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Optimization of the Conductivity and Yield of Chemically Synthesized Polyaniline Using a Design of Experiments

E. Johny Jelmy, S. Ramakrishnan, Sriram Devanathan, Murali Rangarajan, Nikhil K. Kothurkar
Department of Chemical Engineering and Materials Science, Amrita Vishwa Vidyapeetham, Coimbatore 641112, Tamil Nadu, India
Correspondence to: N. K. Kothurkar (E-mail: nikhil.kothurkar@gmail.com).

ABSTRACT: The electrical conductivity and yield of polyaniline (PANi) were optimized using a design of experiments (DOE). PANi samples were synthesized by the chemical oxidative polymerization of aniline using methane sulfonic acid as the dopant acid and ammonium persulfate as the oxidant. The main factors in the synthesis of PANi that can affect the conductivity were identified as (i) the concentration of dopant acid, (ii) oxidant-to-monomer ratio, and (iii) the addition rate of oxidant to monomer. Using a Box-Behnken DOE method the regression equation, main effects plots, contour plots, and optimization plots for conductivity and yield were generated and analyzed. Under the optimized conditions of dopant acid concentration of 0.9*M*, an oxidant addition rate of 30 mL/h and an OM ratio of 0.9, PANi with a conductivity of 1.95 S/cm and yield of 95% was obtained. The observed trends in the four-point probe conductivity measurements were correlated with the polymer structure using fourier transform infrared spectroscopy, X-ray diffraction studies, and scanning electron microscopy. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1047–1057, 2013

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INTRODUCTION

Intrinsically conducting polymers are a special class of polymers, which can conduct electricity without the presence of any external agents. Among them, polyaniline (PANi) is interesting for many reasons such as low monomer cost, a wide range of applications, simple polymerization methods, and a high yield of the polymerization product,[1] and particularly, for its readily tunable properties like electrical conductivity, molecular weight, etc. The electrical conductivity of PANi is relevant for a variety of applications such as in rechargeable batteries, electromagnetic shielding, and microwave absorption. PANi is also used in light-emitting diodes, chemical sensors, electrochromic displays, anodic passivation, corrosion prevention of metals, and electromechanical devices.[2]

Out of the several methods for the synthesis of PANi, the easiest method is the chemical oxidative polymerization of aniline. The electrical conductivity of PANi made by this method depends on many factors including the dopant acid concentration, oxidant-to-monomer ratio (OM ratio), rate of addition of the oxidant to the monomer, temperature of the reaction medium, nature of dopant acids, purity of monomer, and polymerization time.[3–5] Hence, there is a need to optimize the synthesis conditions for maximizing electrical conductivity. While several studies have been done to study the effects of the reaction conditions in improving the conductivity and yield of PANi[3,5,6] there has not been any systematic statistical study of the same. Hence, it is not possible to quantitatively judge the effects of these factors on conductivity or yield or determine the interaction effects. Several such optimization studies using design of experiments (DOE) have been done in many fields.[5,7–9] Hence, a similar study for PANi will be of much relevance.

A study of the literature was conducted in order to determine the most dominant factors affecting the electrical conductivity of PANi. The dopant acid concentration was found to be an important factor and a concentration in the range of 0.5–3*M* was found to yield a polymer with good conductivity. Higher concentrations can disrupt the extended conjugated structure of PANi leading to the reduction in electrical conductivity, while at lower concentrations the formation of nonconducting oligomers may result in reduction in conductivity.[3,6,10,11] Other studies have revealed the effect of the OM ratio on the conductivity of PANi.[4,12] An OM ratio close to 1 can give PANi with good electrical conductivity and yield. Higher OM ratios can lead to over-oxidation of the formed PANi and this can reduce the conductivity and yield of PANi. The rate of addition of the oxidant to the monomer was also found to affect the final

Additional Supporting Information may be found in the online version of this article.

Table I. Levels of Parameters Chosen in the Design of Experiments

Variables	Different levels in Box–Behnken design		
Coded levels	Low (−1)	Middle (0)	High (1)
Dopant concentration, M	0.3	1.05	1.8
OM ratio	0.1	0.8	1.5
Rate of addition (mL/h)	10	30	50

properties of PANi.[13,14] Cao et al. have reported that fast addition rates of the oxidant leads to an overall fine granular morphology of the polymer while a slow addition of the oxidant leads to a coarser morphology.[6] This may be because at higher addition rates, the numbers of nucleation sites are high and this might lead to the formation of smaller aggregates.[15] Since, coral-like morphology with elongated structures can give better conductivity than loose flake-like structures for PANi,[16] the slow addition of the oxidant to the reaction mixture is preferred. Conductivity in PANi is expected to increase with molecular weight due to better interchain and intrachain electron transfer in high molecular weight products. However, several researchers were unable to find a correlation between conductivity and molecular weight.[13,17,18] Cao et al. have reported that yield and electrical conductivity are independent of polymerization temperature at temperatures below 0°C, while synthesis at higher temperatures can lead to greater defects and consequently, poorer conductivity.[6] Hence, a polymerization temperature between 0 and −5°C is suitable for synthesizing defect-free PANi. Studies done by varying the polymerization time revealed that obtaining good electrical conductivity required a polymerization time of 20–24 h.[6]

On the basis of the above discussion and some preliminary experiments, the dopant concentration, OM ratio, and the rate of addition of the oxidant to the monomer were found to be important factors influencing the electrical conductivity and yield of PANi. A statistical DOE was planned to study the effects of these three factors on the electrical conductivity and yield of PANi. The other factors like temperature of reaction medium, polymerization time, nature of the dopant acid, type of oxidant were kept constant in this study. Statistical DOE is a systematic and efficient approach for investigation of a system or process. A series of experiments are designed in which planned changes are made to the input variables of a process or system. The effects of these changes on predefined output are then assessed. DOE is important as a formal way of maximizing useful information obtained regarding underlying relationships between numbers of experiments, thus obtaining maximum understanding of the effects of a set of input variables on the process or outcome of interest.

EXPERIMENTAL

Materials Required

Aniline and ammonium persulfate $(NH_4)_2S_2O_8$ (APS) were procured from Merck (Lab grade). Methanesulfonic acid (MSA) was received from Loba Chemie, Mumbai India. Aniline was distilled under reduced pressure and stored below 4°C. All other reagents were used as received.

Preparation of PANi by Chemical Oxidative Polymerization

PANi was synthesized by the chemical oxidative method as described by Stephen et al.[14] polymerization of aniline was carried out in the presence of an oxidizing agent (APS) in an aqueous medium of dopant acid (MSA). In a two-necked round bottom (RB) flask, distilled aniline (about 5.00 ± 0.01 g) was dissolved in 250 mL of an aqueous solution of a prepared concentration of MSA and was placed inside the cryostat, which was maintained at a temperature of −5°C. The reaction mixture was constantly stirred with a mechanical stirrer. The oxidant (1*M*) was added to the aniline-dopant mixture using a syringe pump at the required flow rate. After constant stirring for 24 h, the formed polymer was vacuum filtered and was washed with 250 mL of same concentration of MSA to remove the unreacted oligomers and monomers. The residue remaining on the filter paper was then dried at 60°C for 24 h to obtain a dark greenish PANi powder. The ranges of the selected parameters and the details of the different experiments are described in Tables I and II.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet, iS10 FTIR spectrometer using KBr pellets in the range of 500–4000 cm^{-1}. A multipoint base line correction was made for all the FTIR spectra and the corrected peak areas were determined using OMNIC 8.1 software. The ratios of peak areas of quinoid to benzoid peaks (A_Q/A_B) for different samples were calculated and analyzed. The morphology of PANi samples were examined using a JEOL JSM-5600 LV field emission scanning electron microscope (FE-SEM). For the conductivity measurements, pellets of 13 mm diameter and ~3 mm thickness were prepared using a hydraulic press (6 ton force for 2 min). Conductivity measurements were made on the pellets (2 replicates) using a four-point probe with a DC and AC current source (Model 6221) and a nanovoltmeter (Model 2182A) from

Table II. The Experimental Design and the Responses Obtained

Run order	Dopant concentration (M)	Rate of addition (mL/h)	OM ratio	Conductivity × 10^{-2} (S/cm)	Yield (%)
1	0.30	10	0.8	11.206	86
2	0.30	30	1.5	15.038	94
3	0.30	50	0.8	1.368	90
4	1.05	50	0.1	0.151	32
5	1.05	10	1.5	1.911	89
6	1.05	30	0.8	153.344	91
7	1.05	30	0.8	253.453	92
8	1.05	50	1.5	6.632	63
9	1.80	10	0.8	0.051	51
10	1.80	50	0.8	0.038	50
11	1.80	30	1.5	0.012	43
12	1.05	30	0.8	191.098	87
13	0.30	30	0.1	0.883	55
14	1.05	10	0.1	0.709	32
15	1.80	30	0.1	0.007	30

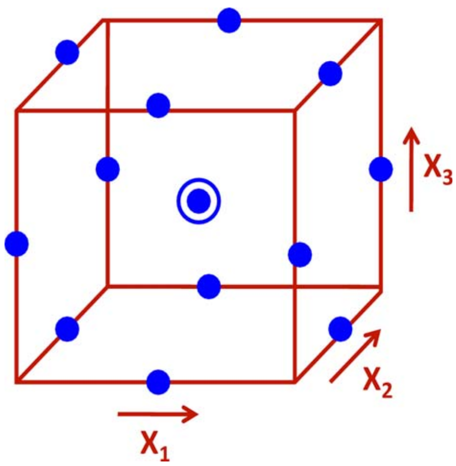

Figure 1. Geometry of the Box-Behnken design for a three variable system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Keithley Instruments. Crystalline structural characterization of PANi samples was performed using X-ray diffraction (XRD) (Brucker AXD D8 Advance, Vertical Configuration) using Cu Kα1 radiation ($\lambda = 1.54056$ Å). The 2θ versus Intensity count data was plotted using Origin 6.1. The Gaussian fits for multiple peaks was carried out to obtain areas of different peaks. The percentage of crystallinity of the samples was estimated from the ratio of crystalline peak area to total peak area.[19]

Experimental Design

A Box–Behnken design was used for the optimization of conductivity and yield for PANi. In a Box–Behnken design each factor is set at one of three equally space values. The treatment combinations are at the mid-point of edges of the process space (visualized as a cube), and at the centre (Figure 1). As such both the Center Composite design and Box–Behnken design allow for modeling quadratic relationship in the data. However, the Box–Behnken design has fewer experiments run for the three factor experiments, and has the added advantage of avoiding simultaneous extremely high or extremely low values of the factors involved. In this study, we have also chosen three replicates for the centre point in order to obtain an adequate estimate of the experimental error. Therefore in the present study, a three-factor, three-level experimental design was used in order to investigate the effect of synthesis parameters on the responses of the formed PANi. In this design, the model relating the response Y to the input parameters X_1, X_2, X_3 is as follows:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1X_2 + a_5X_2X_3 + a_6X_1X_3 + a_7X_1{}^2 + a_8X_2{}^2 + a_9X_3{}^2 + \varepsilon,$$

where a_1, a_3, a_2 are the linear coefficients; a_4, a_5, a_6 are the interaction coefficients; a_7, a_8, a_9 quadratic coefficients and ε is the error term. The factor levels were coded as 1 (for high), 0 (middle), and -1 (low). The regression analysis, analysis of variance (ANOVA), response surface, contour plots and optimizations plots were generated using the statistical software MINITAB 15. The input parameters selected and their ranges are shown in Table I.

RESULTS AND DISCUSSIONS

Optimization Analysis Using Box–Behnken Design

Response Surface Regression Analysis. The experimental runs and the corresponding responses in the Box–Behnken design are given in Table II. The conductivity values reported is the average of four conductivity measurements. The regression equation obtained for conductivity was,

$$Y_1 = -3.3703 + 3.5862X_1 + 0.1454X_2 + 3.2819X_3 - 1.7279X_1{}^2 - 0.0025X_2{}^2 - 2.0003X_3{}^2 + 0.0016X_1X_2 - 0.0674X_1X_3 + 0.0009X_2X_3$$

The equation represents the effect of three selected parameters—dopant concentration (X_1), rate of addition (X_2), OM ratio (X_3), and their interactions, on the conductivity of PANi. The positive sign for the coefficients shows the synergistic effect while the negative sign shows an antagonistic effect. From this equation we can see the direct relationship of each parameter on the response, namely conductivity. The fitness of the model was further analyzed by the value of coefficient of determination, R^2 and adjusted R^2. Since the objective of the experiment is for optimization, the higher R-squared values are favorable and indicate that the model is a good predictor of the responses. R^2 adjusted adjusts the number of explanatory terms in a model. Unlike R^2, the adjusted R^2 increases only if the new term improves the model more than would be expected by chance. The adjusted R^2 can be negative, and will always be less than or equal to R^2. The value of R^2 was calculated to be 94.7% (and that of R^2 adjusted value was 85.2%). This indicates that around 5% of variability in the conductivity cannot be predicted by the model. Furthermore, the significance of the effect of each parameter on a response can be analyzed using the corresponding P-value. The values calculated for the coefficients and their corresponding P-values are given in Table III.

The smaller the P-value (at the chosen level of significance $\alpha = 0.1$), greater the confidence in the significance of the parameter with respect to its effect on the final property of the polymer. Accordingly, the linear terms namely dopant concentration, rate of addition, OM ratio, and the quadratic terms namely dopant concentration × dopant concentration, rate of addition × rate of addition, OM ratio × OM ratio were the most significant factors towards the conductivity of PANi. At the chosen level of significance, the interaction factors did not have a significant effect on the conductivity as their P-values were higher than 0.1. These factors indicate that the quadratic model is significant and thus can be used for further analysis. The final regression equation for conductivity containing only the statistically significant terms is as follows:

$$Y_1 = -3.3703 + 3.5862X_1 + 0.1454X_2 + 3.2819X_3 - 1.7279X_1{}^2 - 0.0025X_2{}^2 - 2.0003X_3{}^2$$

The regression equation for yield is given below,

Table III. Regression Analysis for Conductivity of PANi

Term	Coefficients	*P*-value	Remarks
Constant	−3.3703	0.005	Significant
Dopant concentration	3.5862	0.005	Significant
Rate of addition	0.1454	0.004	Significant
OM ratio	3.2819	0.007	Significant
Dopant concentration × Dopant concentration	−1.7279	0.002	Significant
Rate of addition × Rate of addition	−0.0025	0.002	Significant
OM ratio × OM ratio	−2.0003	0.002	Significant
Dopant concentration × Rate of addition	0.0016	0.885	Not significant
Dopant concentration × OM ratio	0.0674	0.835	Not significant
Rate of addition × OM ratio	0.0009	0.938	Not significant

$$Y_2=0.18+23.17X_1+1.98X_2+133.15X_3-17.11X_1^2-0.03X_2^2-50.76X_3^2-0.08X_1X_2-12.38X_1X_3-0.46X_2X_3$$

The equation represents the effect of three selected parameters—dopant concentration (X_1), rate of addition (X_2), OM ratio (X_3)—and their interactions on the yield of PANi. From this equation we can see the synergic effect of the selected parameter on yield. As in the previous case, the fitness of the model was further analyzed by the value of the coefficient of determination, R^2, and adjusted R^2. The value of R^2 was calculated to be 96.80% (and that of R^2 adjusted value was 91.03%). This indicates that only around 3% of the variability in yield cannot be predicted by the model. The factors, the values calculated for the coefficients, their corresponding *P*-values and their significance on yield are given in Table IV. Note that the *P*-value for dopant concentration is greater than 0.1, but it cannot be dropped from the model since the quadratic term for dopant concentration is statistically significant (with a *P*-value <0.1). It may be noted that all the interaction terms have *P*-value greater than 0.1, and therefore are not statistically significant. The final regression equation for yield containing only the significant coefficients is as follows

Table IV. Regression Analysis for Yield of PANi

Term	Coefficients	*P*-value	Remarks
Constant	0.18	0.992	Not significant
Dopant concentration	23.17	0.248	Not significant
Rate of addition	1.98	0.035	Significant
OM ratio	133.15	0.001	Significant
Dopant concentration × Dopant concentration	−17.11	0.057	Significant
Rate of addition × Rate of addition	−0.03	0.036	Significant
OM ratio × OM ratio	−50.76	0.001	Significant
Dopant concentration × Rate of addition	−0.08	0.752	Not significant
Dopant concentration × OM ratio	−12.38	0.144	Not significant
Rate of addition × OM ratio	−0.46	0.144	Not significant

$$Y_2=0.18+23.17X_1+1.98X_2+133.15X_3-17.11X_1^2-0.03X_2^2-50.76X_3^2$$

Main Effect Plots. Inferences on the relationships between the factors and the responses may generally be drawn using the main effect plots or the interaction plots. However, the analysis shows that the interaction effects are not significant for either of the responses (conductivity and yield). Hence, main effect plots are used to relate the dopant concentration, monomer addition rate, and oxidant-to-monomer ratio with the conductivity and yield of PANi. Figure 2 shows the main effect plots for yield and conductivity of PANi. It can be observed from the plots that the midpoints of the selected ranges of the three factors (dopant concentration, OM ratio, and rate of addition)

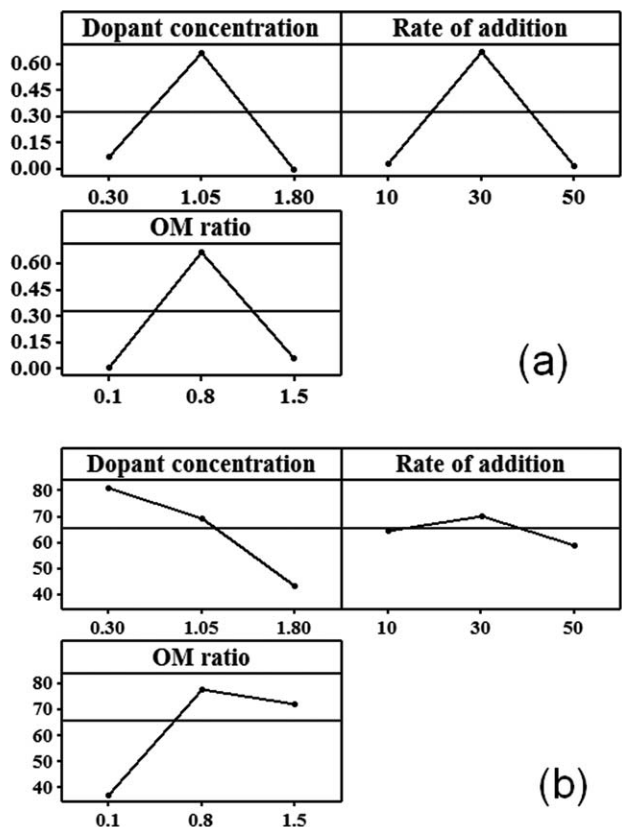

Figure 2. Main effect plots for the (a) conductivity and (b) yield.

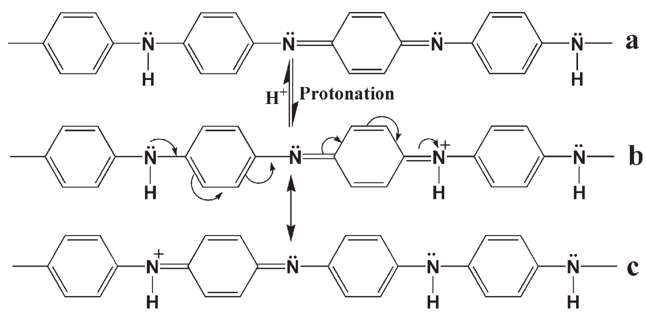

Figure 3. Protonation of polyaniline (emeraldine form).

lead to PANi with the highest conductivity. The concentration of the dopant acid affects the degree of protonation of the polymer, which may in turn affect the electronic conjugation and the electrical conductivity. The protonation of the polymer (a) and the corresponding resonance forms (b and c) are shown in Figure 3. Sengupta and Adhikari have reported that at high dopant acid concentration, the charge localization due to very high amine protonation can lead to molecular association (hydrogen bond formation), which in turn leads to the precipitation of nonconducting oligomers.[10] On the other hand Sapurina and Stejskal have reported that the oxidation of aniline in mildly acidic,[11] neutral or even alkaline media (low dopant acid concentration) yields nonconducting oligomers as the major components of the products.[11] In such media, the level of protonation is very low, thereby the molecules have much lower electronic conjugation. Thus, we can expect the PANi product to have low conductivity at both high and low levels of dopant acid concentrations, due to improper protonation, and high conductivity at intermediate dopant acid concentrations. According to our main effects plots, an intermediate dopant acid concentration ($\sim$1*M*) was found to give a product with high conductivity.

Increasing the amount of oxidant (APS) leads to the formation of more radical cations, which increases the rate of the chemical oxidative polymerization of aniline. Reports reveal that an OM ratio higher than 1.15 may lead to the over-oxidation of PANi.[5,12,20] In the initial stage of the polymerization dimers are formed via the formation of the nitrenium cation and the subsequent propagation happens by a redox process between the growing chain and the aniline monomer.[21] An increased concentration of oxidant will lead to the formation of fully oxidized pernigraniline salt (low conductivity) instead of the partially oxidized emeraldine salt (high conductivity). At very low OM ratio, the oxidant is insufficient to yield the emeraldine form of the polymer. The observed variation in conductivity with OM ratio is in good agreement with the reported results. The main effects plots indicate that an intermediate OM ratio ($\sim$0.8) would be close to the optimum.

The rate of addition of the oxidant to the monomer can also affect the electrical conductivity of PANi. At a higher rate of oxidant addition, the instantaneous concentration of unreacted oxidant in the reaction mixture is high. This can lead to the formation of the pernigraniline form of PANi. The protonated pernigraniline is unstable and, especially in the presence of excess oxidizing agent, it converts into colorless low-molecular-weight oxidation products (1,4-benzoquinone or its derivatives), typically within 10s of minutes in dilute PANi dispersions.[22] This could be the reason for the low conductivity at higher rates of addition of the oxidant. At a very slow addition rate, Cao et al. observed a reduction in inherent viscosity,[6] and this may be due to the formation of small chain dimers and oligomers because of insufficient supply of oxidant, which in turn results in lower conductivity. At moderate rates of addition of the oxidant, PANi in the emeraldine salt form with a well-ordered morphology is formed and it shows high conductivity. A further discussion on the role of morphology is given below.

The main effect plots for the final yield of PANi reveal the importance of the dopant concentration and the OM ratio. The yield was found to decrease with increasing dopant concentration. The reduction in yield at higher concentrations of the dopant acid could be due to the increased hydrolysis rate of poly-emeraldine.[6] With an increasing OM ratio, the yield of PANi increased linearly up to an OM ratio of $\sim$0.9 and then started to decrease. The reduction of yield at higher OM ratio could be due to the formation of soluble oligomers at high concentration of APS. These soluble oligomers would be lost with the washing of the precipitated product and hence would not contribute to the measured yield. The effect of the rate of addition of the oxidant on the yield was found to be very low.

It may be noted that both conductivity and yield reach their maximum values when the factors—dopant concentration, oxidant-to-monomer ratio, and addition rate of oxidant—are at an intermediate value. This is consistent with the presence of quadratic terms for all three factors in the statistical models for both responses.

Response Surface Plots and Contour Plots. Response surface plots, such as contour and surface plots are three-dimensional plots showing the nature of variation of the responses with the selected parameters. These were generated using MINITAB 15. The model contains three factors and the plots can only accommodate two factors and a response. Therefore, one factor is kept constant, and the response was plotted against the other two. Figure 4 shows the response surface diagram for conductivity. The response surface plot for yield is shown in Figure 5. Contour plots were generated to identify the optimized region of responses. The contour plots are two-dimensional graphs drawn for any two out of three parameters, with the third one being kept constant. This is a series of curves that identify different combinations of variables for which the response is constant. Such diagrams illustrate the change in properties when two or more variables vary together and allow predictions to be made for factorial combinations not actually run in the experiment.[23] The regions of maximum response are indicated by the dark colored circles. The contour plot for conductivity and yield are shown in Figures 6 and 7. From these graphs it may be seen that, a rate of addition of 30 mL/h, a dopant concentration of 09*M* and an OM ratio of 0.9 can lead to a PANi product with a conductivity greater than 1.95 S/cm. Likewise, the maximum yield of 95% was obtained at a dopant concentration below 0.6*M* and at an intermediate OM ratio (1–1.5). The rate of

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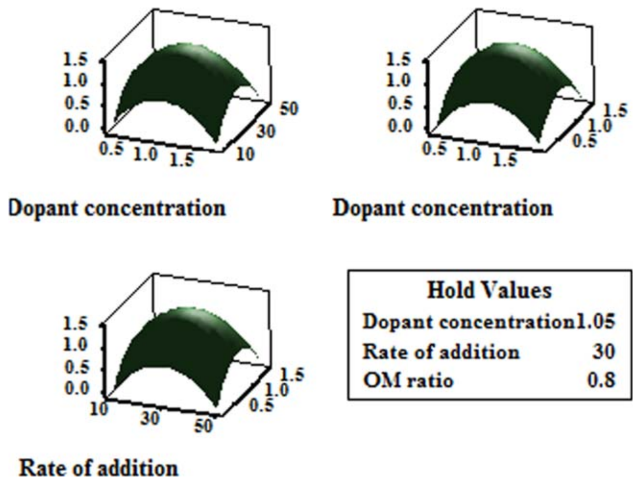

Figure 4. Surface plot for conductivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition does not appear to have any major effect on the yield in the selected range of the factor. For the further analysis, contours and surface plots were drawn for various combinations of the factorial levels chosen in this study.

Overlaid Contour Plots. The contour plots for conductivity and yield were overlaid in order to find out the desirable regions for the two properties. The overlaid portion is the white region in Figure 8. The desired values of all the selected responses can be obtained at any given factorial combination within the optimized region. The plots were overlaid at three different levels of rate of addition.

Validation Experiments. Confirmatory experiments were carried out for the validation of the model. The parameter values selected were not the part of the original experimental design, but were included in the selected experimental region. The three data points selected for the validation experiments were within the selected experimental region but were different from the 15 data points that were part of the design. One of the data points was the optimum as predicted by the model (0.9*M*, 29.8 mL/h, 0.9). The other two data points selected were ±30% from this optimal point, i.e. (0.6*M*, 20.8 mL/h, 0.6) and (1.2*M*, 38.8 mL/h, 1.2). The predicted, observed and the % deviation of conductivity and yield from the actual are given in Table V. The observed values are in good agreement with predicted values and this confirms the adequacy of the selected model and property evaluation.

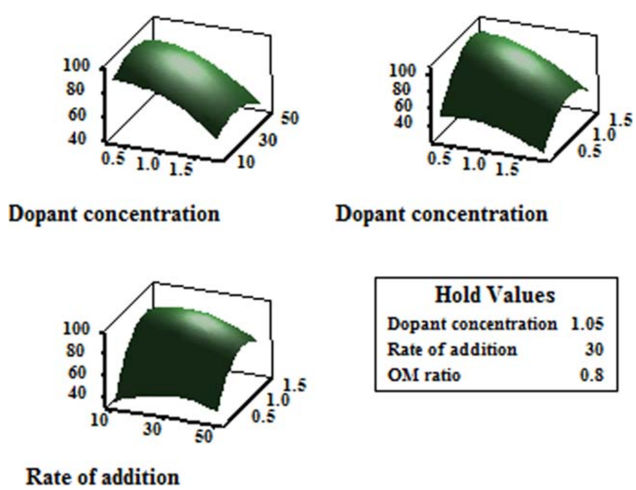

Figure 5. Surface plot for yield. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Optimized Plot for Conductivity and Yield. The optimum values for all parameters to maximize the properties were found out using MINITAB 15. The plot describing the optimal values of all parameters is shown in Figure 9. The "high" and "low" in the plot shows the highest and lowest value within the experimental domain. The desirability of final responses was specified

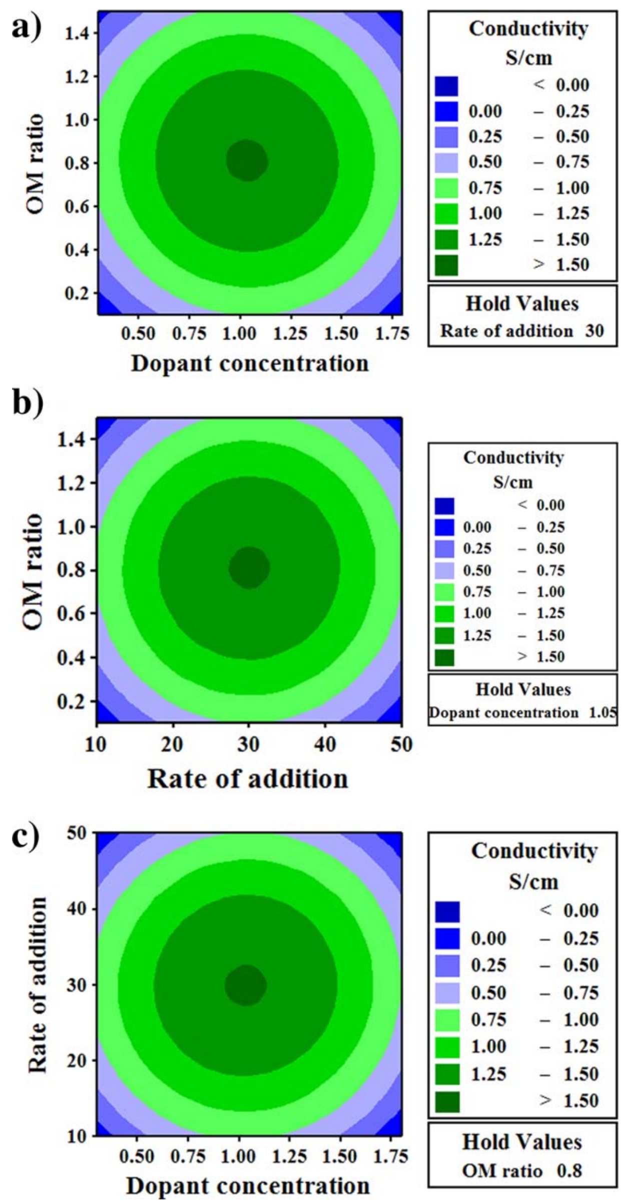

Figure 6. Contour plots for the conductivity at the hold values (a) rate of addition of 30 mL/h, (b) dopant concentration of 1.05*M*, and (c) OM ratio of 0.8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

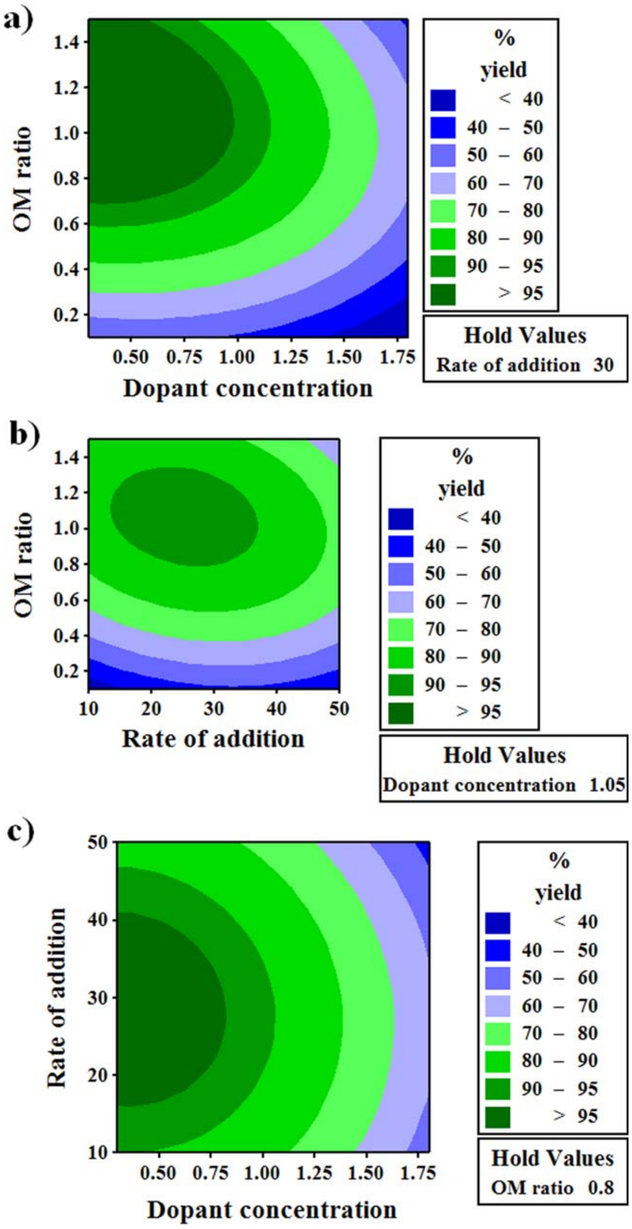

Figure 7. Contour plots for the yield at the hold values (a) rate of addition of 30 mL/h, (b) dopant concentration of 1.05*M*, and (c) OM ratio of 0.8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in MINITAB 15. Its value usually ranges from 0 to 1 and is reflective of the desired closeness between predicted responses and targets. Under the optimized conditions of dopant acid concentration of 0.9*M*, an oxidant addition rate of 30 mL/h and an OM ratio of 0.9, PANi with a conductivity of 1.95 S/cm and yield of 95% was obtained. Note that at this set of (optimal) conditions, the variation in the values of conductivity was significantly higher than the variation in conductivity for other conditions. This is attributed to a combination of measurement error and experimental error. It might be noted that the measurement of electrical conductivity of powder samples by making pellets and placing a four-point probe poses some challenges in getting a good contact. This could be an important contributor to the measurement error. However, the conductivity values for the optimal conditions are two orders of magnitude greater than those seen for any other experimental condition, and hence, the conclusions and inferences stated above are valid in spite of the high error at the center point. For a more detailed explanation of the variation and its probable causes, please see the Supporting Information.

FTIR Analysis

The molecular structure of PANi samples was analyzed using FTIR spectroscopy. The FTIR spectra of all samples have characteristic peaks around 1600 cm^{-1} (quinoid ring stretch),

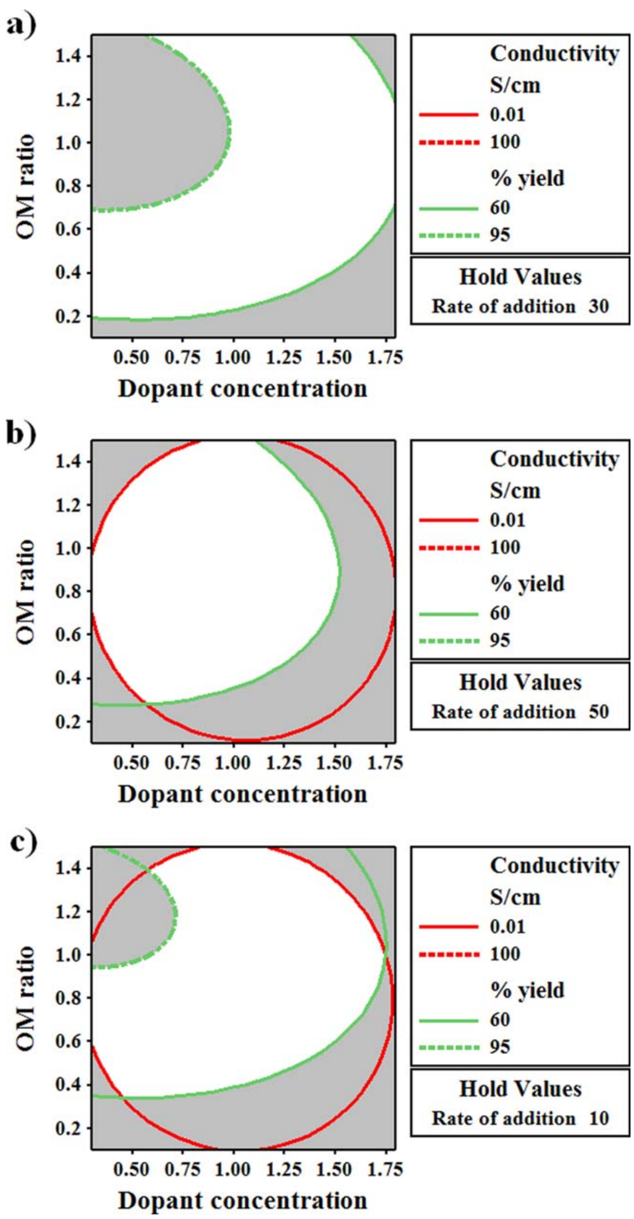

Figure 8. The overlaid contour plots for conductivity and yield at the hold values (a) rate of addition of 30 mL/h, (b) rate of addition of 50 mL/h, and (c) rate of addition of 10 mL/h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Applied Polymer Science

Table V. Comparison of Observed and Predicted Values for Verification Experiments of PANi

Conductivity (S/cm)			Yield (%)		
Predicted	Observed	Deviation (%)	Predicted	Observed	Deviation (%)
1.99	1.81	−9.04	95.43	98.8	3.53
1.39	1.22	−12.23	87.4	92.7	6.29
1.53	1.33	−13.07	81.5	85.3	4.58

1510 cm^{-1} (benzoid ring stretch), 1294 cm^{-1} (N—H bend), 1240 cm^{-1} (asymmetric C—N stretch), 1110 cm^{-1} (—NH^{+}= stretch), and 800 cm^{-1} (aromatic C—H ring bend). The peak around 800 cm^{-1} is characteristic of para-substituted aromatic ring, through which the polymerization is expected to progress. The broad peak around 3450 cm^{-1} is due to the presence of both the free N—H stretch and the O—H stretch from the polymer and the dopant acid, respectively.

Figure 10 shows the FTIR spectra of three representative samples with different electrical conductivities. Samples 11 and 4 have less conductivity as compared to sample 7. The peak areas of quinoid (A_Q), benzoid (A_B) and their relative ratios (A_Q/A_B) in different samples are given in Table VI. It was observed that samples made with an OM ratio of 0.8 have an A_Q/A_B ratio near unity indicating nearly equal amounts of quinoid and benzoid groups, e.g., Sample 7. Thus PANi in sample 7 is in the emeraldine salt form, which is known to have high conductivity. Samples with an OM ratio of 1.5 have an A_Q/A_B ratio > 5, e.g., Sample 11. This may be due to the over-oxidation of the polymer leading to a predominance of the low conductivity quinoid structure. Similarly, PANi synthesized using an OM ratio of 0.1 (Sample 4) showed an A_Q/A_B ratio <0.6 indicating the predominance of the low conductivity benzoid structure. Also, the

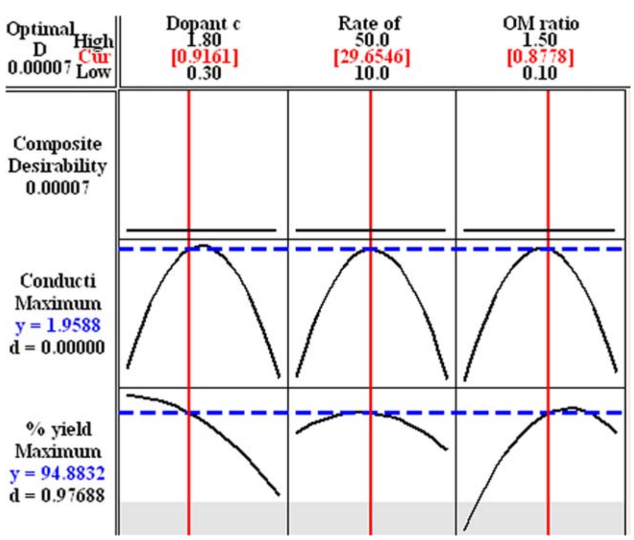

Figure 9. Optimized plot for conductivity and yield. "Cur" represents the current value (optimized value). These values are represented in brackets and in red. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

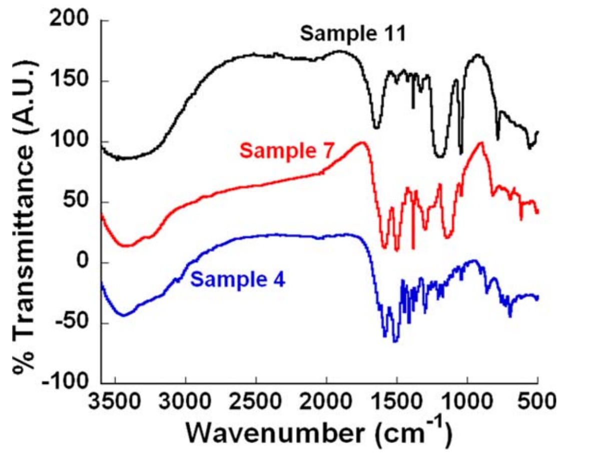

Figure 10. FTIR spectra of PANi samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intensity of the N—H stretching peak of PANi salt is a measure of polymer growth.[10] However, as the peaks of N—H and O—H stretch were overlapping, it was difficult to correlate the concentration of acid and the intensity of N—H stretch band.

XRD Analysis

The XRD plots of different PANi samples are shown in Figure 11 and other details are given in Table VII. The characteristic reflections of PANi were observed in the vicinity of 2θ values of 15°, 21°, and 25°, respectively. The peaks located at 2θ vales of 21° and 15° are the amorphous peaks while the peak at a 2θ value of 25° is the crystalline peak of PANi. In all the samples the crystalline peak at 25° was larger than the amorphous peaks. For samples which showed high conductivity (e.g., Sample 7), the peak at a 2θ value of 25° was higher in intensity than the samples, which showed low conductivity (Samples 4 and 15). Thus, there appears to be a dependence between crystallinity and conductivity of PANi.[19] The high intensity of the peak at a

Table VI. Ratios of Quinoid and Benzoid Forms in PANi

Sample	OM ratio	Peak area (*Q*)	Peak area (*B*)	*Q* : *B*
Sample1	0.8	20.68	10.99	1.9
Sample2	1.5	25.37	0.86	29.3
Sample3	0.8	25.82	24.97	1.0
Sample4	0.1	13.07	24.79	0.5
Sample5	1.5	17.89	1.49	12.0
Sample6	0.8	24.43	15.23	1.6
Sample7	0.8	22.12	15.04	1.5
Sample8	1.5	21.71	3.88	5.6
Sample9	0.8	6.12	6.51	0.9
Sample10	0.8	14.08	9.8	1.4
Sample11	1.5	40.49	1.89	21.4
Sample12	0.8	20.72	17.91	1.2
Sample13	0.1	3.35	5.44	0.6
Sample14	0.1	3.42	5.36	0.6
Sample15	0.1	11.49	18.28	0.6

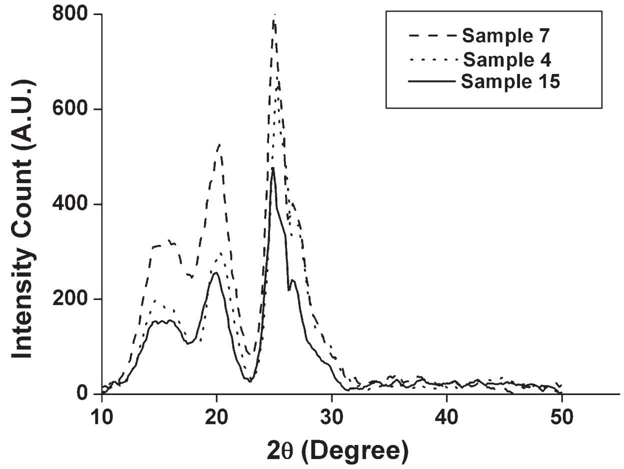

Figure 11. X-ray diffratograms of PANi samples.

2θ value of 25° indicates a more compact molecular arrangement in the sample, which can lead to good intramolecular electron transfer and intermolecular hopping of charge carriers and thus good electrical conductivity.[1,24]

Morphological Analysis

Figure 12 shows the scanning electron microscopy (SEM) images of PANi samples. The morphology of the formed polymers was analyzed in order find the effect of morphology on the electrical conductivity. SEM analysis was conducted for four different samples (Samples 2, 7, 9, and 15) with electrical conductivities of 15.03, 253.4, 0.05, and 0.007 S/m, respectively. This includes the samples with the highest and the lowest conductivities among all the 15 samples. Almost all samples possess either a compact coral-like or a loose flake-like structure. The coral-like morphology was observed for samples with high conductivity (Samples 2 and 7), while a loose flake-like structure was observed for the samples with low conductivity (Samples 9 and 15).

Huang and Kaner have reported the formation of small amounts of nanofibers in the chemical oxidative polymerization of aniline. Nanofibers form during the initial stages of polymerization (primary growth) as the oxidant (APS) initiates polymerization. Later, polymerization is further initiated from the nanofibers (secondary) leading to irregularly shaped agglomerates. Thus, the polymerization product can contain both nanofibers and irregular agglomerates. The instantaneous concentration of oxidant in the reaction bath provides the driving force for initiating the chemical polymerization of aniline. Hence, a rapid addition of the oxidant favors the initiation and primary growth of the polymer leading to high nanofiber content in the product, while a slow addition of the oxidant allows secondary growth of the polymer leading to a more agglomerated morphology.[25] In the present work, the instantaneous concentration of unreacted oxidant in the reaction bath is determined by the rate of addition of the oxidant to the monomer and by the OM ratio. Since, all the three rates of addition chosen for these experiments were relatively gradual (10, 30, and 50 mL/h), both primary (nanofibers) and secondary growths (agglomerates) are expected in all the four samples. However, Figure 12 shows some differences in the nature of the secondary growth among the samples, which might have contributed to the differences in electrical conductivity.

The overall electrical conductivity is a function of inter chain and intra chain electron transfer in PANi. Two distinct morphologies were observed in the samples studied. Samples 2 and 7, which had a high electrical conductivity, displayed a highly connected coral-like morphology that allows for good inter- and intra-chain electron transfer within PANi. Samples 9 and 15, which had a poor electrical conductivity, displayed a loose flake-like morphology with poor connectivity between PANi particles. As a result, we can expect poor interchain electron transfer in these samples resulting in a low conductivity.

The connected coral-like morphoplogy as seen in sample 7 appears at medium values of all three factors. This sample also has the highest electrical conductivity (253.45 S/m). Sample 2 also shows a similar morphology and a relatively high electrical conductivity (15.04 S/m). The electrical conductivity of sample 2 is somewhat lower than sample 7 due to the detrimental effect of a low dopant concentration and a high OM ratio as discussed in the section "Main Effects Plots." In samples 9 and 15, due to the low values of the rate of addition and the OM ratio, respectively, the driving force for initiation of the polymerization was low. As a result, greater amounts of secondary growth can be expected. This is consistent with the observed irregular, loose morphology and the resultant poor electrical conductivity. Additionally, both the samples had high values of dopant acid concentration, which as per the discussion in the section "Main Effects Plots," leads to poor conductivity.

CONCLUSIONS

The electrical conductivity and the yield of PANi were optimized using a DOE approach. A three-level, three-factor Box–Behnken design was used. The three factors identified for the study were (i) the concentration of dopant acid, (ii) oxidant-monomer (OM) ratio, and (iii) the addition rate of the oxidant to the monomer. The responses were analyzed using MINITAB 15 software. The contour plots generated using MINITAB were overlaid to find the optimal regions for specified properties. Under the optimized conditions of dopant acid concentration ~0.9*M*, an oxidant addition rate ~30 mL/h and an OM ratio ~0.9, the polymer yield obtained is 95% and the electrical conductivity obtained is 1.95 S/cm. The verification experiments confirmed the prediction of the properties and the adequacy of the model chosen. The samples were further characterized using different techniques. Characterization studies on a few representative samples from the DOE, revealed that the chosen factors affect the electrical conductivity of PANi by altering the oxidation form, crystallinity and morphology of PANi. The form of

Table VII. X-ray Diffraction Analysis of PANi

Samples	Conductivity (S/cm)	Crystallinity (%)	2θ
Sample 7	2.53000	42.73	25.10°
Sample 4	0.00150	33.48	25.09°
Sample 15	0.00007	24.91	25.40°

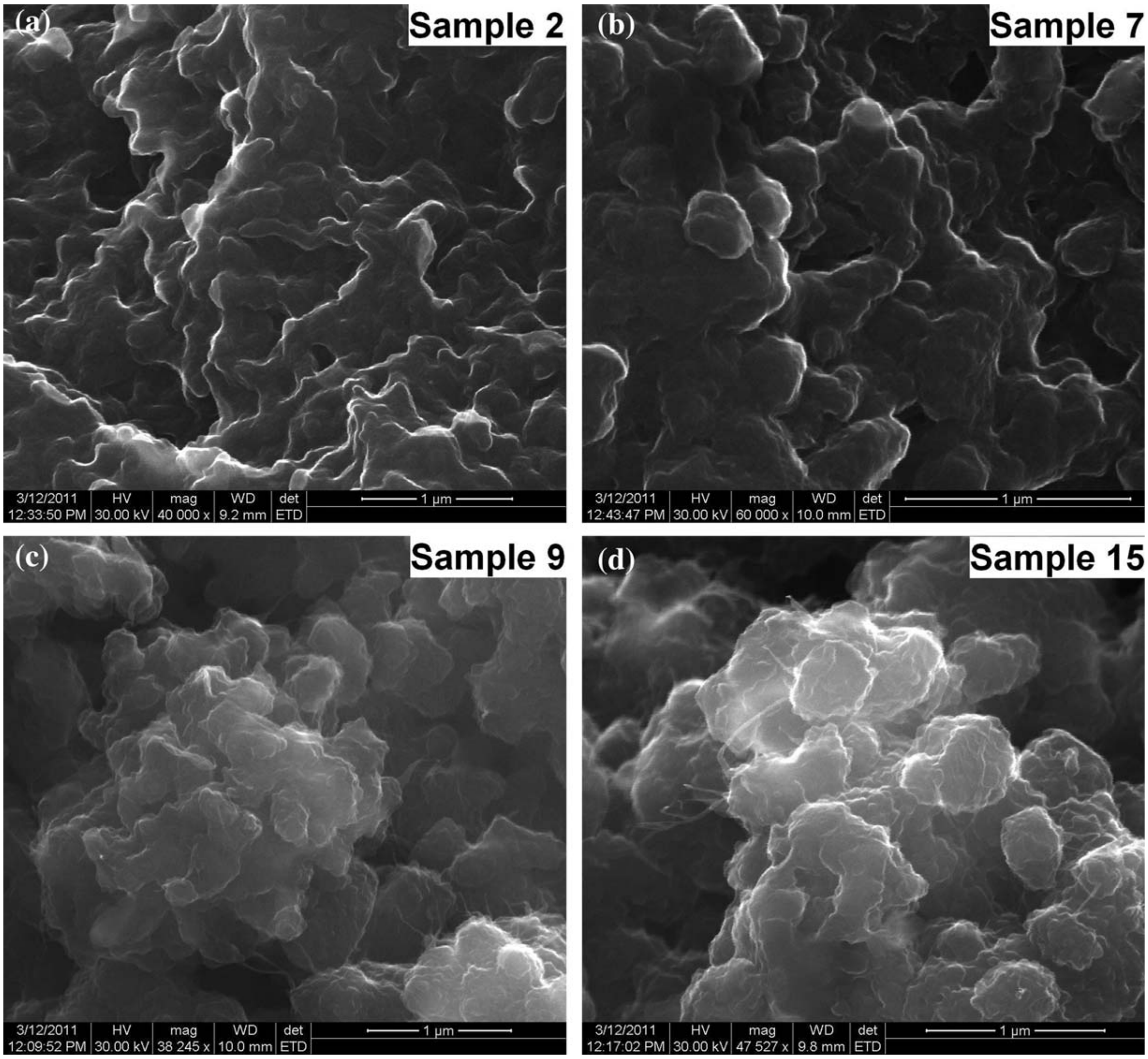

Figure 12. (a, b) SEM images of PANi with high conductivity and (c, d) low conductivity.

PANi was determined by FTIR studies while the crystallinity and morphology were studied by XRD and SEM, respectively. The highly conductive samples had a roughly equal proportion of the benzoid and the quinoid structures (emeraldine salt form of PANi), high crystallinity and an interconnected coral-like morphology. The low conductivity samples had largely unequal proportions of the benzoid and the quinoid structures (more of pernigraniline or more of leucoemeraldine forms of PANi), low crystallinity and a loose flake-like morphology.

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