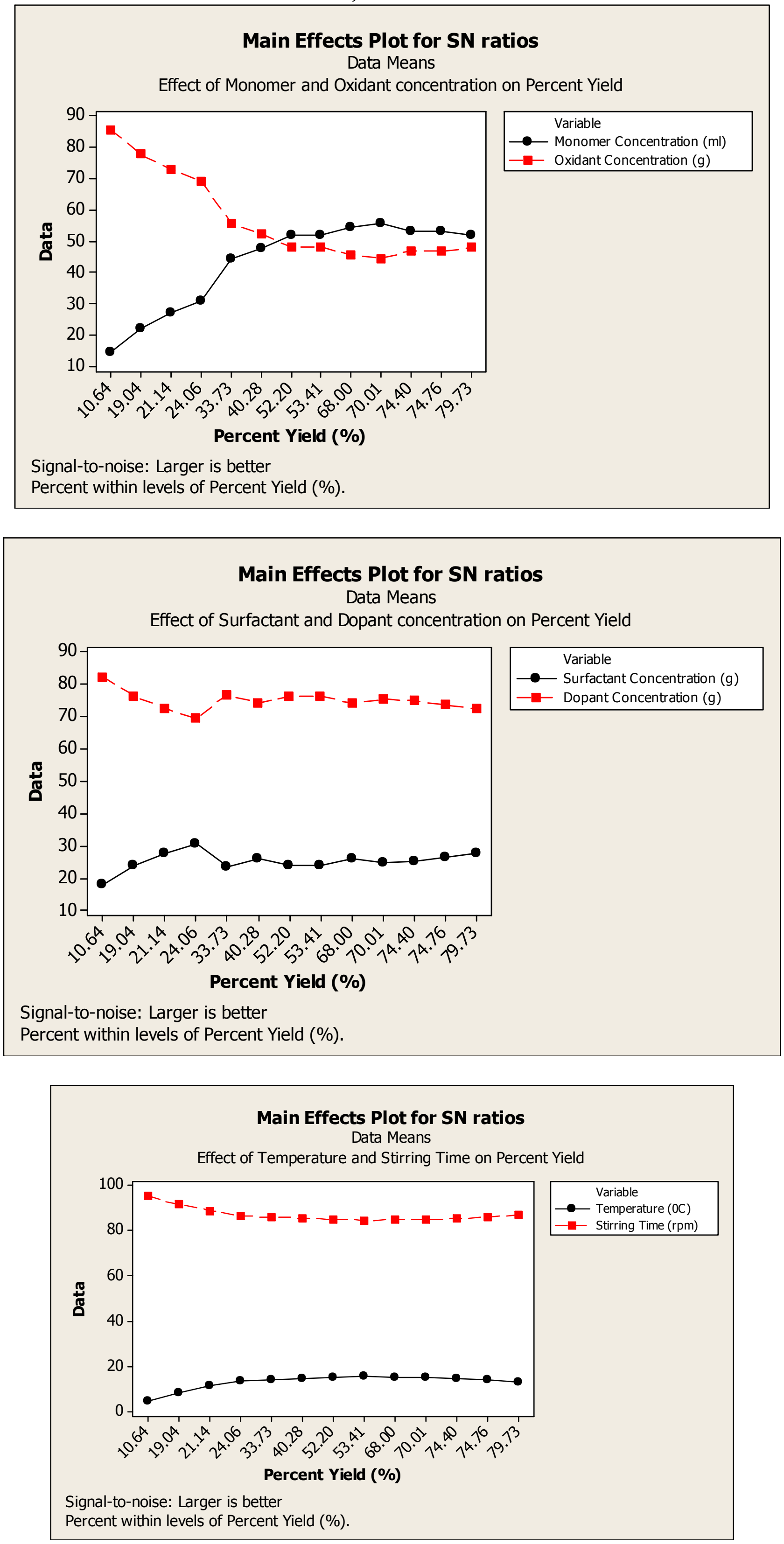

Figure: 2 Effect of process parameters on percent yield of polypyrrole

The percent yield increases with the increasing concentrations of monomer, surfactant, oxidant and dopant. However, it can be seen from the graphs that with the increasing monomer and surfactant concentration, there is a steady increase in the percent yield of polypyrrole. This may be due to the increasing monomer chains on the polymer backbone, and kinetic effects were favoured in the polymerization process by inverted emulsion polymerization technique.

IV. Discussion

Analysis of Variance (ANOVA)

ANOVA is a statistical, objective decision making tool for detecting any differences in the average performance of groups of items tested. ANOVA tests the significance of all the main factors and their interactions by comparing the mean square against an estimate of the experimental factors at specific confidence levels. ANOVA estimates 3 sample variances: a total variance based on all the observation deviations from the grand mean, an error variance based on all the observation deviations from their appropriate treatment means and a treatment variance. The treatment variance is based on the deviations of treatment means from the grand mean, the result being multiplied by the number of observations in each treatment to account for the difference between the variance of observations and the variance of means.

The fundamental technique is a partitioning of the total sum of squares *SS* into components related to the effects used in the model. For example, the model for a simplified ANOVA with one type of treatment at different levels.

$SS_{Total} = SS_{Error} + SS_{Treatments}$

The percentage contribution P can be calculated as:

$P = SS_d/SS_T$, where SS_d = the sum of the squared deviations. The one way ANOVA results are shown in the following form:

Source	DF	SS	MS	F	P
Factor	3	260554	86851	76.44	0.000
Error	48	54536	1136		
Total	51	315089			

S = 33.71 R-Sq = 82.69% R-Sq(adj) = 81.61%

Level	N	Mean	StDev
Stirring Time (rpm)	13	176.15	62.79
Percent Yield (%)	13	47.80	24.40
Monomer Conc.(ml)	13	3.27	2.25
Oxidant Conc. (g)	13	3.38	1.42

Pooled StDev = 33.71

One way ANOVA compares means of two or more samples in which samples in two or more groups are drawn from populations with the same mean values. The one way ANOVA results show the standard deviation for stirring time at 62.79 and the standard deviation of percent yield at that deviation of stirring time was found to be 24.40 which was maximum at any level.

Statistically, there is a tool called an F-test which indicates which design parameters have a significant effect on the quality characteristic.

In this analysis, Factor 3, i.e., oxidant concentration was shown to have a significant impact on the percent yield of polypyrrole salt with an F value of 76.44. As the oxidant concentration increases, the percent yield of polypyrrole was also found to increase.

In recent years, emulsion polymerization and micro-emulsion polymerization techniques have acquired significant importance in the preparation of polypyrrole, Saravanan et.al. (2006), Helmers (1973), and Karambelkar et.al. (2011) . These techniques offer several advantages over conventional synthesis methods. For example, the polymerization process is easy to control due to physical state of the emulsion system, thermal and viscosity problems are less significant, high reaction rates can be achieved and the product obtained can be utilized without further purification.

Polypyrrole is usually prepared employing electrochemical and chemical-oxidative polymerization techniques using water soluble oxidizing agents, Chen et.al.(1992). However, inverted emulsion polymerization technique which employs oil soluble oxidizing agents, offers several distinct advantages like high yield of the polymer with respect to the monomer used, high electrical conductivity and reduced reaction duration, Karambelkar et.al. (2011).

Attempts have been made to synthesize high conducting polypyrroles using benzoyl peroxide as a novel oxidizing agent, Saravanan et.al.(2006). In the research presented herein, synthesis of polypyrrole salt using methanesulfonic acid as a novel dopant employing inverted emulsion polymerization technique has been successfully accomplished with a very high percentage yield (83.77%), with respect to the amount of monomer used and significantly reducing the reaction time, Karambelkar et.al.(2011) (one hour and ten minutes) avoiding toxic and hazardous chemicals with a relatively pure polypyrrole salt.

V. Conclusions

Synthesis of polypyrrole salt was successfully accomplished through Taguchi technique of robust experimental design. Polypyrrole salt was obtained in a very high percentage yield with respect to the amount of monomer used (83.77%) using inverted emulsion polymerization technique.

Optimum control parameters were fixed and polymerization reaction was carried out by varying various control factors to obtain high yielding polypyrrole salt. Polymer chemists working with conducting polymer synthesis may find this method more useful should they have more than five experimental parameters to vary. Inverted emulsion polymerization reaction is useful to synthesize fused five membered heterocyclic rings which are otherwise difficult to synthesize and process. Synthesis of conducting polymers through this innovative method and applying the principles of Taguchi method would ensure error free experimentation and would help to set up optimum control parameters by reducing variation.

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