Modeling, Prediction, and Multifactorial Optimization of Radiation-Induced Grafting of 4-Vinylpyridine onto Poly(vinylidene fluoride) Films Using Statistical Simulator

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ABSTRACT: The traditional method for obtaining best combination of reaction parameters for graft copolymerization of 4-vinylpyridine onto poly(vinylidene fluoride) films was modified using Box-Behnken factorial design available in the response surface method (RSM). A computer-assisted statistical simulator was used to obtain the optimum absorbed dose, monomer concentration, grafting time and reaction temperature to achieve the highest degree of grafting ($G\%$) based a quadratic model. The validity of the developed model was confirmed by experimental data, which only deviated by a 2% from the predicted value of $G\%$ confirming the effectiveness of RSM in optimization of the reaction parameters in the present grafting system. A comparison was also made between the obtained model and that of 1-vinylimidazole/poly(ethylene-*co*-tetrafluoroethylene) grafting system. The chemical structure, morphology and thermal stability of the obtained graft copolymers was investigated by means of Fourier transform infrared, filed emission scanning electron microscope, and thermogravimetric analysis, respectively. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Radiation-induced grafting is an attractive method to overcome the theoretical and technological challenges in combining hydrophilic monomers with hydrophobic polymers to develop new functional copolymers.[1] Such materials have the merit of a simple preparation procedure, tailor-made physicochemical properties caused by controlling the reaction parameters and flexible selection of starting polymeric forms (bead, fiber or film). In addition, various irradiation sources are available for initiation the reaction.[2]

Poly(vinylidene fluoride) (PVDF) film is a partially fluorinated polymer having interesting electrical properties, resistance to weathering, durability, biocompatibility, and processibility in addition to high resistance to ionizing radiation.[3] Thus, PVDF film has been used as a substrate for preparation of a number of cation/proton exchange membranes with sulfonic acid functionality after being grafted with styrene or styrene/crosslinker mixture followed by a sulfonation.[4–8] A review of previous studies on sulfonic acid membranes based on PVDF films and other fluorinated films can be found in Nasef 2008.[9]

4-Vinylpyridine (4-VP) is an interesting vinyl monomer of heterocyclic structure that has been radiochemically grafted onto various polymers to prepare functional membranes in many occasions.[10–16] Grafting of 4-VP confers the polymer film a weak basic character that can be further enhanced by a quaternization reaction. Table I shows a summary of previous studies involving grafting 4-VP onto various polymer films. However and up to the knowledge of the authors, there is no reports on radiation-induced grafting of 4-VP onto PVDF film.

Recently, radiation-induced grafting of 4-VP onto poly(ethylene-*co*-tetrafluoroethylene) (ETFE) was used to introduce a pendant —C=N⁺ group to form a membrane precursor that can be doped with phosphoric acid to yield an acid/base membrane for possible use in a high temperature proton exchange membrane fuel cell (PEMFC).[11,12,17] Earlier grafting of 4-VP onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) for water desalination application was also reported in literature.[18]

Achieving a favorable degree of grafting ($G\%$) in the membrane is highly necessary to ensure obtaining graft homogeneity and

Table I. Summary of Previous Studies on Radiation-Induced Grafting of 4VP onto Various Base Polymer Films

Monomer system	Base polymer	Radiation source/method	Refs.
4VP	FEP[a]	γ-radiation/direct irradiation	10
4VP	FEP; ETFE[b]	EB (1MeV)/preirradiation	11
4VP	ETFE	γ-radiation(60-Co)/preirradiation	12
AAc[c]/4-VP	LDPE[d]	γ-radiation(60-Co)/direct irradiation	13
4VP	PTFE[e], LDPE	γ-radiation(60-Co)/direct irradiation	14
4VP/DVB[f]	ETFE	γ-radiation/direct irradiation	15
4VP/MAN[g]	PE[h]	γ-radiation(60-Co)/direct irradiation	16

[a]FEP, Poly(tetrafluoroethylene-co-hexafluoropropylene), [b]ETFE, Poly(ethylene-co-tetrafluoroethylene), [c]AAc, acrylic acid, [d]LDPE, low-density polyethylene, [e]PTFE, polytetrafluoroethylene, [f]DVB, divinylbenzene, [g]MAN, methacrylonitrile, [h]PE, polyethylene.

uniformity meeting PEMFC requirements. However, such aim is not an easy task and can be only achieved by optimizing the reaction parameters that can be achieved using commercial statistical packages employing factorial strategies.[17] This allows achieving a maximum $G\%$ with a minimum number of experiments and cost reduction.

In a previous study, radiation induce grafting of 1-vinylimidazole (1-VIm) onto ETFE film using the preirradiation method with electron beam (EB) was statistically modeled using Box-Behnken factorial design available in response surface method (RSM) for the first time.[17] The obtained results revealed the effectiveness of the Box-Behnken module in predicting $G\%$. The optimum combination of reaction parameters that allowed achieving an experimental $G\%$ with a minor deviation of 3% from the value predicted by the model was determined.

The objective of the present study is to apply the Box-Behnken module for optimization of the reaction parameters for grafting of 4-VP onto PVDF films and predict the response ($G\%$) using a statistical model based on factorial strategies. This would confirm the validity and flexibility of such method in addressing the variation in the nature of grafting system components i.e., monomer, solvent, and polymer film. The evidence for grafting of poly(4-VP) into PVDF film based on material research aspects is also provided.

EXPERIMENTAL

Materials
PVDF films with thickness of 50 μm and density of 1.76 g cm^{-3} were obtained from Goodfellow (UK). 4-VP, purity of 95% (Aldrich) was used without any further purification. Other chemicals, such as solvents and reagents, were research grade and used as received.

Irradiation of PVDF Films
PVDF films were washed with ethanol and then dried in a vacuum oven. The dried films were irradiated by an electron beam (EB) accelerator (Curetron, EBC-200-AA2, Japan) at the following conditions: acceleration energy of 200 KeV, beam current of 2.0 mA, N$_2$ atmosphere and at a room temperature. The total dose was in the range of 20–100 kGy obtained at 10 kGy

per pass. The irradiated films were quickly sealed in an evacuated polyethylene bag and stored at -60°C until used.

Graft Polymerization
Graft copolymerization of 4VP onto PVDF film was performed by placing the irradiated PVDF film in a glass tube reactor, which was tightly sealed and evacuated to remove air. A nitrogen-bubbled grafting solution composed of monomer and solvent with specific concentrations was introduced to the reactor through a special connection and the reaction was carried out by putting the sealed reactor into a heated thermostat bath allowing a control over reaction temperature at desired reaction time. The grafted film was removed and extracted in a methanol-containing vessel placed in an ultrasonic machine for several hours to remove the unreacted monomer and/or homopolymer. The obtained membrane was thoroughly dried under vacuum at 60°C for 24 h. The degree of grafting ($G\%$) was calculated as follows:

$$G\% = \frac{W_g - W_o}{W_o} \times 100, \tag{1}$$

where, W_o and W_g are the weights of original and grafted PVDF films, respectively.

Characterization of the Grafted Films
The evidence for successful grafting of poly(4-VP) onto PVDF films was monitored through the investigation of chemical, morphological, and thermal properties. The chemical composition was determined using Fourier transform infrared spectroscopy (FTIR). The analysis was performed on a Perkin Elmer Spectrum 400 FTIR/FIR spectrophotometer in the transmittance mode in a wave number range of 4000–450 cm^{-1} with a resolution of 4 cm^{-1}.

The morphology of the PVDF film before and after grafting were studied by the field emission scanning electron microscopy (FESEM) using a Leo Supra 35VP FE SEM coupled with an energy dispersive X-ray (EDX) analyzer. Representative samples were cut, loaded on the sample holder and sputtered with gold prior to analysis.

Table II. Reaction Parameters and Their Levels for Optimization of Grafting of 4-VP onto PVDF Films

Variables	Level 1	Level 2	Level 3	Level 4
Monomer conc. (vol %)	10	30	40	50
Absorbed dose (kGy)	20	60	80	100
Grafting temperature (°C)	55	60	65	70
Grafting time (h)	2	4	6	8

Thermogravimetric analysis (TGA) was conducted onto pristine and grafted samples under N_2 atmosphere using a Mettler Toledo TG/SDTA 851 analyzer with a heating rate of $20°C\ min^{-1}$ in the range of 30–750°C.

Experimental Design and Optimization
Radiation-induced grafting of 4-VP onto PVDF was optimized using Box-Behnken module of RSM available in the design expert software. The grafting parameters (independent parameters); absorbed dose, monomer concentration, grafting time, and temperature were varied in four levels in correlation with G% (the response). The vital ranges of these selected parameters were obtained in the preliminary experiments as shown in Table II. The experimental design array made by Box-Behnken set the desired combinations of the grafting parameters to achieve maximum G% as presented in Table III.

Response Fitting
The average of three runs of the independent parameters in correlation with the responses was recorded. The obtained results were introduced to the Box-Behnken model available in the Design Expert-6® software. The software was used to fit the

Table III. Various Combinations Run According to RSM Array

Run	Factor 1 A: Monomer Conc. (vol %)	Factor 2 B: Absorbed dose (kGy)	Factor 3 C: Grafting Temp. (°C)	Factor 4 D: Grafting Time (h)	Response G (%)
1	30	60	74	2	19.2
2	50	100	55	8	112.2
3	30	20	63	2	12.2
4	50	100	70	8	78.7
5	10	100	70	8	7.6
6	10	20	55	8	8.5
7	30	60	63	4	29.5
8	10	20	70	8	3.4
9	50	20	55	8	59
10	30	100	63	2	24.3
11	60	60	63	2	85.8
12	10	100	55	8	4.4
13	10	60	63	2	7
14	30	60	51	2	2.3
15	30	60	63	8	15.8
16	50	20	70	8	43.2

Table IV. ANOVA Analysis of the Impact of the Noise on the Data

Source	Degree of freedom	F-value	Prob > F	Significance
Model	4	24.65	< 0.0001	Significant
A	1	75.19	< 0.0001	Significant
B	1	5.71	0.0359	Significant
A^2	1	11.56	0.0059	Significant
AB	1	6.15	0.0305	Significant

Factor A: monomer concentration and B: absorbed dos.

responses to a quadratic polynomial regression model with respect to the independent parameter of grafting as shown in the following general equation:

$$y_i = b_0 + \sum b_i x_i + \sum b_{jj} x_i^2 + \sum\sum b_{ij} x_i x_j + e \quad (2)$$

where, y_i is the response, b is the regression coefficient, x is the independent parameter and e is the experimental error. An automatic backward reduction of the insignificant parameters was met at a significance level of $P \leq 0.05$. Finally, the software was used to perform ANOVA and produce 3D surface plots for the optimum results space.

RESULTS AND DISCUSSION

Statistical Analyses of the Response
The average of three runs of the independent parameters in correlation with the responses is presented in Table III. A quadratic polynomial regression model with a significance level of $P \leq 0.05$ was obtained after the response data were fitted to eq. (2) leading to the following equation.

$$y_i = 30.84x_1 + 8.5x_2 + 14.57x_1^2 + 11.07x_1x_2 + 20.59 \quad (3)$$

The significant factors in eq. (3) were maintained whereas the insignificant ones were automatically eliminated using a backward reduction method. The significance of each parameter, both individual and during interaction, was estimated using a probability function analysis available in the software. Finally, the impact of the noise on the data was assessed using ANOVA and presented in Table IV. As can be seen, the F-value, ratio of noise to response, for the model is 24.65 and this implies that the model is significant. There is a 0.01% chance that a "model F-value" this large could occur due to the noise. The values of "Prob > F" less than 0.05 indicate the model terms are significant.

It can be also seen that not all the four parameters have significant effect on the response. For instance, only the monomer concentration (A) and absorbed dose (B) showed the most significant effects on the response (G%) among the independent parameters. Figure 1 shows a one factor plot illustrates the effect of monomer concentration solely on the G%. It can be seen that the quadratic term of the monomer concentration is showing a significant effect on the response and linear term with an exponential growth of G% with the increase in the monomer
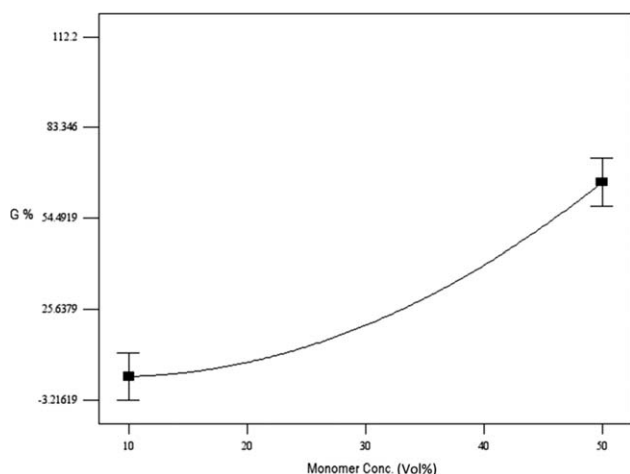
Figure 1. One factor plot illustrates the effect of monomer concentration solely on the degree of grafting.

Figure 3. 3D surface plot illustrates the effect of monomer concentration and absorbed dose on degree of grafting at 5 h grafting time and 62°C grafting temperature.

concentration. Such exponential increase in $G\%$ is attributed to the increase in monomer diffusion and the availability at the grafting sites in PVDF film. Such behavior emphasizes that the concentration of the monomer in the bulk solution has a greatest effect on the $G\%$.

On the other hand, ANOVA table shows another source of impact on the response due to the interaction between the monomer concentration and absorbed dose (AB). Figure 2 depicts a contour plot illustrating the interaction effect of the monomer concentration and absorbed dose at 62°C and 5 h on the $G\%$ (response) in 3D surface and 2D contour plots. It is clear that $G\%$ exhibits nonlinear increase as the monomer concentration and/or the absorbed dose increase. Finally, it was shown from the ANOVA that the absorbed dose (B) also exerts a linear impact on the response ($G\%$). This trend can be ascribed to the increase in the amount of radicals formed in the
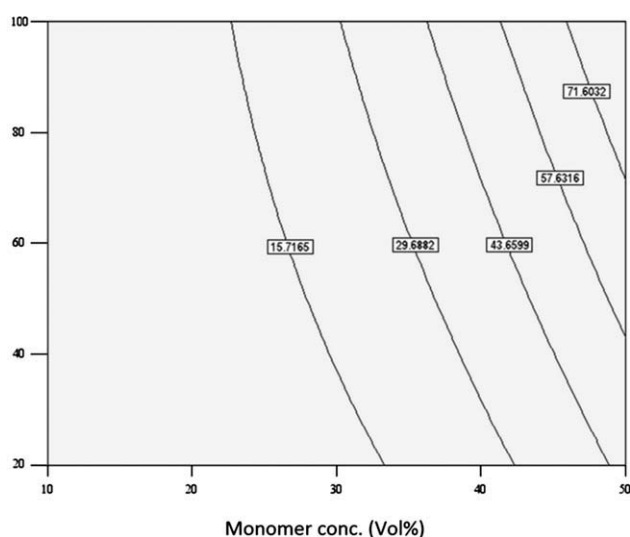
film with absorbance of more doses leading to more participation in the reaction with the monomer molecules available in the grafting sites.

Figure 3 shows a 3D surface plot illustrates the effect of monomer concentration and absorbed dose on the $G\%$, at 5 h grafting time and 62°C grafting temperature. It can be observed in the (absorbed dose-$G\%$) plane that the absorbed dose exerts a linear effect on the $G\%$. Such linearity is in accordance with ANOVA analysis presented in Table IV. It can be concluded that the absorbed dose and monomer concentration are the significant quadratic terms in the model out of the four linear significant terms: absorbed dose, monomer concentration, reaction time, and temperature. These results suggest that the grafting of 4-VP onto PVDF film is a diffusion controlled process and grafting mainly depends not only on monomer concentration but also on the absorbed dose.

Figure 4 presents the relation between the natural logarithm of residuals (y-axis) and lambda (x-axis), where; Box-Cox transform takes the form $\frac{y^{\lambda}-1}{\lambda}$, thus as λ tends to approach the value

Figure 2. Contour plot illustrates the effect of monomer concentration vs. absorbed dose on degree of grafting at 5 h grafting time and 62°C grafting temperature.
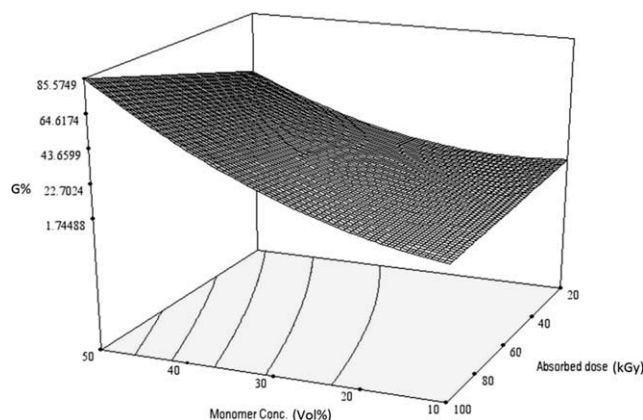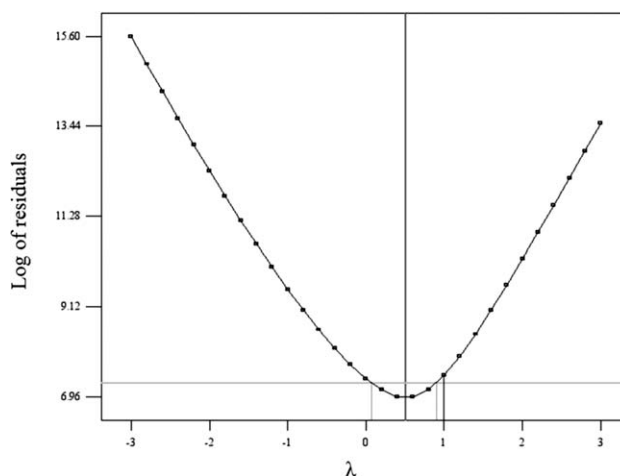

Figure 4. Box-Cox plot for power transform.

of 1, the fitting tends to exhibit linear behavior. On the other hand, as the value of λ approaches zero, the fitting of model tends to owe a logarithmic behavior. From Figure 4, one can notice that the current fitting of the response data has been met at $\lambda = 1$, which indicates the robustness of the response fitting and shows no violation to the normality in all fitting cases. Such plot shows that the linear fitting is still robust; however, the software suggested transforming the data before fitting. The model was found to run the significant parameters through a quadratic equation to produce ten valid solutions for the response optimization.

Finally, an optimization study for predicting the optimum results beyond the borders of the experimental results was performed. A desirability function was implemented on the results of the experiment using the design expert 6 software. The goal of the optimization was set to maximize the degree of grafting up to 60%, a desired value that meet PEMFC requirement when dope with phosphoric acid. Figure 5 shows a 3D surface plot of desirability vs. monomer concentration and absorbed dose. The 3D-surface plot was produced using the numerical optimization process to represent set of solutions that achieve the goal of maximizing $G\%$. At a desirability of 1, the optimum main parameters, i.e., monomer concentration and adsorbed dose to achieve maximum $G\%$ were 48 vol % and 61 kGy, respectively.

A summary of the overall optimum reaction parameters investigated to obtain a G of 60% is presented in Figure 6. They are 48% monomer concentration, 61 kGy absorbed dose, optimum grafting time ranges in the range of 2–8 h and optimum grafting temperature in the range of 55–70°C. The validation experimental value for $G\%$ obtained at 48% monomer concentration, 61 kGy absorbed dose, 5 h reaction time and 62°C temperature was found to be 58%. Such value agrees very well with the predicted one and provides a strong evidence for the model success in the prediction of $G\%$ and optimization of the reaction parameters.
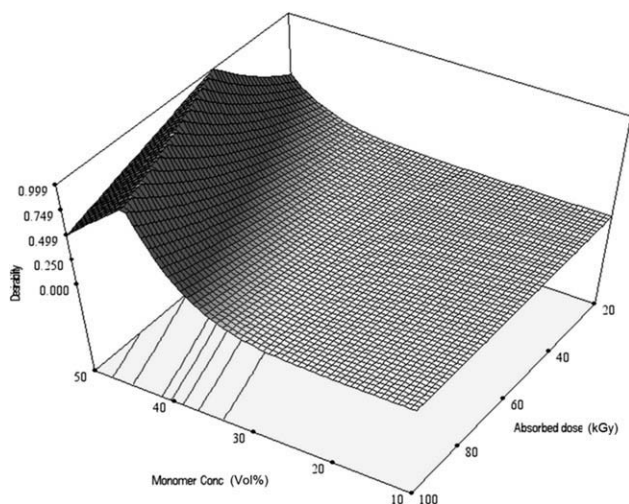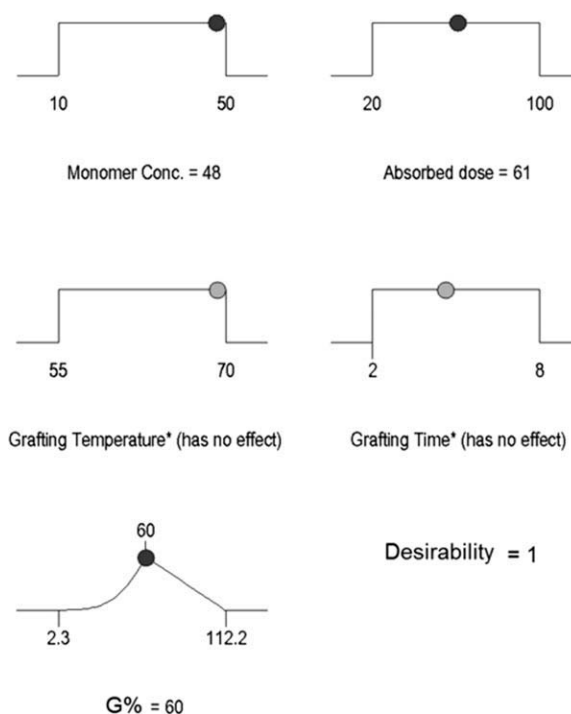

Figure 6. Ramp report showing the optimum parameters at 1 desirability level: (●) more significant parameters and (○) less significant parameters in affecting degree of grafting.

Comparison Between Models for 4-VP/PVDF and 1-VIm/ETFE Grafting Systems

To confirm the validity of Box-Behnken model of RSM for optimization of radiation-induced grafting of 4-VP onto PVDF films and its flexibility in addressing the variation in the nature of monomer solution and polymer film, a comparison between the present grafting system and that involving grafting of 1-VIm onto ETFE film is made and summarized in Table V. As can be seen, the linear terms of all reaction parameters (monomer concentration, absorbed dose, grafting temperature, and time) were found to be significant in the two models, i.e., these parameters have direct effects on the $G\%$ (response). However, the model proved to be sensitive to the difference between the behavior of 1-VIm and 4-VP during grafting onto ETFE and PVDF films, respectively, as indicated by the obvious differences in the terms of the equations. For instance, the quadratic terms of the models show that monomer concentration and grafting temperature are the most significant parameters when 1-VIm diluted with water (50/50 v:v) was grafted onto ETFE film whereas in grafting of 4-VP diluted with ethanol (50/50 v:v) onto PVDF film, the monomer concentration and absorbed dose are the most significant parameters. Such behavior means that when 1-VIm is grafted onto ETFE film, the $G\%$ shows a great sensitivity to the medium temperature in addition to monomer concentration. On the other hand, the absorbed dose shows a rapid effect on $G\%$ for grafting 4-VP onto PVDF together with short time dependence. This behavior can be attributed to the differences in (1) physical and chemical properties of 1-VIm and 4-VP despite their common basic nature and heterocyclic molecular structure and (2) the difference between ETFE and PVDF both of which have similar

Figure 5. 3D surface plot of desirability versus monomer concentration and absorbed dose.

Table V. Comparison Between Results of Optimization of Grafting of 1-VIm and 4-VP onto ETFE and PVDF Films

Comparison points	Grafting of 1-VIm onto ETFE film[a]	Grafting of 4-VP onto PVDF film
Model equation	$y_i = \text{Inv} \begin{bmatrix} 9.25*10^{-3}x_1 - 0.013x_2 - 0.016x_4 \\ +0.024x_1^2 + 0.015x_2^2 - 6.582*10^{-3}x_1x_4 \\ -0.017x_2x_4 + 0.028 \end{bmatrix}$	$y_i = 30.84\,x_1 + 8.5x_2 + 14.57\,x_1^2 \\ + 11.07\,x_1\,x_2 + 20.59$
Type	Quadratic polynomial	Quadratic polynomial
Significant linear terms	Monomer concentration, absorbed dose, grafting temperature and grafting time	Monomer concentration, absorbed dose, grafting temperature and grafting time
Significant quadratic terms	Monomer concentration and grafting temperature	Monomer concentration and absorbed dose
Significant interacting terms	(Absorbed dose - monomer concentration) and (absorbed dose-grafting temperature)	(Absorbed dose - monomer concentration)
Optimum values of significant parameters	–Monomer concentration: 55 vol %	–Monomer concentration: 48 vol %
	–Absorbed dose: 100 kGy	–Absorbed dose: 61 kGy
	–Grafting time: 14–20 h	–Grafting time: 2–8 h
	–Grafting temperature: 61°C	–Grafting temperature: 55–70°C
Optimum experimental G% value	57%	58%
Predicted G% value	60%	60%

[a]Reported in Ref. 17.

chemical compositions but different molecular structures and molecular weights. For instance, the density of 1-VIm (1.039 g/mL) is higher than that of 4-VP (0.975 g/mL) suggesting a slower diffusion in the former than the latter. Thus, the temperature is more significant in affecting VIm viscosity and its diffusion through ETFE film during grafting reaction. In addition, VIm is more basic than 4-VP and its diluting with water forms stronger hydrogen bonds than diluting 4-VP with ethanol[19] making VIm less reactive during the grafting reaction. On the other hand, PVDF film, which has a less chain packing density (1.76 g/cm^3 for PVDF compared to 1.9 g cm^{-3} for ETFE) seems to form more stable radicals than EFTE because the rise in its crystallinity upon irradiation at low doses, unlike ETFE, which has a crystallinity decrease caused by the presence of radiation-sensitive tetrafluoroethylene component in its molecular structure leading to less radical stability.[20] The observations obtained for the comparison of the two models of the two grafting systems confirm the sensitivity of Box-Behnken of RSM to the variation in the monomer nature and its effective optimization for the reaction parameters together with the accuracy in predicting G%.

Evidence of Grafting

FTIR Spectroscopy. Figure 7 shows typical FTIR spectra of grafted PVDF films and its corresponding pristine PVDF and pure poly(4-VP) homopolymer films. The pristine PVDF film is characterized by the presence of symmetric and asymmetric stretching vibrations of CH$_2$ groups at 2854 and 2923 cm^{-1}. The characteristic bands at 1120–1280 cm^{-1} are assigned to the stretching vibration of the —CF$_2$ groups present in the PVDF film. Poly(4-VP) film exhibited inherent peaks at 1595, 1547,

and 1408 cm^{-1} due to C=C and C=N of the pyrdine ring stretching vibrations together with peaks at 3022 and 2983 cm^{-1} of aromatic C—H stretching vibration and its out-of-plane bending vibration at 829 cm^{-1}. The spectra of 4-VP grafted PVDF films clearly show a combination of characteristic peaks originated from the pyridine ring and PVDF film features. These results confirm the grafting of 4-VP onto PVDF films.

FESEM Analysis. Figure 8(a,b) shows surface SEM images for the pristine PVDF and poly(4-VP) grafted PVDF film. As can be seen, the surface of the pristine PVDF appears to be rough,
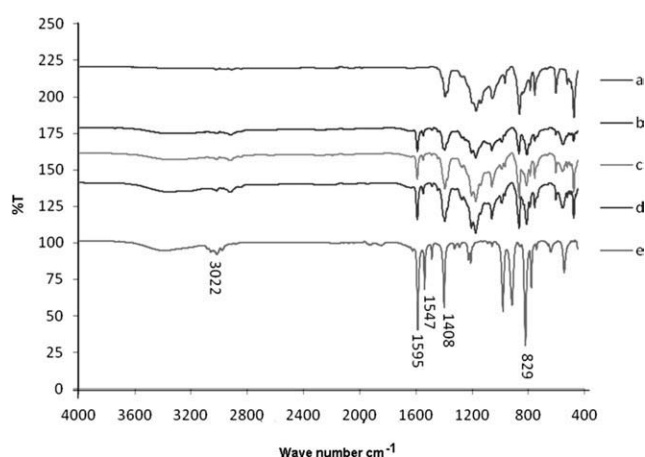
Figure 7. FTIR spectra of: (a) the pristine PVDF, poly(4-VP) grafted PVDF films with various G%: (b) 28%, (c) 48%, (d) 81%, and (e) pure poly(4-VP) homopolymer.

which became rougher with heterogeneous look when poly(4-VP) grafts was attached to the surface after grafting. Figure 8(c,d) shows the qualitative elemental analysis of pristine PVDF and poly(4-VP) grafted PVDF films obtained by EDX. The appearance of N peak in the spectrum of the grafted film is an indication of the formation of poly(4-VP) in the grafted films.

Thermogravimetric Analysis. Figure 9 shows TGA thermograms of pristine PVDF and poly(4-VP) grafted PVDF films having various $G\%$. The pristine PVDF film shows a thermal stability up to about 400°C followed by one–step degradation pattern of polymer molecular chains. The incorporation of poly(4-VP) grafts in PVDF backbone introduces a multistep degradation pattern start below 100°C followed by two degradations commencing at about 300 and 400°C, respectively. The first degradation step is due to the removal of moisture attached to the basic pyridine groups in the grafted film. The second transition occurred at 300°C corresponds to the decomposition of the poly(4-VP) grafts of the copolymers while the massive weight loss at $\sim$ 400°C is due to the degradation of PVDF backbone. It can be noticed that the grafted films did not undergo a complete dissociation with some residues were left at the end of each thermograms unlike the pristine PVDF film, which was completely dissociated. This is most likely caused by the formation of inorganic residue complexes
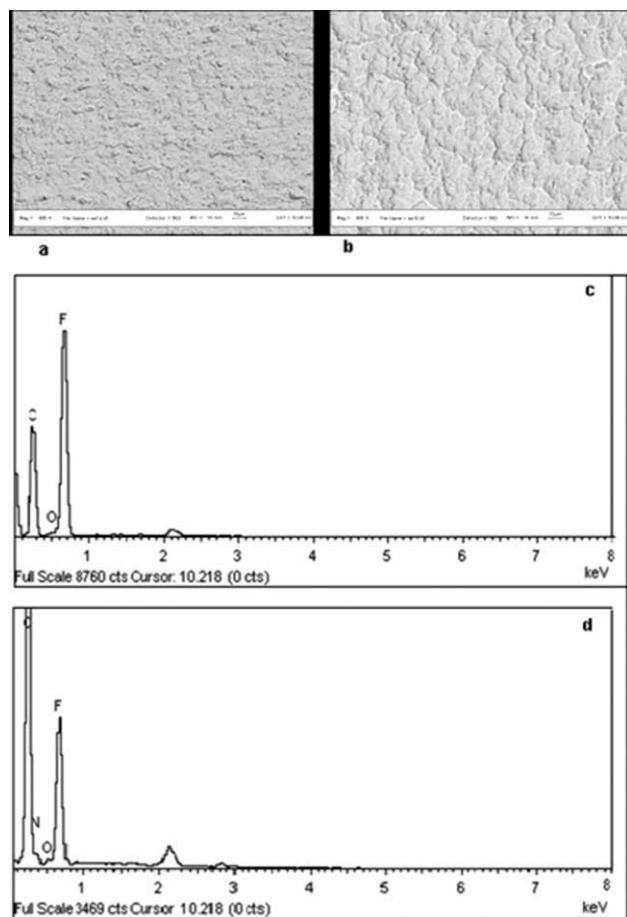

Figure 8. SEM Images of: (a) pristine PVDF and (b) poly(4-VP) grafted PVDF films together with spectra of EDX analysis of: (a) pristine PVDF and (b) poly(4-VP) grafted PVDF films.
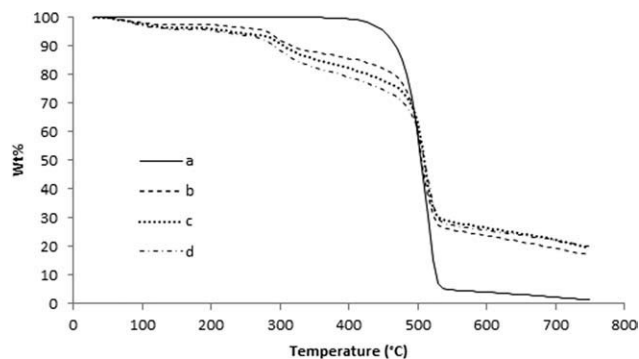

Figure 9. TGA thermograms of: (a) pristine PVDF film and PVDF-g-4-VP copolymer having various degrees of grafting: (b) 15%, (C) 33%, and (d) 51%.

composed of nitrogen originated from poly(4-VP) and carbon of the polymer backbone.

CONCLUSIONS

Grafting of 4-VP onto PVDF film was successfully performed using radiation-induced grafting under controlled reaction parameters, which were optimized by adopting factorial strategies using the Box-Behnken of RSM available in the Design-Expert®6 software. A quadratic model was developed to predict the response i.e., $G\%$. A maximum $G\%$ value of 60 was predicted at a combinational set of optimum reaction parameters. The application of this optimum parameters; monomer concentration of 48 vol %, absorbed dose of 61 kGy, reaction time of 5 h (range of 2–8 h) and a temperature of 62°C (in the range of 55–70°C) produced an experimental $G\%$ value of 58, which confirms the success of the model in predicting the degree of grafting for grafting 4-VP onto PVDF film. A comparison between the present grafting system and that of 1-VIm onto ETFE films further confirms the validity and reliability of the develop statistical models of both grafting systems in predicting $G\%$, optimizing the grafting parameters and tolerating the variation in the types of the monomer and base polymers during radiation-induced grafting reactions. The formation of poly(4-VP) grafts in PVDF films was evident from the chemical, morphological, and thermal properties of the grafted films.

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