CONCURRENT OPTIMIZATION OF THE MECHANICAL AND ELECTRICAL PROPERTIES OF POLYANILINE MODIFIED KENAF PAPER

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Response surface methodology (RSM) was used to simultaneously optimize the tear index and electrical conductivity of newly developed conductive paper made from kenaf fiber and polyaniline (KF-PANI). The Design of Experiment (DOE) was used to study the effect of process parameters. The measured tear index and electrical conductivity values were in good agreement with those of the predicted optimized process. The scanning electron microscopy (SEM) image of the optimized KF-PANI paper revealed no significant fiber damages.

Keywords: kenaf, polyaniline, conductive paper, electrical conductivity, mechanical properties, numerical optimization, response surface methodology

INTRODUCTION

Natural fibers coated with conducting polymers have recently gained wide attention due to their anti-static, electro-magnetic shielding, electrical conductivity and anti-bacterial properties, for applications in manufacturing papers and packaging products.[1-6] Among the conducting polymers used for coating cellulosic fibers, polyaniline (PANI) is one of the most promising due to its ease of preparation,[7] excellent electrical,[8] optical,[9] anticorrosive properties[10] and biocompatibility.[11] Hardwood[1-5] and some agro-waste crops[6] fibers have been used to prepare such conductive paper composites. Though a desirable conductive sheet can be achieved by the addition of PANI, one of the drawbacks of the combination is that the mechanical integrity of the processed sheet can be easily lost once the synthetic conducting polymers are introduced. Reduction of tear[6] and tensile[1] indexes up to 35 and 54% has been reported, respectively. Growing environmental awareness and depletion of the wood resources worldwide are among the vital factors enticing to explore the potential of agro crops and lignocellulosic materials as an alternative source of fiber material.

Kenaf (*Hibiscus cannabinus* L., *Malvaceae*) is a warm season annual fiber crop. Various applications of kenaf fiber (KF) have been explored including as feed stock, adsorbent material, paper, insulation board and as reinforcement in composites.[12-15] The advantages include low cost, comparable specific tensile properties to those of synthetic fibers, non-abrasiveness, non-irritation to the skin and reduced energy consumption.[16] Therefore, combining KF with PANI is a good strategy to obtain electrically conductive paper, originating from inexpensive pulp and having good mechanical properties.

Our earlier work described the possibility of modifying KF with PANI.[17-20] Though desirable properties were achieved, the optimum process parameters for obtaining the best combination of mechanical and electrical properties of the resulting paper sheets are still unclear. Several factors can affect the electrical conductivity and strength of the conductive paper, such as initial treatment of KF, dopant type, dopant concentration, PANI amount and molar ratio. Furthermore, it is problematic to deduce the influence of these independent variables and correlate them with the properties of the conductive paper. A statistical method using the Design of Experiment (DOE) can be utilized to optimize the conditions,[21] which would produce KF-PANI paper with a defined property. A systematic experimental design to find the parameters that can affect conductivity and strength can be employed by utilizing the response surface methodology (RSM) procedure coupled with a central composite design (CCD) and further subjected to regression analysis. RSM reduces the number of required experimental runs to achieve a statistically validated result.[22] Thus, the main aim of this study is to prepare electrically conductive KF-PANI paper, which would present the best combination of tear index and electrical conductivity.

EXPERIMENTAL

Preparation of KF-PANI paper

The preparation of KF was described in detail elsewhere.[17,18] Briefly, kenaf bast fibers (KF) (Everise Crimson (M)) were treated with active alkali charge of 15% and sulphidity of 17.5%. The mercerized fibers were washed with running water. The pulp was then mechanically disintegrated by a three-bladed mixer for 2 min. In situ polymerization of aniline in presence of KF pulp was performed in formic acid (dopant) solution (Merck). The required amount of aniline monomer (Acros) with respect to KF and oxidant (ammonium persulfate, Merck) was separately dissolved in the dopant solutions. The monomer to oxidant molar ratio was prepared accordingly. The blended KF were initially immersed in the reaction mixture containing aniline solution, followed by the addition of oxidant solution to initiate the polymerization process. The temperature of the reaction mixture was maintained at 10 °C in an ice bath. The reaction medium was vigorously stirred with a mechanical stirrer for 4 h and was left for 24 h. The obtained KF-PANI pulp was then washed several times by deionized water until the suspension was clear from excess oxidants and clear green fibers could be seen. The KF-PANI pulp was formed into paper sheets by hand, screened via a flat-plate screen with 0.15-mm slits, pressed for 4 min using a hydraulic press and further conditioned at 90 °C for at least 6 h. Following the above mentioned procedures, KF-PANI paper samples were prepared varying the factors, based on the design matrix.

Characterization

Tear test was performed using the Elmendorf Tear method (ASTM D-1922). The tear index of the paper was calculated using average tearing force (mN)/average grammage (g/m^2), whereby the average tearing force is given by (16 × 9.81 × average scale reading). DC electrical conductivities of the prepared KF-PANI paper were measured using a resistance meter (Advantest) by the four probe method under ambient conditions. Samples were dried for 4 h at 90 °C prior to testing to remove the adsorbed moisture and then stored in a desiccator filled with silica gel. Paper morphology was examined using a Leo Supra 50VP scanning electron microscope (SEM). Fourier transform infrared (FTIR) spectra of the sample were obtained using a model 2000 Perkin Elmer spectrometer.

Statistical analysis using Design of Experiment

Design Expert Software, version 6.0.6 (Stat-Ease Inc., USA) based on RSM in conjunction with CCD was used to perform the statistical analysis and generate the regression model to analyze the correlations between the variables of KF-PANI paper and the responses. The selected responses were tear index (Y_1) and electrical conductivity (Y_2). The variables in this study included three numerical factors: that of PANI amount (x_1), acid concentration (x_2) and molar ratio (x_3). The three variables together with their respective ranges were chosen based on the experimental studies described in our previous work.[17,18] The ranges of the independent variables and design level are shown in Table 1.

The number of experimental runs determined from CCD was 20, corresponding to 6 factorial points, 6 axial points and 6 centre point replications. An α value of 1 was used. The experimental sequence was randomized in order to minimize the effects of uncontrolled factors. Each response was used to develop an empirical model, which correlated the response to the variables used. The general quadratic equation model[23] is given by Equation 1, where Y represents the response, β_0 is the constant coefficient, β_i, β_{ii} and β_{ij} are coefficients for the linear, quadratic and interaction effects, respectively. x_i and x_j are the independent variables, and ε is the standard error.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^{\,2} + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon$$

The coefficient of determination, R^2, was used to evaluate the quality of the developed model, which was then followed by ANOVA analysis to check the statistical significance of the models. Numerical optimization was computed by the software to give out the optimum combinations of the parameters in order to fulfil the requirements as desired. Optimizations were conducted for tear index (Y_1) and electrical conductivity (Y_2). The ultimate goal of the optimization was to obtain the combination of maximum responses (tear index and electrical conductivity) that would simultaneously satisfy all the variable properties. Experimental validation was done based on the suggested runs with the highest combination of desirability, D, function[24,25] given in Equation 2. Y_i is the determined level of the response i,

$d_i(Y_i)$ is the converted desirability score of the associated response and k_i being the relative importance of that response compared to others. Desirability function, D, will take a value between 0 and 1, where being as close as possible to 1 is desired.

$$D = (d_1(Y_1)^{k_1} \times d_2(Y_2)^{k_2} \times \dots \dots . d_n(Y_n)^{k_n})^{\frac{1}{\sum k_i}} \quad (2)$$

Table 1
Independent variables and their coded variables

Variables	Code	Coded variable levels		
		-1	0	1
PANI amount, wt%	x_1	1	5.5	10
Acid concentration, *N*	x_2	5	15	25
Molar ratio	x_3	0.5	1	1.5

Table 2
Experimental design matrix and responses

	Variables			Response	
Run	x_1	x_2	x_3	Y_1	Y_2
1	10.0	5.00	1.5	19.95	7.67
2	10.0	25.00	0.5	19.8	8.15
3	5.50	15.00	1	20.75	8.78
4	5.50	5.00	1	21.04	7.50
5	1.00	25.00	0.5	20.8	5.24
6	10.0	15.00	1	19.9	7.04
7	5.50	15.00	1	20.8	8.82
8	5.50	15.00	1	20.6	8.88
9	5.50	15.00	0.5	20.6	8.50
10	5.50	25.00	1	20.0	9.30
11	1.00	5.00	0.5	21.2	4.35
12	5.50	15.00	1	20.8	8.78
13	5.50	15.00	1	20.7	8.80
14	1.00	5.00	1.5	21.2	4.51
15	10.0	5.00	0.5	19.9	6.53
16	1.00	25.00	1.5	20.8	5.52
17	5.50	15.00	1	20.8	7.85
18	1.00	15.00	1	21.0	4.64
19	10.0	25.00	1.5	19.7	8.45
20	5.50	15.00	1.5	20.8	8.95

RESULTS AND DISCUSSION

Development of Regression Model Equation

The complete design matrix for preparing KF-PANI paper and the responses are given in Table 2. The tear index was found to range from 19.7 to 21.2 mN·m^2/g and the electrical conductivity from 4.35 to 9.30 x 10^{-3} Scm^{-1}. The quadratic model was suggested for both responses, according to the sequential model sum of squares. The final empirical formula model for tear index (Y_1) and electrical conductivity (Y_2) in terms of their coded factor after excluding the insignificant factors are given as Equations 3 and 4, respectively.

$$Y_1 = 20.71 - 0.57x_1 - 0.22x_2 \quad (3)$$

$$Y_2 = 8.56 + 1.36x_1 + 0.61x_2 - 2.58x_1^2 \quad (4)$$

The quality of the models was evaluated based on standard deviation and the value of the correlated coefficient, R^2. The capability of the model to predict the response is translated to small standard deviation and a value of R^2 closer to unity. The standard deviations of Equations 3 and 4 are 0.17 and 0.37 with R^2 of 0.9237 and 0.9749, respectively. These indicate that 92.4% (tear index) and 97.5% (electrical conductivity) of the total variation were attributed to the experimental variables studied.

ANOVA analysis

ANOVA has been employed to further justify the significance of the models. The statistical significance of the quadratic model for each response is determined by F-value and Prob.>F. F-value is a measurement of variance of data about the mean, based on the ratio of mean square of group variance due to error. A significant model possesses high F-value and Prob.>F less than 0.05. The ANOVA results for the quadratic model of tear index and electrical conductivity are presented in Tables 3 and 4, respectively. The quadratic model of tear index exhibits an F-value of 15.39 and Prob>F of 0.0001. x_1 and x_2 are the significant model terms to the response. As for the electrical conductivity, the obtained F-value is 43.08 and Prob>F of < 0.0001. x_1, x_2, and x_1^2 are the significant model terms to the response. This implies that both models are significant. Based on the statistical analysis, the models are adequate enough to predict the tear index and electrical conductivity within the range of the variables.

Table 3
ANOVA results for tear index of KF-PANI paper

Source	Sum of squares	Degrees of freedom	Mean square	F-value	Prob > F
Model	4.22	9	0.47	15.39	< 0.0001
x_1	3.31	1	3.31	108.57	< 0.0001
x_2	0.48	1	0.48	15.75	0.0026
x_3	0.00225	1	0.00225	0.074	0.7913
x_1^2	0.12	1	0.12	3.88	0.0772
x_2^2	0.052	1	0.052	1.70	0.2213
x_3^2	0.00502	1	0.00502	0.16	0.6933
x_1x_2	0.025	1	0.025	0.83	0.3834
x_1x_3	0.0003	1	0.0003	0.01	0.9213
x_2x_3	0.00281	1	0.00281	0.092	0.7674

Table 4
ANOVA results for electrical conductivity of KF-PANI paper

Source	Sum of squares	Degrees of freedom	Mean square	F-value	Prob > F
Model	52.16	9	5.80	43.08	< 0.0001
x_1	18.44	1	18.44	137.08	< 0.0001
x_2	3.72	1	3.72	27.66	0.0004
x_3	0.54	1	0.54	4.04	0.0723
x_1^2	18.29	1	18.29	135.92	< 0.0001
x_2^2	0.00095	1	0.00095	0.0071	0.9345
x_3^2	0.26	1	0.26	1.92	0.1961
x_1x_2	0.031	1	0.031	0.23	0.6402
x_1x_3	0.12	1	0.12	0.93	0.3578
x_2x_3	0.065	1	0.065	0.48	0.5035

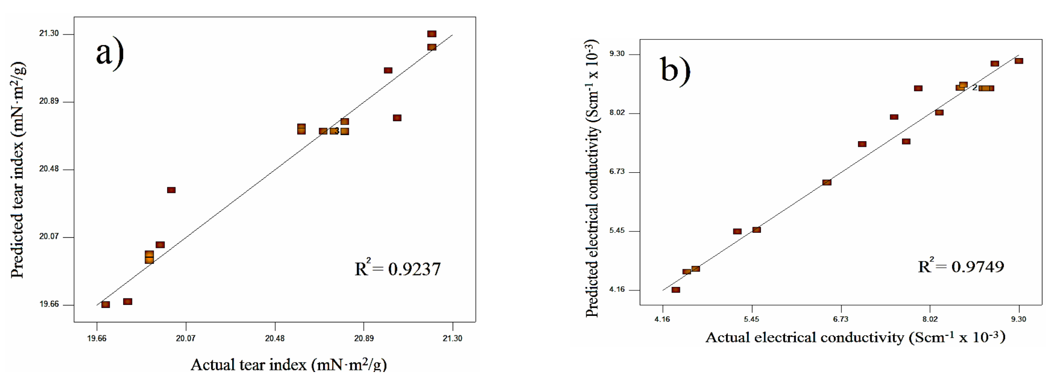

Figure 1: Comparison between the actual and experimental values for a) tear index b) electrical conductivity

Figure 1 (a and b) shows the predicted values versus the experimental values of the responses. It can be seen that the response models show good fits to the experimental data, which is reflected in the good predictions of the models. It is essential to check the interaction effect between the model terms based on their significant effects and the model equation. These interactions can be depicted clearly by plotting both variables on a 2D plot and 3D surface plot. Since the model has more than two variables, only the targeted variables were varied while the others were held constant. Based on *F*-values, the PANI amount gives the greatest impact on both responses. The molar ratio is set at zero level (1.0). Figure 2 (a and b) shows the 2D and 3D plots of the interaction of the PANI amount and acid concentration towards the tear index of the KF-PANI paper. It can be observed from the plots that the maximum tear index of the KF-PANI paper is provided at the lower limit, 1 wt% of PANI for both acid concentrations (5 and 25 *N*). By using an acid concentration of 5 *N*, it is possible to obtain a higher tear index for the KF-PANI paper than that obtained at 25 *N* at the same PANI amount. The plots imply that an acid solution and PANI coating have an adverse effect on the mechanical strength of the conductive paper. Highly acidic condition during the in situ polymerization might promote the degradation of the fibers by hydrolysis of the cellulose chain.[26] It has been reported that for a dilute hydrolysis process, high temperature, pressure and catalyst are needed for the reaction to happen.[27] The low reaction temperature (10 °C) however inhibits the hydrolysis and confines the dopant ions ($HCOO^-$) strictly on the fiber surfaces as a protonating agent to PANI.

Increasing the amount of PANI leads to poor strength due to the poor mechanical properties of PANI and the difference in crystallinity/polarity of the two surfaces (PANI and KF). Furthermore, the tendency of the monomer to polymerize outside the vicinity of the KF surfaces is increased when the aniline amount is increased. The 2D and 3D surface plots of the interaction of the PANI amount and acid concentration towards the electrical conductivity of the KF-PANI paper are shown in Figure 3a and b. From the examination of the contour plot (Figure 3b), it can be noted that the process may be slightly more sensitive to changes in PANI amount than to changes in acid concentration. An optimum conductivity can be observed as the amount of PANI is increased. This is attributed to the presence of the more dominant conducting PANI phase in the KF paper. The drop might reflect that the detachment of PANI from the KF surface has occurred.

Process optimization

Table 5 gives the constraints of each variable for the numerical optimization. Table 6 exhibits the five possible runs that fulfilled all the specified constraints of Table 5 to obtain the optimum value for the tear index and electrical conductivity. A useful approach to optimization of multiple responses is to use the simultaneous optimization technique by using the desirability, *D*, function.[28] All the runs in Table 6 gave high *D* values. The optimum conditions in any of the five given runs can be chosen for further validation. Runs 1 to 4 in Table 6 obtained the highest combined *D*. The runs could be used to validate the actual performance of the final product. In this case, Run 1 (5 wt% PANI, acid concentration of 11.39 *N* and molar ratio of 1.5) was selected. For further validation of the developed model, the experimental runs were carried out under the conditions stated in Table 6, Run 1. Experimental runs were done to further validate the developed model. The experiments were repeated three times to ensure the validity of the results. Table 7 shows the three repeated runs for the model validation. The accuracy of the equations derived from ANOVA can be evaluated by calculating the percentage of error between the predicted and the experimental responses of tear index and electrical conductivity. The results confirm the predictability of the ANOVA model for both responses under the experimental conditions. The errors of the predicted and experimental values for tear index and electrical conductivity were less than 6%. It can be justified by the developed model and process optimization that the properties of the KF-PANI paper can be optimized using all the possible runs. The improvement can be justified as summarized: 1) optimum PANI inclusion imparted electrical properties without significant loss in the mechanical properties, 2) optimum dopant concentration could reduce mechanical deterioration caused by the hydrolysis of cellulose chains and 3) the combination of optimum PANI amount and dopant concentration resulted in optimized responses due to better KF-PANI surface interactions and morphology of adhered PANI, which facilitated electron conduction, while maintaining its mechanical integrity.

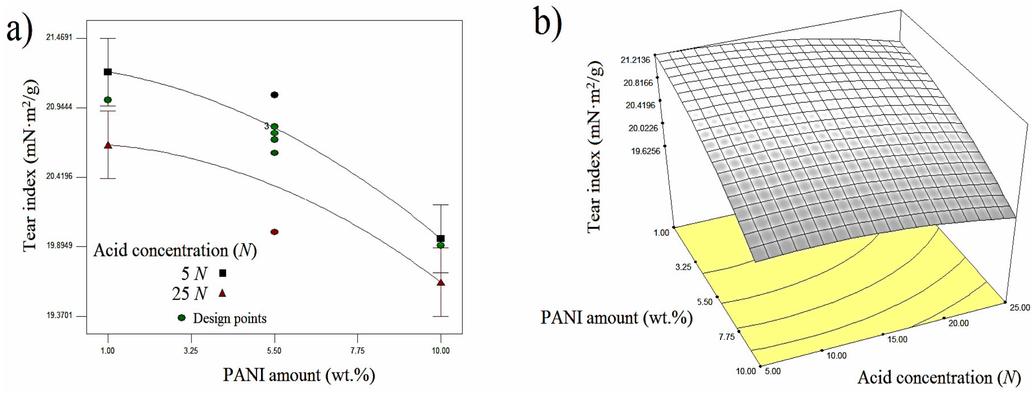

Figure 2: 2D and 3D response surface plot for tear index

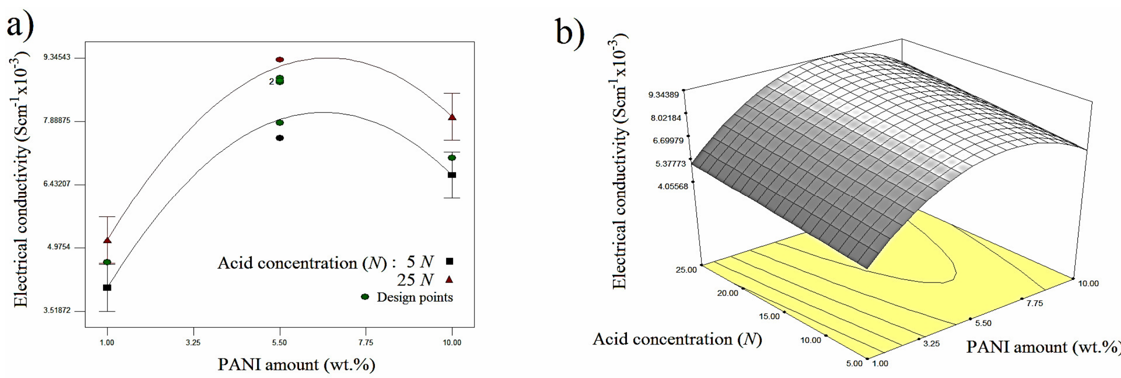

Figure 3: 2D and 3D response surface plot for electrical conductivity

Table 5
Constraints of each variable for the numerical optimization of tear index and conductivity

Type of variable	Goal	Lower limit	Upper limit
PANI amount, wt%	in range	1	10
Acid concentration, *N*	in range	5	25
Molar ratio	in range	0.5	1.5
Tear index, mN·m^2/g	maximize	19.7	21.2
Electrical conductivity, Scm^{-1} x 10^{-3}	maximize	4.35	9.30

Table 6
Optimum conditions to obtain the maximum tear index and electrical conductivity

	Numerical factors			Tear index, mN·m^2/g	Electrical conductivity, Scm^{-1} x 10^{-3}	Combined *D*
Run	PANI amount, wt%	Acid concentration, *N*	Molar ratio			
1	5.00	11.39	1.50	20.897	8.715	0.839
2	5.03	11.24	1.50	20.896	8.718	0.839
3	4.97	11.87	1.50	20.895	8.720	0.839
4	4.93	14.43	0.50	20.815	8.400	0.780

Table 7
Results of validated experiments conducted under optimum conditions as obtained from DOE for tear index and electrical conductivity

Run	Numerical factors			Predicted tear index, mN·m^2/g	Experimental tear index, mN·m^2/g	Error, %	Predicted electrical conductivity, Scm^{-1} x 10^{-3}	Experimental electrical conductivity, Scm^{-1} x 10^{-3}	Error, %
	PANI amount, wt%	Acid concentration, *N*	Molar ratio						
1	5.00	11.39	1.5	20.897	19.865	4.94	8.715	8.254	5.29
2	5.00	11.39	1.5	20.897	20.256	3.06	8.715	8.355	4.13
3	5.00	11.39	1.5	20.897	19.873	4.90	8.715	8.271	5.09

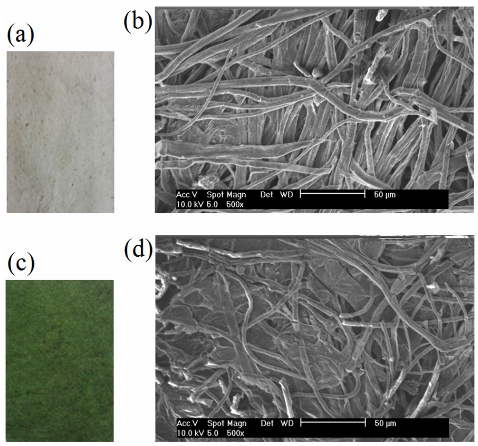

Figure 4: Photographs and electron micrographs of (a-b) unmodified KF paper, (c-d) optimized KF-PANI paper

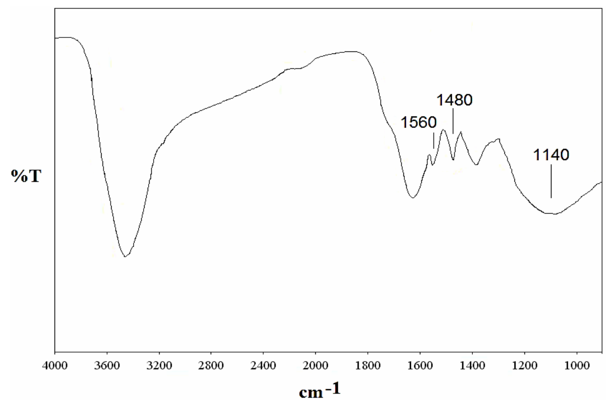

Figure 5: FTIR spectra of optimized KF-PANI paper

Morphological characterization and FTIR spectroscopy

Figure 4 (a and b) illustrates the photograph of unmodified KF paper and its SEM image, respectively. The sample exhibits typical surface features of lignocellulosic fibers. The in situ modification of the KF pulp with PANI leads to paper green in colour (Figure 4c); this essentially indicates the presence of the PANI component in its doped state.[17] Its corresponding SEM micrograph (Figure 4d) reveals that the morphology of the fibrous sheet is still intact, no fiber rupture and damages are observed. This is a positive indication of a possible way to obtain conductive paper, while preserving its fiber characteristics.

The FTIR spectrum of the KF-PANI paper sample (Figure 5) shows the clear presence of benzoid and quinoid ring vibrations at 1480 cm^{-1} and 1560 cm^{-1}, respectively, indicating the oxidation state of emaraldine salt of PANI. The strong band around 1140 cm^{-1} is the characteristic peak of PANI conductivity and is considered to be the measure of the degree of delocalization of electrons.[17,18] The absence of the C-H stretching peak at 2900 cm^{-1} might suggest that the surface hydroxyl groups of the KF have been dominated by the PANI component. This can be associated by the overlapping of C-H stretching of KF by the broad absorption of PANI N-H stretching. Their surface interaction is provided by the formate ion, which dopes the PANI chains and possibly forms H bonding with the KF. This is also accompanied by potential H bonding between the amide group of PANI and the KF surface hydroxyl, as observed by the broad N-H stretching in the spectrum.

CONCLUSION

It has been demonstrated that the KF-PANI paper achieved the desirable combination of electrical and mechanical properties, using the suggested models of the DOE. The effects of molar ratio, PANI wt% and acid concentration on the electrical conductivity and tear index of conducting KF-PANI paper were successfully studied using RSM equipped with CCD. Two quadratic models were given to correlate the process variables to the responses. The DOE revealed that the PANI amount had the most significant influence on both responses. Optimum process conditions were obtained at PANI of 5 wt%, acid concentration of 11.39 *N* and molar ratio of 1.5, which resulted in tear index and electrical conductivity of 19.87 $mN \cdot m^2/g$ and 8.254×10^{-3} Scm^{-1}, respectively. SEM images of the optimized conductive paper revealed no fiber damages by the in situ modification. The vibrational analysis indicated the presence of the doped PANI component and good surface interaction between the KF and PANI. This novel conductive paper can find interesting applications for electrostatic and charge dissipation materials, which require mechanical integrity and bio-derived resources.

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