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Optimization of reaction parameters of radiation induced grafting of 1-vinylimidazole onto poly(ethylene-co-tetraflouroethene) using response surface method

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ABSTRACT

Radiation induced grafting of 1-vinylimidazole (1-VIm) onto poly(ethylene-co-tetraflouroethene) (ETFE) was investigated. The grafting parameters such as absorbed dose, monomer concentration, grafting time and temperature were optimized using response surface method (RSM). The Box–Behnken module available in the design expert software was used to investigate the effect of reaction conditions (independent parameters) varied in four levels on the degree of grafting (*G*%) (response parameter). The model yielded a polynomial equation that relates the linear, quadratic and interaction effects of the independent parameters to the response parameter. The analysis of variance (ANOVA) was used to evaluate the results of the model and detect the significant values for the independent parameters. The optimum parameters to achieve a maximum *G*% were found to be monomer concentration of 55 vol%, absorbed dose of 100 kGy, time in the range of 14–20 h and a temperature of 61 °C. Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate the properties of the obtained films and provide evidence for grafting.

1. Introduction

Radiation induced grafting (RIG) in an interesting method to impart new functional groups to preformed polymers having various morphologies without significant alterations in their inherent properties (Nasef et al., 2011a). The application of this method introduces changes to polymer wettability, adhesion, printability, metalization, anti-fog properties, anti-statics properties and biocompatibility. Thus, it has been used to develop various forms of functional polymers suitable for medical, biological, environmental, chemical and solid state applications (Nasef et al., 2011b).

RIG is most suitable for the development of functional membranes and provides obvious advantages compared to conventional grafting methods. This includes an ability to combine virtually unlimited number of base polymers with many monomers under controlled reaction conditions to achieve membrane compositions and properties for specific application. RIG is simple in practice and can be initiated with various high energy radiation sources (e.g. γ-rays and EB). It also overcomes membrane shaping problem as the reaction starts with a polymer matrix in a sheet form. This made RIG an attractive method for addressing the challenge of the development of proton exchange membranes (PEMs) for fuel cells (Nasef and Hegazy, 2004).

RIG has been used to develop a variety of PEMs bearing sulfonic acid groups suitable for proton conduction in the PEM fuel cells at temperatures in the range of 50–80 °C. Such membranes were prepared by radiation induced grafting of styrene (Li et al., 2004; Gürsel et al., 2007) or styrenic derivatives (Nasef et al. 2011a; Yamaki et al., 2004), with crosslinking agents (Nasef and Saidi (2003); Li et al. (2005); Chen et al., 2006a, 2006b; Yamaki et al., 2007) or co-monomers (Gübler et al., 2009; Ben Youcef et al., 2009) followed by sulfonation reaction. The latest progress in radiation grafted PEMs has been recently reviewed in literature (Nasef, 2008; Gubler and Scherer, 2010). Recently, radiation grafted precursors doped with phosphoric acid have been proposed as proton conducting membranes for high temperature PEM fuel cells (Schmidt and Schmidt-Naake, 2007). The membrane precursor preparation was carried out by radiation induced grafting of heterocylic monomers such as 1vinylimidazole (1-VIm) onto irradiated fluorinated polymer films such as poly(ethylene-co-tetraflouroethene) (ETFE). The selection of VIm was motivated by the presence of–N–that forms a basic center, which conducts protons at a temperature above 100 ºC when forming an acid/base complex with phosphoric acid (Schmidt and Schmidt-Naake, 2007). ETFE was selected for its inertness, thermal stability and mechanical integrity. In addition, it has high

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radiation resistance and forms stable radicals (Nasef et al. 2003). However, the details of the effect of the grafting parameters on the degree of grafting (G%) of VIm onto ETFE films and its optimization using statistical tools have not been reported. Since the grafting level in the membrane precursor is affecting the structure and properties of the resultant membrane to a large extent, it is highly necessary to determine the optimum reaction parameters required to obtain G% suitable for PEM fuel cell.

The objective of this work is to report on the optimization of the reaction parameters for grafting of 1-VIm onto ETFE films using response surface method (RSM). The Box–Behnken model was selected to correlate the four independent parameters having four levels with one dependent parameter (Lenth, 2009). The formulated model was analyzed using analysis of variance (ANOVA) by means of design expert software.

2. Experimental

2.1. Materials

Films of ETFE of 0.125 mm thickness and 1.9 g/cm^3 density were purchased from Good fellow (Cambridge, England). 1-Vinylimidazole (Fluka, Switzerland) with purity >99% was used without further purification. Hydrochloric acid of 37% (JT Bakers) and ion free water (NANOpure® DIamond™) were used.

2.2. Irradiation of ETFE films

The ETFE samples were kept in evacuated thin polyethylene bags and irradiated using a universal electron beam accelerator (NHV—Nissin High Voltage, EPS 3000, Cockroft Walton type, Japan) operated at 2 MeV to a total dose in the range of 40—100 kGy with 10 kGy per pass. The irradiated films were kept in a low temperature freezer at −60 °C before use.

2.3. Grafting of 1-VIm

The Box–Behnken experimental design was applied to minimize the number of experiments and optimize the conditions for grafting of 1-VIm onto ETFE films. The G% was selected as the dependent parameter (response). The monomer concentration, absorbed dose, reaction time and medium temperature were chosen as the independent parameters. Some preliminary exploratory trials were made to assist in the selection of the number of levels and ranges as shown in Table 1.

Grafting of 1-VIm onto ETFE films was performed following the procedure reported by Rohani et al. (2007). The desired combination of grafting parameters was set according to the experimental design array made by Box–Behnken model as shown in Table 2. The irradiated ETFE film (dose 40–100 kGy) of known weight was placed in a glass ampoule, which was tightly sealed and evacuated (1 mbar). The monomer solution of a prescribed concentration (40–70%) diluted with deionized water was bubbled with purified N_2 for 30 min and transferred to the evacuated ampoule containing the ETFE film. The reaction was allowed to continue for chosen periods of time (14–20 h) under a controlled temperature (50–80 °C). At the end of the reaction, the grafted films were removed and rinsed in a 0.1 M HCl solution in an ultrasonicator for 16 h. This is to remove the residues and homopolymer occluded on surfaces of the films. The grafted films were dried at 60 °C in a vacuum oven for 16 h. Finally, the films were weighted and G% was obtained using the following equation:

Table 1
Levels and parameters of optimization study for grafting of VIm onto ETFE films.

Variables	Level 1	Level 2	Level 3	Level 4
Monomer conc. (vol%)	40	50	60	70
Grafting time (h)	12	14	16	18
Grafting temp. (°C)	50	60	70	80
Absorbed dose (kGy)	40	60	80	100

Table 2
Various combinations runs according to RSM array.

Run	Factor 1 Monomer conc. (vol %)	Factor 2 Absorbed dose (kGy)	Factor 3 Grafting temperature (°C)	Factor 4 Grafting time (h)	Response Degree of grafting (G%)
1	65	24	21	40	24
2	80	100	80	14	17
3	60	40	42	17	9
4	80	100	80	20	15
5	40	100	80	20	22
6	40	100	50	14	19
7	60	32	17	60	8
8	40	100	50	20	23
9	80	100	50	14	19
10	60	40	87	17	29
11	90	40	65	17	9
12	40	100	80	14	22
13	30	40	65	17	13
14	60	40	65	12	23
15	60	100	65	17	53
16	80	100	50	20	33

$$G(\%) = \frac{m_g - m_o}{m_g} \times 100 \quad (1)$$

where, m_g and m_o are the weights of the grafted and pristine ETFE films, respectively.

2.4. Characterization of the grafted films

Fourier transform infrared (FTIR) measurements of the samples were recorded on a Nicolet 5700 spectrophotometer in a transmittance mode at a frequency range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were detected and analyzed using Essential FTIR™ commercial software.

Thermal gravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851. All the heating runs were made in a temperature range of 50–700 °C at a constant heating rate of 20 °C min^{-1} and under N_2 atmosphere.

Differential scanning calorimetry (DSC) measurements were recorded on a Mettler Toledo DSC 822 under N_2 atmosphere in a temperature range of 50–300 °C at a constant heating rate of 20 °C min^{-1}. The degree of crystallinity was calculated by taking the heat of melting of 100% crystalline ETFE into account and correcting the recorded values of the heat of melting of the grafted films by dividing over the weight fraction of ETFE as described elsewhere (Nasef and Saidi, 2005).

2.5. 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 software (version 1.6). The software was used to fit the responses to a quadratic polynomial regression equation with respect to the independent parameter of grafting as

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

where y_i is the response, b is the regression coefficient, x is the independent parameter and e is the experimental error.