Radiation Physics and Chemistry 151 (2018) 283–291

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Highly flexible method for fabrication of poly (Glycidyl Methacrylate) grafted polyolefin nanofiber

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ARTICLE INFO

Keywords:
Electrospinning
Polypropylene
Response surface method
Nanofiber
Radiation induced grafting
Glycidyl methacrylate

ABSTRACT

This paper describes the development of highly flexible and simple approaches toward fabrication of syndiotactic polypropylene (s-PP) nanofibers of desired morphology and functionalization with modifiable poly (glycidyl methacrylate) (PGMA) of desired level. To this end, the nanofibers were fabricated by electrospinning. Optimization of electrospinning process was carried out using Box-Behnken design (BBD) of response surface method (RSM) and a linear mathematical model was developed to relate various electrospinning parameters to the average fiber diameter. According to the model calculation, a minimum fiber diameter of 336 nm was supposed to be obtained at a flow rate of 4 ml/min, applied voltage of 16 kV and needle tip to collector distance of 20 cm, which was confirmed by the experiment with only 2.2% error. Furthermore, prediction capability experiments of the model revealed maximum 5.3% and 8.9% deviation from the model-predicted values for applied high voltage and flow rate, respectively. Radiation induced grafting of glycidyl methacrylate (GMA) on the electrospun nanofibers was carried out to impart desired density of oxirane groups to the nanofibrous s-PP.

1. Introduction

Functionalized hydrocarbon materials have found diverse applications in various fields such as energy and environment, healthcare, etc. Typically, the materials in a nanofibrous form have been successfully used for water and air filtration (Chen et al., 2018), biosensors (Guler Gokce et al., 2018), drug delivery (Adepu et al., 2017), wound dressings (Liang et al., 2018), enzyme immobilization (Wu et al., 2018) and energy (Abouzari-lotf et al., 2016). Furthermore, nanofibers have been used as catalysts (Chang et al., 2015) and as membranes (Abouzari-lotf et al., 2017) in electrochemical energy-associated devices. In order to design such materials, controlling the morphology and developing flexible methods for introducing various functionalities are of great concerns. In fact, it is quite difficult to plan the morphology and functionalization levels for specific substrates.

Electrospinning is a very simple and robust method for producing nano- and micro-fibers from a wide range of polymers. In electrospinning, a high voltage is applied between a needle and a conductive collector placed in a distance from the needle tip. This voltage induces charges with the same polarity on the surface of the solution droplet at the tip of the needle and a polymeric jet is ejected toward the collector. Electrospun polymeric nanofibers have several advantages over regular fibers including very high surface area and controllable porosity and composition with the aim of achieving different characteristics (Bhardwaj and Kundu, 2010). In order to control and predict the morphology of electrospun nanofibers, various techniques, most importantly response surface methodology (RSM), have been used (Khanlou et al., 2015; Bösiger et al., 2018).

RSM is a preferred optimization technique owing to its simplicity and ability to study the interaction between various parameters (Ziabari et al., 2010). It is a collection of statistical and mathematical techniques capable of allowing the construction of an approximation model for descripting the relationship between a response and a set of predictor variables, on the basis of the empirical data obtained using an

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https://doi.org/10.1016/j.radphyschem.2018.07.002
Received 15 April 2018; Received in revised form 5 July 2018; Accepted 6 July 2018
Available online 09 July 2018
0969-806X/

appropriate experimental design. Thus it is possible to carry out a simultaneous investigation of the effect of the single variables and their mutual interaction on the response, with the possibility of defining quantitatively optimized parameters to be applied in a given process (Boaretti et al., 2015). Central-Composite design (CCD) and Box–-Behnken design (BBD) are the two most commonly used techniques employing RSM experimental designs and optimization processes. However, having ≥ 3 factors makes the quadratic response surface model with BBD more advantageous compared to the CCD (Ray and Lalman, 2011).

While nanofibers are very promising materials in different applications, they usually need to be modified using different techniques to promote their applications by imparting functional or ionic groups of desired characteristics. There are several methods for modifying polymeric nanofibers such as dip-coating, interfacial polymerization, and graft polymerization which can be initiated chemically, photo-chemically, thermally and radiochemcially (radiation induced grafting) (Nasef et al., 2016). Among others, radiation induced grafting (RIG) is a very flexible modification technique because of its potency to modify chemical and physical characteristics of polymeric substrates in various physical forms (films, particles or fibers) without changing their inherent properties (Mahmoud Nasef et al., 2016). RIG involves the use of high energy radiations (e.g. γ-rays and electron beam) to form active sites on the main polymeric backbone. These active sites react with desired monomers to start polymerization reaction and as a result, side chain grafts are formed on different sites of the main polymer (Nasef and Hegazy, 2004).

The main aim of this work is to develop a highly flexible method for the fabrication of grafted hydrocarbon nanofibers with desired morphology and functionality level, capable of hosting various groups for potential utilization in a variety of applications such as wound dressing, adsorption, catalysis and filtration. Polypropylene (PP) was used as a substrate due to its good mechanical properties, chemical resistance and thermal stability (Aizenshtein and Efremov, 2006). In fact, electrospinning of polyolefins, including PP, was limited to melt electrospinning because of their low solubility and high electrical resistivity. Thus, studies on PP electrospinning from solution are scarce. Typically, syndiotactic polypropylene (s-PP) with average fiber diameters of 650 and 510 nm were obtained by dissolving the polymer in the solvents mixtures of cyclohexane/acetone/dimethylformamide and decalin, respectively (Lee et al., 2009; Watanabe et al., 2011; Tomoki Maeda and Hotta, 2013). Alternatively, higher temperatures were also used to obtain better PP nanofibers using electrospinning (Liu et al., 2013). However, optimization of electrospinning to control fiber diameter and the development of a model that can predict the diameter under the effect of various parameters has not been reported in the literature. Glycidyl methacrylate (GMA) is chosen to functionalize nanofibrous polyolefin substrate since it contains oxirane group that is capable of hosting various functional groups when treated with appropriate agents under mild conditions, which is suitable for different applications.

For this purpose, s-PP nanofibers were prepared by electrospinning technique under different spinning conditions and the average fiber diameter (AFD) was obtained for each electrospun s-PP nanofiber. This is followed by development of a statistical model for optimization of the electrospinning parameters in order to control and predict the fiber diameter using Box-Behnken design (BBD) of RSM. The electrospun s-PP nanofibers were functionalized with GMA using radiation-induced grafting method under controlled grafting parameters. Finally, a nanofibrous structure containing oxirane rings, susceptible for ring-opening reaction for introducing various functionalities for different applications was achieved.

2. Experimental

2.1. Materials

Syndiotactic polypropylene (M_w = 174,000; M_n = 75,000), decahydronaphthalene (decalin) (reagent grade, 98%), dimethylformamide (DMF, ≥ 99.8%), GMA (purity ≥ 99%), and tetrahydrofuran (THF) (anhydrous, ≥ 99.9%) were purchased from Sigma-Aldrich. Acetone (Analytical grade, Fischer Scientific) and methanol (Merck Millipore) were used as received without further purification. N_2 gas (> 99.99%) was supplied by Linde AG (Malaysia). Deionized water was used for preparation of solutions.

2.2. Electrospinning

s-PP of known weight was dissolved in a mixture of decalin, acetone and DMF (80:10:10 wt%) at 65 °C to prepare 7.5 wt/v% polymer solution, unless stated otherwise (Watanabe et al., 2011). The solution was electrospun using an automated lab-scale electrospinning machine with a rotary drum collector, dual syringe spinneret system and chamber temperature control (Electroris, FNM Co. Ltd, Iran) at 45 °C.

The electrospinning conditions such as applied voltage, needle tip to collector distance (TCD), and flow rate (considered as independent parameters) were varied according to the combinations obtained by Box-Behnken design (BBD) of RSM as presented in Table 1. The average diameter of electrospun nanofibers was chosen as the dependent parameter. The employed BBD was in a form of an incomplete three-level factorial design. Each independent parameter was placed at three equally spaced coded values as −1, 0 and + 1 (Box and Behnken, 1960). Design expert software, version 7, was used to perform the experimental design and data manipulation. The selection of meaningful ranges for each independent parameter was made based on preliminary studies conducted by our group.

2.3. Grafting of GMA

The s-PP nanofibrous sheets were sealed inside polyethylene thin plastic bags and irradiated using a universal electron beam accelerator (NHV—Nissin High Voltage, EPS3000, Cockroft Walton type, Japan) that was operated at 1 MeV and a beam current of 10 mA with a total dose in the range of 40–200 kGy. After irradiation, samples were kept inside a freezer at − 40 °C before being used for grafting within 3 days.

Pre-irradiation technique in which irradiation and introduction of

Table 1
Box-Behnken design array of experiments and response results.

Runs	Applied voltage (kV)	Distance (cm)	Flow rate (ml/h)	Average diameter (nm)	Fiber evaluation[a]
1	12	15	2.5	553	+
2	16	10	2.5	628	+
3	16	15	1.0	589	+ +
4	12	20	1.0	655	+
5	8	15	4.0	505	–
6	12	15	2.5	540	+
7	16	20	2.5	438	+ +
8	12	10	1.0	670	+
9	12	15	2.5	506	+
10	8	20	2.5	594	–
11	8	10	2.5	668	+
12	12	15	2.5	582	–
13	12	20	4.0	391	–
14	12	10	4.0	384	–
15	16	15	4.0	386	–
16	8	15	1.0	738	+ +
17	12	15	2.5	523	+

[a] fibers were classified as: very good (+ +), good (+) and poor (-).