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Modeling and optimization aspects of radiation induced grafting of 4-vinylpyridene onto partially fluorinated films

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HIGHLIGHTS

- Comparative study of radiation induced grafting of 4-VP onto PVDF and ETFE films.
- Optimization of reaction parameters for both grafting systems was made using RSM.
- Single factor design for both grafting systems was used as a reference.
- Two quadratic regression models were developed for prediction of grafting yield.
- RSM is an effective tool for handling grafting reactions under different conditions.

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ABSTRACT

Modeling and optimization aspects of radiation induced grafting (RIG) of 4-vinylpyridine (4-VP) onto partially fluorinated polymers such as poly(ethylene-*co*-tetrafluoroethene) (ETFE) and poly(vinylidene fluoride) (PVDF) films were comparatively investigated using response surface method (RSM). The effects of independent parameters: absorbed dose, monomer concentration, grafting time and reaction temperature on the response, grafting yield (*GY*) were correlated through two quadratic models. The results of this work confirm that RSM is a reliable tool not only for optimization of the reaction parameters and prediction of *GY* in RIG processes, but also for the reduction of the number of the experiments, monomer consumption and absorbed dose leading to an improvement of the overall reaction cost.

1. Introduction

Radiation induced grafting (RIG) is a powerful technique for preparation of novel materials for meeting the growing demands in the field of separation and purifications in a wide range of applications (Nasef and Hegazy, 2004) and Nasef and Güven (2012). Particularly, RIG of 4-vinyl pyridine (4-VP) is a fascinating reaction for producing graft copolymers precursors suitable for preparation of various functional membranes (Rath et al., 2008; Schmidt and Schmidt–Naake, 2007; Şanli and Gürsel, 2011; Nasef et al., 2011). Particularly, precursors obtained by RIG of 4-VP onto poly(ethylene-*co*-tetrafluoroethene) (ETFE) films possess a basic nitrogen that can be converted to proton conducting membranes by doping with phosphoric acid. RIG of 4-VP onto poly (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) was earlier used to prepare membranes for water desalination application (Kaur et al., 2001).

Response surface methodology (RSM) is an approximation technique having a collection of mathematical and statistical techniques that can be used for: (i) modeling and optimization of experiments, (ii) determining factors and levels that simultaneously satisfy a set of desired responses, and (iii) determining a region of the factor space in which operating specifications are satisfied. The use of RSM for optimization purposes reduces the cost of expensive analysis methods and their associated numerical noise (Myers et al., 2004).

RSM dates back to the work by Box and Wilson (1951) and was early applied in the chemical industry and currently extended to cover quality improvement and product design (Myers et al., 2009). However, applying RSM in modeling and optimization of RIG reactions is unpopular. Majority of experimental design in such field rely on the single factor design that leads to data waste, excessive monomer consumption and longer reaction time in addition to lack of reproducibility upon scaling-up reactions.

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Recently, we proposed RSM for modeling and optimization RIG of 1- vinylimidazole (1-VIm) and 4-VP onto ETFE film using pre-irradiation method with electron beam (EB) for the first time (Nasef et al., 2011, 2012). However, the flexibility of RSM in optimizing and modeling other reaction involving grafting of 4-VP onto PVDF is not investigated.

The objective of this article is to investigate the modeling and optimization aspects of the reaction parameters for RIG of 4-VP onto PVDF and ETFE films using RSM. The obtained results of grafting yield (GY) are compared with the corresponding data obtained by RIG of 4-VP onto PVDF and ETFE films using a single factor design.

2. Experimental design and optimization

RSM was used to model RIG reaction of 4-VP onto PVDF and ETFE films and optimization of its parameters using RSM through Box–Behnken module of response available in the design expert software (Version 6.0). The independent grafting parameters i.e., monomer concentration (A), absorbed dose (B), temperature (C) and grafting time (D) were varied in four levels versus *GY* (the response). Other parameters such as film thickness and storage of film after EB irradiation were kept constant and excluded from the study to simplify the models. Diluting solvents were selected after a prior screening. The vital ranges of investigated parameters were obtained based some preliminary experiments and from the literature review leading to the values presented in Table 1.

2.1. Fitting of the response

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 software (version 6.0). The quantitative form of relationship between the desired response and independent input parameters in RSM is represented as $y=F(x_1, x_2, x_3, x_4)$. Where, y is the desired response and F is the response function (or response surface).

In the procedure of analysis, the approximation of y was performed using a quadratic polynomial regression model as a function of grafting parameters using Eq. (1), which has linear and quadratic terms in addition to an interaction term features:

$$y_i = b_0 + \sum b_i x_i + \sum b_{jj} x_i^2 + \sum\sum b_{ij} x_i x_j + e \tag{1}$$

where, yi is the desired response *GY*, b is the regression coefficient, x is the independent parameter and e is the experimental error.

An automatic backward reduction iteration function available in Design Expert software was used to eliminate the insignificant parameters at a significance level of $p \leq 0.05$. Probability function analysis was used to estimate the significance of parameters individually and upon interaction. The obtained data was subjected to analysis of variance (ANOVA) using the same software to assess the impact of noise on the data.

Table 1
Reaction parameters and their levels for optimization of grafting of 4-VP onto. PVDF and ETFE films.

Parameters	Level 1	Level 2	Level 3	Level 4
Monomer concentration (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

3. Experimental

3.1. Materials and irradiation

PVDF (thickness of 50 μm and density of 1.76 g/cm^3) and ETFE (thickness of 125 μm and density of 1.69 g/cm^3) films were obtained from Goodfellow (UK). 4-VP, purity of >99% (Aldrich), was used without any further purification. Other chemicals, such as solvents and reagents, were research grade and used as received. The films were washed with ethanol, vacuum dried, sealed under vacuum in thin PE bags and irradiated (at room temperature) to the desired dose using EB accelerator (NHV-Nissin High Voltage, EPS 3000, Cockroft Walton type, Japan). The irradiated films were stored at −60 °C prior to their use for 7 days.

3.2. Grafting procedure

Grafting reaction was performed by introducing a mixture of 4-VP/solvent of desired concentration to the irradiated film in a special ampoule, which was then flushed for 30 min with a purified N_2 and tightly sealed. The ampoule was kept in a water bath at a 60 °C for a desired period of time. After the reaction, the grafted films were extracted under sonication followed by washing and vacuum drying. *GY* was gravimetrically calculated as follows:

$$GY = [(W_g - W_o/W_o) \times 100] \tag{2}$$

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

4. Results and discussion

4.1. Statistical analysis of the response

The average of three runs of the independent parameters for grafting 4-VP onto PVDF and ETFE films in correlation with the responses is presented in Table 2. In RIG of 4-VP onto PVDF, a quadratic polynomial regression equation with a significance level of $p \leq 0.05$ was obtained after the response data were fitted to Eq. (1) leading to the final estimated response model (based on the actual value) as in Eq. (3).

$$y_i = 30.84x_1 + 8.5x_2 + 14.57x_1 + 11.07x_1 x_2 + 20.59 \tag{3}$$

Table 2
Various combination runs for grafting of 4-VP onto PVDF and ETFE according to RSM array.

Run	A: Monomer concentration (vol%)	B: Absorbed dose (kGy)	C: Grafting temperature (°C)	D: Grafting time (h)	*GY* (%) 4-VP/ PVDF	*GY* (%) 4-VP/ ETFE
1	30	60	74	2	19.2	19.5
2	50	100	55	8	112.2	82.0
3	30	20	63	2	12.2	14.7
4	50	100	70	8	78.7	57.6
5	10	100	70	8	7.6	6.0
6	10	20	55	8	8.5	3.6
7	30	60	63	4	29.5	28.7
8	10	20	70	8	3.4	2.2
9	50	20	55	8	59.0	54.3
10	30	100	63	2	24.3	20.2
11	60	60	63	2	85.8	83.4
12	10	100	55	8	4.4	1.7
13	10	60	63	2	7.0	5.1
14	30	60	51	2	2.3	1.5
15	30	60	63	8	15.8	17.3
16	50	20	70	8	43.2	36.3