Wat.Ener.Food.Env.J 1, No. 1,73-86 (2020)

Water, Energy, Food and Environment Journal
An International Journal

http://dx.doi.org/10.18576/wefej/010105

Surface Modification of Seven Bores Hollow Fiber Membranes by Grafting Sulfonic Group, a Modeling Approach to Quantify the Degree of Sulfonation

Elham El Zanati[*]

National Research Center, El Buhouth St., Dokki, Cairo, Egypt., P. Code 12622.

Received: 1 Apr. 2019, Revised: 22 Apr. 2019, Accepted: 15 May. 2019.

Abstract: The active sulfonic group was grafted on a preprepared Seven Bore Hollow Fiber membranes (SBHF) of PolyEtherSulfone (PES), it is used for esterification catalyzation as a novel catalytic membrane with a smart surface and excellent mechanical properties. A kinetic model incorporated the grafting mechanism, describes the polymerization physically and mathematically. Surface chain grafting occurs by both monomer and backbone polymer. The kinetics of isothermal (25°C) graft polymerization of the active functional group onto the prepared SBHF PES mem-branes was previously studied. The polymerization initiated with 0.5N H_2SO_4, then use the Styrene monomer of concentrations ranging 12 vol. % for polymerizations, which was terminated using a 0.5N H_2SO_4 formulating the active sulfonic groups attached to the pores of the SBHF PES membranes. The degree of sulfonation was determined using the experimental results and compared with that forecasted by several methods: determine the conversion of the activation step experimentally, by the acid-base back titration method, calculation by the H+ and predicted by the developed mathematical model. It has a good harmony with such experimentally achieved results. The degree of sulfonation is determined, using four approaching ways, they are very close: 21.89, 23, 21.57 and 22.67%. The IEC was, also, determined and it equals 0.1316 meq/g.

Keywords: Multi Hollow channel, Membrane Grafting, Modeling.

1 Introduction

Recently, membrane processes are reputable and exceptional technologies for separation, concentration, purification, and catalysis. It is recognized by its fast-moving, energy-saving and environmentally friendly.

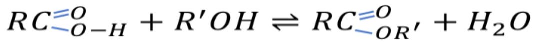
The membranes catalysis is used for chemical reactions, it has an influential immobilized functionalized group, a potential concern of the catalytic membranes is the efficient elimination of the equipment corrosion especially in the case of the acid catalyst [1]. The membrane grafting is used to implant the functional catalytic group onto the membrane.

The grafting copolymerization is a prominent way to adjust the properties of the polymer according to appropriate specifications designed for particular applications. The selection of optimum synthetic monomers and the handling of the grafting conditions allow the modification of the natural polymers into customized materials for various applications [2,3].

Surface grafting can produce covalent bonding between the membrane surface and the graft molecules, leading to more permanent and well-mannered layer on the membrane surface. The chemical, enzymatic, gamma rays, Ultra Violet, plasma, etc. are used for grafting process triggering [4].

Correspondingauthore-mail: eelzanati@hotmail.com

The esterification reaction was taken as an example to study the grafting of the suitable functional group on a membrane, the esters have chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is heating a carboxylic acid; R-CO-OH with alcohol; R'-OH (Equation 1) in the presence of an acidic catalyst [5]. A mineral acid is usually used as a catalyst to push the esterification reaction in the forward direction. At the end of the reaction, the acid catalyst should be neutralized, precipitated and separated, in order, to isolate the product [5, 3,4].



$$RC\genfrac{}{}{0pt}{}{=O}{-O-H} + R'OH \rightleftharpoons RC\genfrac{}{}{0pt}{}{=O}{-OR'} + H_2O \qquad (1)$$

Here, the membrane catalysis is an excellent candidate used to avoid the separation, neutralization and purification steps. The catalytic membrane reactor (CMR) is a unit that acts simultaneously as a reactor/separator [6-7].

PolyEtherSulfone is a smart polymer using as a membrane base material due to its excellent characteristics as film-forming, proper chemical resistance, thermal and mechanical stability, and adequate reactivity in electrophilic substitution [8-12].

In recent years, the development of the catalytic membrane reactors is increasing up and giving more attention. They have a membrane in a different configuration; flat sheet, spiral wound and hollow fiber membranes.

A Multi Bore Hollow Fiber (MBHF) membrane is a newly emerged configuration, offered an alternative of the single bore hollow fiber membranes of an exceptional high mechanical strength, high stability and optimum configuration [13]. Therefore, an earlier prepared Seven Bore Hollow Fiber (SBHF) PolyEtherSulfone (PES) membrane was used in this work.

The grafting of a functionalized sulfonic group on the SBHF PES membrane is developed for application in a catalytic membrane reactor as an alternative to traditional catalysts [11,12]. The grafting process is conducted through permeating the initiator, monomer, and terminator through the membrane channels and pores. During the initiation step the sulfonic group attaches the polymer backbone, then, the styrene monomer joins the sulfonic group. The monomer permits multiples polymerization step, where, it makes more than 100 repeated unit of the polymer chain in one pore [14,15]. The grafting reaction is ended by the termination followed activation steps, where the sulfonic functional group attached to the chains of styrene monomer. Many mathematical models were developed to study the grafting process, to obtain the desired catalytic efficiency and to optimize the affecting parameters [16].

The present work is a part of an integrated project designed to prepare SBHF membrane of PolyEtherSulfone and to apply it for preparation 2-ethyl hexanoate (Ester) which is used in laundry dishwashing, lubricants and greases products, and produce biodiesel and biofuels.

It is aiming to study the grafting process of the sulfonic group on SBHF PES theoretically via developing a mathematical model, determine the catalytic efficiency and the degree of sulfonation. The model is verified using earlier experimental results [17].

2 Model Developments

2.1 Grafting Process Description

A previously prepared SBHF PES membranes, in an earlier project, were used in the current research (Figure 1) [17]. Therefore, a brief exploration of the previous experimental work is mandatory herein to facilitate the understanding of the model derivation.

All grafting steps were carried out using a glass membrane reactor (Figure 2). It comprises a glass tube of 3 cm diameter filled with 13 fibers of Seven Bores of PolyEtherSulfone. The reactants were heated to the desired temperature (25 ºC) and pumped to the glass reactor using a peristaltic pump.

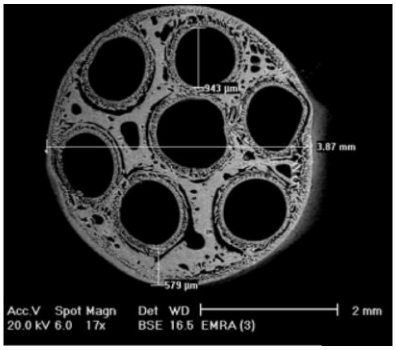
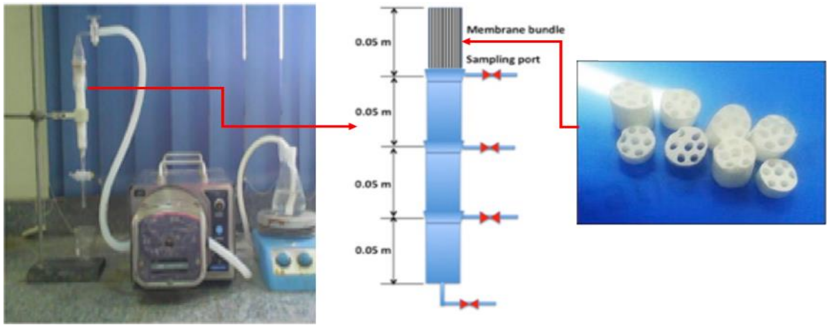


Fig.1: Developed SBHF PES membrane.



Experimental Set-up Glass Membrane Reactor Seven Bore Hollow Fiber Membranes

Fig.2: Membrane reactor of Seven Bore Hollow Fibers.

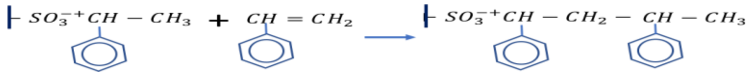
A mathematical model was developed to describe the grafting of a functional sulfonic group onto the SBHF PES membrane. It depends on studying the three steps of grafting process; initiation, polymerization, and activation, it is solved simultaneously and verified using the formerly obtained experimental results of the grafting process.

2.1.1 Initiation

The surface of the thirteen fibers of SBHF PES membranes was modified, and exposed to 0.5N H_2SO_4 at 25 ºC for 1 h. The solution was permeated throughout the PES membranes to determine the optimum time for complete initiation step, the changes of the H_2SO_4 concentration with time was recorded.

2.1.2 Polymerization (propagation)

The polymerization is the essential step of the grafting process, where the styrene monomer was grafted into membrane pores to give chains of the polymer, which holds the functional groups (sulfonic groups). Equation (2) illustrates the propagation step of the polymerization reaction. The styrene monomer carbon-carbon double bond can provide linkages that undergo chain polymerization. In the chain polymerization, the repeating process of the polymer due to the double bond of styrene monomer and the polymerization composed of monomer growth by more cationic polymerization [17].



(2)

In the polymerization step, the styrene mixture (styrene/toluene, 12%) was permeated throughout the membrane reactor (13 SBHF PES membrane fibers), at 25 ºC for 1 h, the change of styrene concentration with time was monitored [16,18].

The polymerized membranes were stored in water for conditioning, and preventing cracking due to drying.

2.1.3 Activation

Activation of the polymerized membranes is the final grafting step, where the active sulfonic group was attached to the styrene, however, the free branch of the styrene polymer inside pores can hold the sulfonic group of negative charge. The change of concentration of the activator; [H_2SO_4] with time was documented during permeating 0.5N H_2SO_4 on the polymerized membrane at 25ºC. After reaction completion, the active sulfonic groups were grafted on the membrane bores as shown in Figure (3).

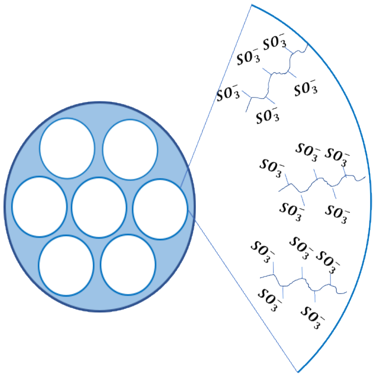


Fig.3: The grafted polystyrene and attached active sulfonic group in a membrane pores.

The grafted SBHF PES membranes were characterized to confirm the occurrence of the grafting process and determination of the degree of sulfonation as well.

Fourier transforms infrared spectra (FTIR) was used to assure the introducing of the sulfonic group in the pores of SBHF PES membrane. The experiments were carried out at room temperature, on the sulfonated, polymerized membranes, and activated sulfonated SBHF PES membrane as well. Figure (4) depicts the FTIR spectra on the sulfonated, polymerized, and activated sulfonated SBHF PES membrane.

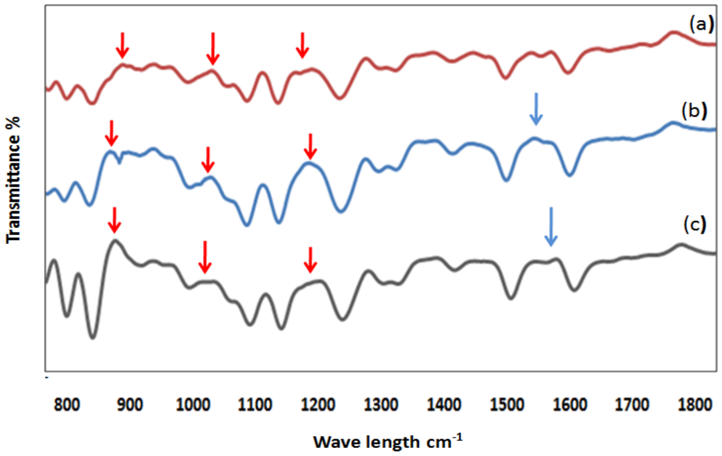


Fig. 4: FTIR for (a) sulfonation membrane (initiation step), (b) polymerized membrane and (c) grafted membrane (termination step).

Moreover, the structure of the sulfonated SBHF PES membrane was determined by NMR analysis using the *Jeol* spectrometer at a resonance frequency of *500-MHz* at different time intervals up till 60 min. This technique was used to determine the degree of sulfonation.

The sulfonated SBHF PES membrane was also characterized using the NMR spectroscopy [17]. The presence of a sulfonic group causes a significant down-field shift ranged from 7.3 to 7.5 ppm of the hydrogen located in the ortho-position at the aromatic ring. The H-NMR spectrum (Figure 5) was measured over a wide spectral range with a very short spacing of the two consecutive pulses to avoid the dumping of the broad signal components. It is clear from the figure (5) that the peak of the sulfonic group (~ 7.5 ppm) is getting obvious by time, it became significant after 15 min, it took the well-formed shape at 30 min.

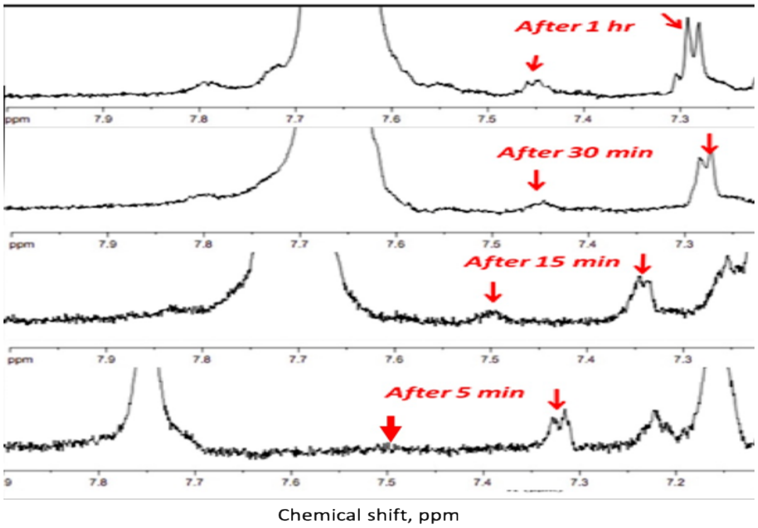


Fig.5: H-NMR analysis of the membrane after activation step at different time.

2.2 Kinetic Study of Grafting Process

2.2.1 Tentative Polymerization (propagation) Mechanism Equations

The polymerization (propagation) mechanism for the grafting of active functional group SO_3^- on SBHF PES membranes was described, as given in Table (1), by the customary initiation, propagation, and activation steps.

Table 1: Polymerization mechanism equations.

1- Initiation	
1	$H_2SO_4 \overset{k_d}{\rightarrow} HSO_3^o + OH^-$ (3)
2	$T \overset{k_s}{\rightarrow} T^o$ (4)
2- Propagation	
3	$HSO_3^o + S \overset{k_{i,M}}{\longrightarrow} S^o + HSO_3^-$ (5)
4	$T^o + S \overset{k_{i,s}}{\longrightarrow} S^o + T^-$ (6)
5	$S^o + S \overset{k_p}{\rightarrow} S_n^o + S_m^o$ (7)
3- Activation	
6	$S^o + [H_2SO_4] \overset{k_t}{\rightarrow} S[SO_3]^- + H^+ + OH^-$ (8)
7	$S^o{}_n + [H_2SO_4] \overset{k_t}{\rightarrow} S_n[SO_3]^- + H^+ + OH^-$ (9)
8	$S^o{}_m + [H_2SO_4] \overset{k_t}{\rightarrow} S_m[SO_3]^- + H^+ + OH^-$ (10)

Where: the forward rate coefficients for the initiator converting to the free radical of the sulfonic group (Equation 3) is given by k_d. The reaction rate coefficient for the changing of the solvent (Toluene) to the free radical is given by k_s (Equation 4). The formation and dissociation rate coefficients of the monomer–initiator associate (Equation 5) is denoted by $k_{i,M}$, the initiation rate coefficients of the free radicals and grafted polymer by the initiator radical are given by $k_{i,M}$ and $k_{i,S}$ (Equation 6). The polymer propagation (polymerization) rate coefficient is given by k_p (Equation 7). The rate coefficients for chain-transfer reactions of a terminating grafted polymer and an activated sulfonic group k_t are given by (Equations 8-10). We have assumed here that three termination and activation steps are governed by the same rate coefficient. Termination by disproportionation was of negligible importance and has been omitted.

2.2.2 Rate of Polymerization Reactions

The rate expressions for the various species in the reaction mixture are obtained, according to the proposed kinetic mechanism (Table I), and depicted in the table (2).

Table 2: Rate Expressions of grafting process.

Rate of reactions according to the polymerization scheme equations

$$r_1 = k_d\, C_{H_2SO_4} \tag{11}$$

$$r_2 = k_s\, C_T \tag{12}$$

$$r_3 = k_{i,M}\, C_{HSO_3^o}\, C_S \tag{13}$$

$$r_4 = k_{i,s}\, C_{T^o}\, C_S \tag{14}$$

$$r_5 = k_p\, C_{S^o}\, C_S \tag{15}$$

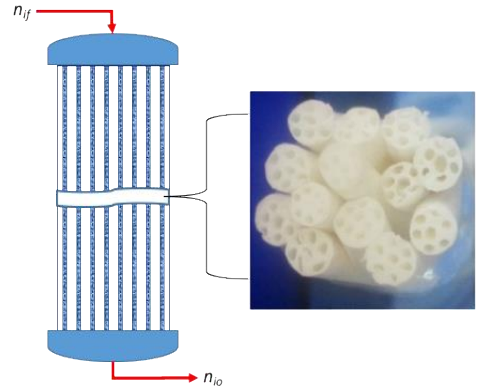
$$r_6 = k_t\, C_{S^o}\, C_{[H_2SO_4]} \tag{16}$$

$$r_7 = k_t\, C_{S_n^o}\, C_{[H_2SO_4]} \tag{17}$$

$$r_8 = k_t\, C_{S_m^o}\, C_{[H_2SO_4]} \tag{18}$$

2.2.3 Kinetic Model Derivation

The grafting process was carried out in a glass membrane reactor, which contains 13 SBHFs of PES membranes (Figure 6), it is operating isothermally at 25°C. Figure (6) illustrates that the reactants are fed from the top, while the products are collected from the bottom. It is designated that (n_{if}) is the number of moles of component (i) in the feed stream, (n_{io}) is the number of moles of component (i) in the product stream and (N) is the number of components.



i component and *j* reactions Inside reactor cross section

Fig.6: Mass flow diagram of chain reaction in membrane reactor.

The mass balance design equations derived for a time increment (Δt) inside the reactor for each reaction in the chemical engineering system of j consecutive reactions of reaction rates r_{ij} ($r_{i1}, r_{i2}, \ldots r_{ij}$), where j is equal to 8, and i components ($i=1,2, \ldots .N$) equal to 16, as follows:

$$n_i + \Delta n_i = n_i \sigma_i r_i \Delta t \tag{19}$$

$$\frac{\Delta n_i}{\Delta t} = \sigma_i r_i \tag{20}$$

$$\frac{dn_i}{dt} = \sigma_i r_i \qquad (21)$$

For multiple reactions, it was written as:

$$\frac{dC_i}{dt} = V \sum_j^N \sigma_{ij}\, r_j \qquad (22)$$

At $t = 0$; $C_i = C_{if}$, and at any t; $C_i = C(t)_i$, where V is the reactor volume, cm^3. Table (3) demonstrates the rate of change of the concentration of each component with time.

Table :3 Change of concentration of component *i* with time.

Change of concentration with time	
$\frac{dC_{H_2SO_4}}{dt} = -r_1$ (23)	$\frac{dC_{S^o}}{dt} = +r_3 + r_4 - r_5 - r_6$ (31)
$\frac{dC_{HSO_3^o}}{dt} = +r_1 - r_3$ (24)	$\frac{dC_{T^-}}{dt} = +r_4$ (32)
$\frac{dC_{OH^-}}{dt} = +r_1 + r_6 + r_7 + r_8$ (25)	$\frac{dC_{S_n^o}}{dt} = +r_5 - r_7$ (33)
$\frac{dC_T}{dt} = -r_2$ (26)	$\frac{dC_{S_m^o}}{dt} = +r_5 - r_8$ (34)
$\frac{dC_{T^o}}{dt} = +r_2 - r_4$ (27)	$\frac{dC_{S[SO_3^-]}}{dt} = +r_6$ (35)
$\frac{dC_{HSO_3^-}}{dt} = +r_3$ (28)	$\frac{dC_{S_n[SO_3^-]}}{dt} = +r_7$ (36)
$\frac{dC_S}{dt} = -r_3 - r_4 - r_5$ (29)	$\frac{dC_{S_m[SO_3^-]}}{dt} = +r_8$ (37)
$\frac{dC_{H^+}}{dt} = +r_6 + r_7 + r_8$ (30)	$\frac{dC_{[H_2SO_4]}}{dt} = -r_6 - r_7 - r_8$ (38)

2.3 Degree of Suffocation

The Degree of Sulfonation (DS) shows the number of hydrogen atoms (H) that have been substituted with sulfonate (~SO_3H) group in the polymer chain. The DS reflected the success of the sulfonation process, also, its magnitude signifies the number of active sulfonic groups (SO_3^-) substituting H atoms in aromatic groups. The DS value indicates the ability to absorb water on the membrane, and characterizes the accomplishment of the sulfonation process. Its value signifies the number of sulfonic groups (SO_3^-) substituting H atoms in Styrene. It indicates the ability to absorb water (produced water during the esterification reaction) on the membrane process. The DS was measured by several methods.

2.3.1 Acid-base Back titration

The acid-base back titration method (phenolphthalein as the indicator) was used to determine the DS, a sample of the sulfonated SBHF PES membrane was weighed soaked in 0.1 M NaCl solution for 24 h. The mixture was filtered, and the obtained filtrate was titrated with 0.02 M NaOH. The degree of sulfonation is determined using equation (39), and the IEC is calculated by equation (40).

$$DS\% = \frac{V_{NaOH} \cdot M_{NaOH} \cdot \ MR\ Monomer\ Styrene}{Sample\ weigt} * 100 \qquad (39)$$

$$IEC = \frac{V_{NaOH} \cdot M_{NaOH}}{Sample\ weigt} \qquad (40)$$

Where: V_{NaOH}= volume of NaOH (mL), M_{NaOH} = concentration of NaOH (M).

2.3.2 NMR

For more accurate determination of the DS is the proton nuclear magnetic resonance (H-NMR) techniques. It was used to indicate the attachment of the sulfonic group to the polymer backbone. The equations (41-43) used to calculate the DS.

$$\frac{\nu}{(\alpha-2\nu)} = \frac{AH_E}{\sum AH}, \qquad (41)$$

$$\frac{AH_E}{\sum AH} = Z, \qquad (42)$$

$$DS\% = \frac{\alpha Z}{(1+2Z)} * 100 \qquad (43)$$

Where DS is the degree of sulfonation (mole %), AH_E is the area of H_E (number of hydrogen atoms on adjacent to the sulfonic acid group), ΣAH is integral of the area of other aromatic hydrogen atoms.

2.3.3 Experimental Approach

The DS was calculated from the experimental results of the concentration at any time t of the activator, where, the activator converted to the active sulfonic group (SO_3^-).

$$DS\% = \left[\frac{C^0_{[H2SO4]} - C^t_{[H2SO4]}}{C^0_{[H2SO4]}}\right] * 100 \qquad (44)$$

Where, $C^0_{[H2SO4]}$ is the concentration of the activator at time = 0, while $C^t_{[H2SO4]}$ is the concentration of the activator at any time = t.

2.3.4 Predicted by Developed Model

The developed model was solved to determine the change of the concentration of every intermediate and final product, then it was verified using the experimental results. The DS is calculated using equation (45).

$DS\%$ = ($\sum$active Sulfonic groups/Initial concentration of activator) *100 (45)

3 Results and Discussion

3.1 Model Development and Verification

A little investigation was made on the kinetics of the reaction of grafting of the sulfonic group on PES membranes. The expressions for the rate of polymerization of styrene and activation are based on the set of reactions described by equations (3-10).

The set of rate equations of each intermediate and final product described by equations (31-38) are solved numerically using Matlab b2014 Simulink; figure (7) illustrates the block diagram of the numerical Simulink solution. The model was then verified with the formerly obtained experimental results illustrated in table (4) [18].

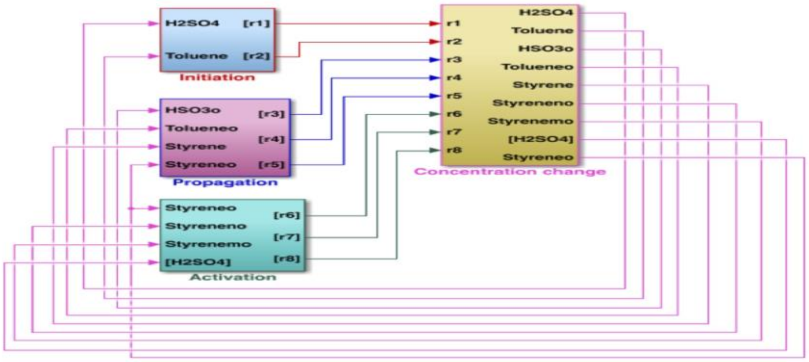


Fig.7: the Simulink diagram of the model solution.

Table 4: The change of the initiator (H_2SO_4), Styrene, Activator ($[H_2SO_4]$), Conversion with time.

Time, min	H_2SO_4, mol/l	Styrene, mol/l	$[H_2SO_4]$, mol/l	Toluene, mol/l	Monomer conversion, X
0	0.51	1.047	0.51	7.68	0
5	0.506	0.760	0.505	7.55	0.273
10	0.504	0.600	0.502	7.41	0.427
15	0.502	0.360	0.5	7.28	0.656
20	0.50	0.150	0.49	7.18	0.857
25	0.50	0.10	0.49	7.03	0.904
30	0.50	0.02	0.48	6.91	0.990
35	0.50	0	0.47	6.79	1
40	0.49	0	0.46	6.67	0.999
45	0.49	0	0.45	6.55	0.999
50	0.49	0	0.43	6.44	0.999
55	0.49	0	0.42	6.33	1
60	0.48	0	0.4	6.23	1

The rate of consumption of Styrene and its free radicles is expressed by equations (29 and 31).
In this context, the rate of production of the Styrene free radicals is equal the rate of depletion, therefore, depending on equation (31):

$$+r_3 + r_4 - r_5 - r_6 = 0 \qquad (46)$$

$$+r_3 + r_4 = r_5 + r_6 \qquad (47)$$

$$r_3 k_{i,M}\, C_{HSO_3^o}\, C_S + k_{i,s}\, C_{T^o}\, C_S = k_p\, C_{S^o}\, C_S + k_t\, C_{S^o}\, C_{[H_2SO_4]} \qquad (48)$$

By rearrangement and simplification, the rate of polymerization is [19]:

$$Rp = k_p\, C_S^2 \frac{k_d C_{H2SO4} + k_{i,S} C_T}{k_p C_S + k_t C_{[H2SO4]}} \qquad (49)$$

The polymerization rate is calculated using the reaction rate constants that verified the developed model and provide the fair fitting for both results derived either from the experimental work or predicted by the model, these reaction constants are k_d, ks, $k_{i,M}$, $k_{i,S}$, k_p, *and* k_t: 0.0009012 s^{-1}, 0.003525 s^{-1}, 0.0051 $cm^3mol^{-1}s^{-1}$, 1 $cm^3mol^{-1}s^{-1}$, 5 $cm^3mol^{-1}s^{-1}$, and 0.0055 cm^3 mol^{-1} sec^{-1} respectively. Figure (8) illustrates the predicted polymerization rate, it is apparent that the reaction is almost terminated at t = 30 min, therefore, the reaction time can be optimized and stopped at this time. Furthermore, as depicts in figure (9), after 30 min, the conversion of the polymerization step (X) approaches 1. Meanwhile, it is clear to notice that, there is a fair agreement between the conversion calculated using the experimental results and that predicted by the verified mathematical model. Figures 8 and 9 confirmed that the polymerization step is approximately completed within 30 min. Furthermore, it is noticeable from the figure (5) that the peak of the sulfonic group (~ 7.5 ppm) is getting obvious by time, it became significant after 15 min, it took the well-formed shape at 30 min., which is compatible with the polymerization rate and with the polymerization conversion.

The kinetic model provides excellent agreement with the experimental initiator (H_2SO_4), monomer (Styrene) and activator ($[H_2SO_4]$) concentration changed with time. The figure (10) illustrates the change of concentration with time for both initiation and activation steps, the iterative model solution gives fair agreement of the experimental results of monitored concentrations and the corresponding predicted values, which obtained from the model. Figure (10) illustrates that the concentration of the initiator (H_2SO_4) is decreased slowly with time, it may be referred to the initiator which is contributed in one reaction (equation 3) just to start the grafting process, while, the change of the concentration of the activator ($[H_2SO_4]$) is decreased relatively faster more than the initiator, it is attributed to its consumption during three simultaneous reactions, which are responsible for attaching the active sulfonic group to the free side of styrene (equations 8-10).

Figure (11) depicts the change of concentration of monomer (styrene) with time as predicted from the developed

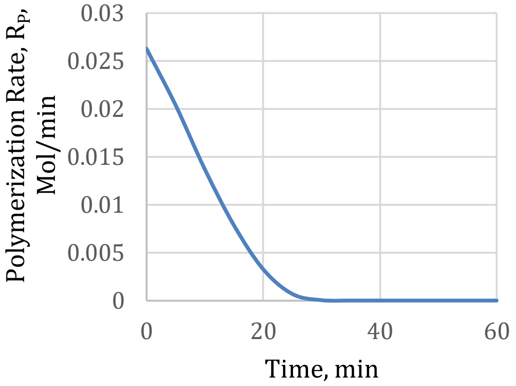


Fig.8: Change of polymerization rate with time.

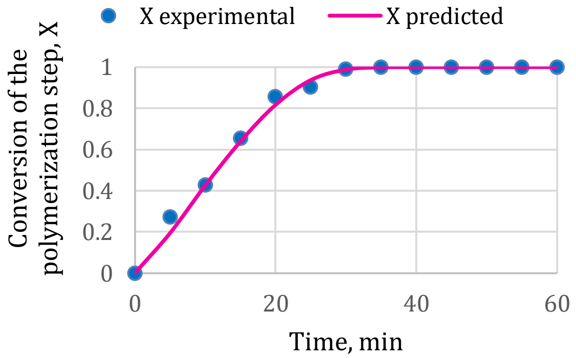


Fig. 9: Monomer (Styrene) Conversion.

model, which has a good agreement with the corresponding experimental results of styrene. Furthermore, figure (11) illustrates the changes of all intermediate styrene free radical concentration with time, moreover, it is obvious, that the styrene monomer is consumed during 30 min, while, in the beginning, the free radicals of styrene (S^o, S_n^o, S_m^o and the total sum of free radicals) is increased, then decreased, because they are consumed at the end of the grafting process when the active sulfonic groups are formed.

The free radicals of styrene can carry the sulfonic groups in the activation step; figure (12) depicts the change in products concentration with time; these products namely are: $S.SO_3^-$, $S_n.SO_3^-$ and $S_m.SO_3^-$, the sum of the three active component gives the product of the active functional group (SO_3^-).

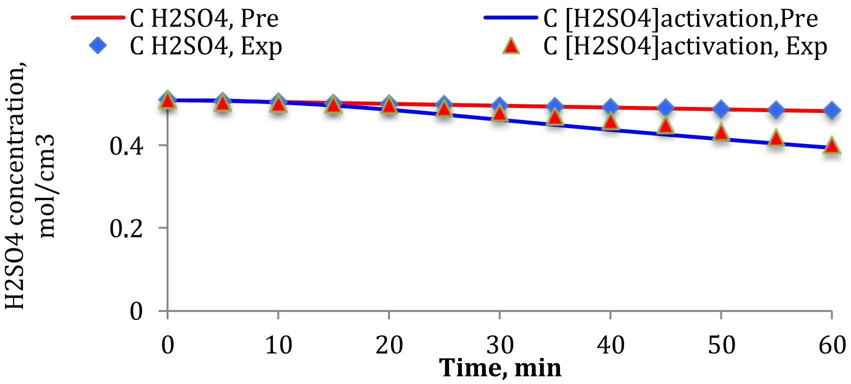


Fig.10: The change of initiator concentration; C_{H2SO4} and activator concentration; $C_{\mathrm{[H2SO4]}}$ with time at initiation and activation steps.

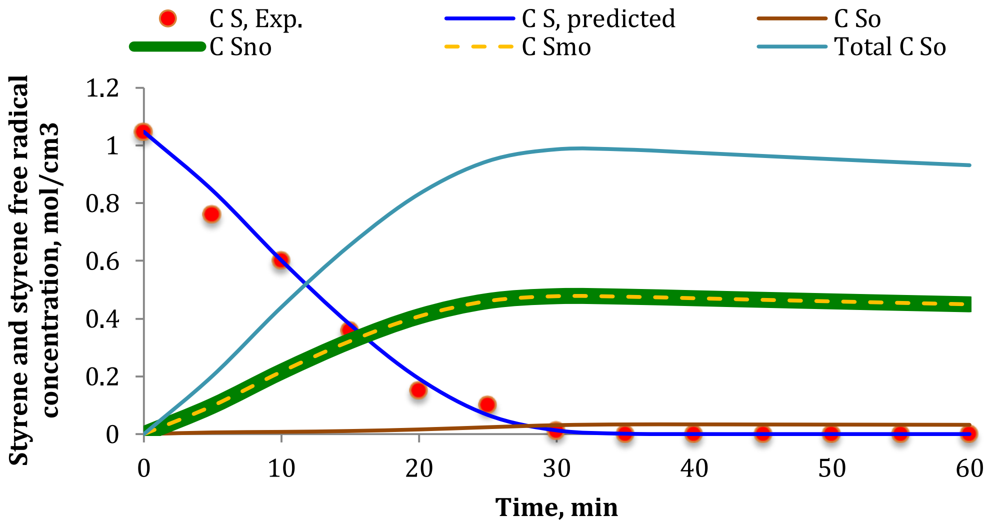


Fig.11: The predicted change of styrene concentration with time.

3.2 Determination of DS

3.2.1 Acid-base Back Titration

3.2.1.1 Degree of Sulfonation

The DS was determined quantitatively via the titration method. At the end of the grafting process, a sample of the developed sulfonated SBHF PES membrane of 0.38 g was soaked in 0.1 M NaCl solution for 24 h. The filtrate was titrated with 0.02 M NaOH. The degree of sulfonation is determined using equation (39). The DS was calculated and depicted in figure (13), it equals 21.89%.

3.2.1.2 Ion Exchange Capacity

Ion exchange capacity (CEC) shows the number of milli-equivalents per gram of polymer weight. The purpose of this analysis is to determine the ability of Sulfonated SBHF PES membrane to exchange the cations attached to their functional group with other cations given to the system. The value of ion exchange capacity (IEC) is determined using equation (40). It equals 0.1316 mequ/g, and it depicted in figure (13).

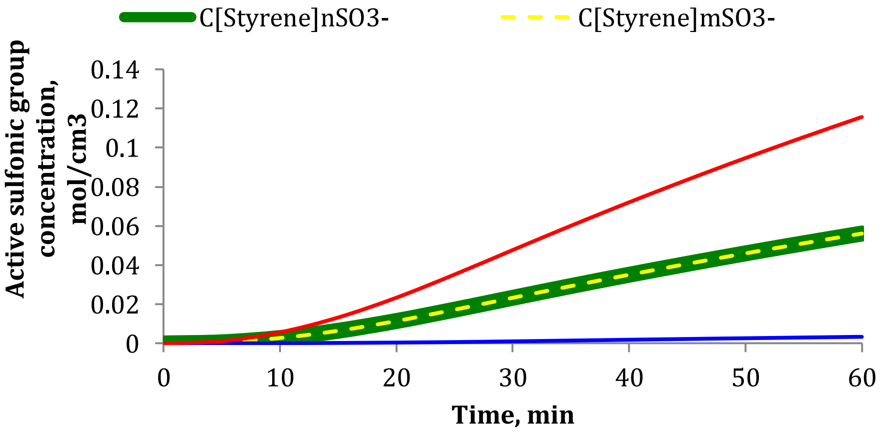


Fig.12: The predicted change of concentration of the activation group with time.

3.2.1.3 NMR

The DS is calculated by the proton nuclear magnetic resonance (H-NMR) techniques. The equations (41-43) are used to calculate the DS. It is calculated and it equals 23%.

3.2.2 Experimental Approach

The degree of sulfonation was determined using the results of the experiments that was mentioned on 2.1. The change of degree of sulfonation with time, obtained from experimental, is calculated from equation (44), The maximum degree of sulfonation as illustrated in figure (13) is equals 21.57%.

3.2.3 Predicted by Developed Model

The change of predicted sulfonic group with time was calculated as the percentage of the (total produced active group/initial concentration of the activating agent), it was 22.67% (figure 13).

These results of calculated DS are perfectly matched with each other. In this context, the verified model will be a reliable tool used for scaling up and grafting process design.

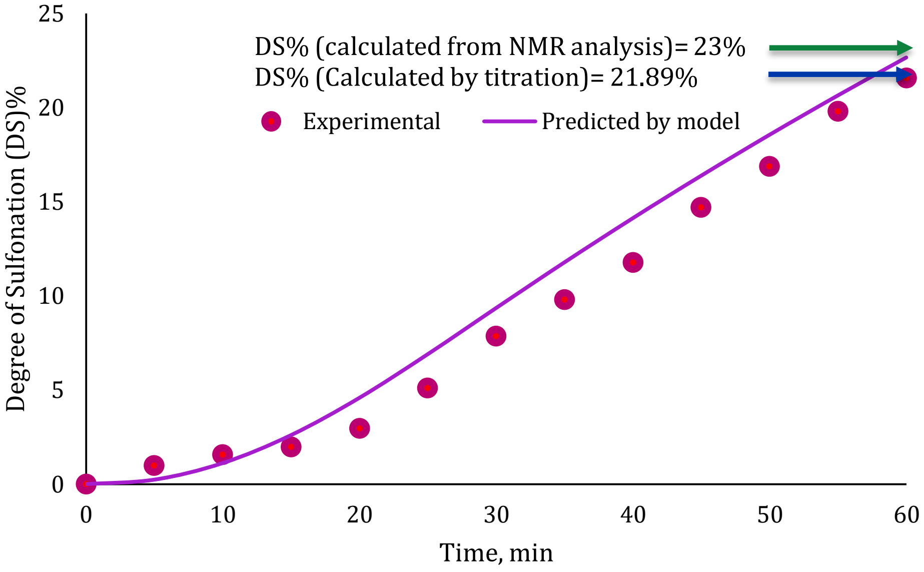


Fig.13: Degree of sulfonation predicted by the model and calculated from experimental results.

Conclusions

A mathematical model of grafting process of Seven Bore Hollow Fiber PES Membranes was developed, te grafting process comprises three steps; initiation, polarization, and activation. The developed model is solved using Matlabb2014, Simulink, and verified using the experiment results of the grafting step. The reaction constants of all grafting steps are determined, which are: decomposition rate constant; k_d; 0.0009012 s^{-1}, rate of solvent constant k_s; 0.003525 s^{-1}, monomer initiation rate constant $k_{i,M}$; 0.0051 $cm^3mol^{-1}s^{-1}$, solvent initiation rate constant $k_{i,S}$; 1 $cm^3mol^{-1}s^{-1}$, propagation rate constant k_p; 5 $cm^3mol^{-1}s^{-1}$ and termination rate constant k_t; 0.0055 cm^3 mol^{-1} sec^{-1}.

The degree of sulfonation is determined using four approaching ways; the titration, the NMR analysis, experimental results of grafting process and predicted by the developed model, they are: 21.89, 23, 21.57 and 22.67%. The IEC was also determined and it equals 0.1316 mequ/g.

List of symbols

AH_E : the integral of H_E (number of hydrogen atoms on adjacent to the sulphonic acid group)

ΣAH is integral of other aromatic hydrogen atoms
C_i: concentration of component i,
C_{if}: feed concentration of component i
DS: the degree of sulfonation (mole %)
H^+: hydrogen cationic ions
C_{H2SO4}: Concentration of the initiator, mol/cm^3
$C_{[H2SO4]}$: Concentration of the activator, mol/cm^3
$C_{[H2SO4]}^0$: Concentration of the activator at time= 0, mol/cm^3
$C_{[H2SO4]}^t$: Concentration of the activator at any time= t, mol/cm^3
C_{HSO3^-}: Concentration of the bisulfite active group, mol/cm^3
C_{HSO3^o}: Concentration of the initiator free radical, mol/cm^3
C_{OH^-}: Concentration of hydroxyl group anionic ions, mol/cm^3
C_S : the monomer (Styrene), mol/cm^3

$C_{S_i^o}$: Concentration of Styrene (monomer) free radical, where i= 1, n or m, mol/cm^3
C_T: Concentration of the Toluene (solvent of Styrene), mol/cm^3
C_{T^o}: Concentration of the Toluene (solvent of Styrene) free radical, mol/cm^3
DS : Degree of sulfonation
k_d: is the decomposition rate constant; cm^{3}mol^{-1}sec^{-1}
k_S : is the solvent rate constant; cm^{3}mol^{-1}sec^{-1}
$k_{i,M}$: is the initiation rate constant of polymer; cm^{3}mol^{-1}sec^{-1}
$k_{i,s}$: is the initiation rate constant of solvent; cm^{3}mol^{-1}sec^{-1}
k_p : is the rate of chain propagation; cm^{3}mol^{-1}sec^{-1}
k_t : is the termination constant. cm^{3}mol^{-1}sec^{-1}
N: The number of components
n_i: The number of moles of component (i) at any time, mole
n_{if}: The number of moles of component (i) in the feed stream, mole
n_{io}: The number of moles of component (i) in the product stream, mole
$r_{ij:}$ reaction rate of component i at reaction j, mol/s
Rp: Polymerization rate, mol/s
SO_3^-: Active sulfonic group

t: Time at any time t

V: Volume of reactor, cm^3

α: The total number of Hydrogen with different electron density in the aromatic rings, equal to 8 for SPES

ν is the number of H_E hydrogen atom

σ equal -1 for reactants and +1 for products

References

[1] W. Shi, B. He, J. Li, Esterification of acidified oil with methanol by SPES/PES catalytic membrane, Bioresource Technology., **102(9)**, 5389–5393, 2011.

[2] E. ElZanati, S. Ritchie, H. Abdallah, R. Ettouny, M. El–Rifai, Esterification Catalysis through Functionalized Membranes, Int. J. Chem. React. Eng. 9 Note S6, 1-20, 2011.

[3] I. Noordergraaf, T. Fourie and P. Raffa, Free-Radical Graft Polymerization onto Starch as a Tool to Tune Properties in Relation to Potential Applications. A Review, Processes., **6(31)**, 1-14, 2018.

[4] M. Ghulam, W. Kenny, V. Pieter, B. Anita, M. Vera, Antifouling grafting of ceramic membranes validated in a variety of challenging wastewaters, J. Membr Sci., **470**, 369–377, 2014.

[5] E. El Zanati, R & D towards a Novel Method for Production of Biofuel Using Membrane Catalysis, Project ID: 1090, Project Type: Chemical Engineering, funded by Science and Technology Development Fund, Ministry of Scientific Research Ministry, Egypt., 2013.

[6] K. Peyman, A. Ali Akbar, Preparation of non-permselective sulfated zirconia catalytic membrane for use in a catalytic membrane reactor, Chem. Eng. Res. Des., **104**, 472–478, 2015.

[7] M. Sasidharan, A. Patra, Y. Kiyozumi, A. Bhaumik, Fabrication, characterization and catalytic oxidation of propylene over TS-1/Au membranes, Chem. Eng. Sci., **75**, 250–255, 2012.

[8] A. Venault, Y. Chang, D. Wang, D. Bouyer, A. Higuchi, and J. Lai, PEGylation of anti-biofouling polysulfone membrane via liquid and vapor-induced phase separation membrane processing, J. Membr. Sci., **403-404**, 47-57, 2012.

[9] F. Fayyazi, E. Feijani, and H. Mahdavi. Chemically modified polysulfone membrane containing palladium nanoparticles: Preparation, characterization and application as an efficient catalytic membrane for Suzuki reaction, Chemical Engineering Science., **134**, 549–554, 2015.

[10] B. Domènech, M. Muñoz, DN. Muraviev, J. Macanás, Catalytic membranes with palladium nanoparticles: from tailored polymer to catalytic applications, Catal. Today., **193(1)**,158–164, 2012.

[11] GQ. Lu, JC. Diniz, M. Duke, S. Giessler, R. Socolow, R. Williams, T. Kreutz, Inorganic membranes for hydrogen production and purification: a critical review and perspective, J. Colloid Interface Sci., **314**, 589–603, 2007.

[12] E. El Zanati, H. Abdallah, Development of Functionalized Catalytic Membrane for Ethyl Ester Production, IJETED., **5(2)**, 505-521, 2012.

[13] K. Arvind, B. Ankushi, B. Babita, L. Suman, S. Siddharth, Mater. Chem. Phys., **172**, 189-196, 2016.

[14] N. Abdurahman, Y. Rosli, N. Azhari, , Development of a Membrane Anaerobic System (MAS) for Palm Oil Mill Effluent (POME) Treatment, Desalination., **266**, 208–212, 2011.

[15] H. Abdallah, F. Said, E. Ahmed, O. El-Ardy, E. El Zanati, Development and Preparation of Microfiltration of Polyethersulphone Membrane for Catalytic Membrane Application, JASR., **9(3)**, 1623-1634, 2013.

[16] E. El Zanati, S. Ritchie, H. Abdalla, S. Elnashaie, Mathematical Modeling, Verification and Optimization for Catalytic Membrane Esterification Micro-reactor, Int. J. Chem. React. Eng., **13**, 71-82, 2015.

[17] E. El Zanati, Novel Membranes with Multiple Hollow Holes (MMHH) for Reaction Catalysis to produce biofuel, Project ID: 9185, Project Type: STDF - National Challenges Program (STDF-NCP), funded by Science and Technology Development Fund (STDF), Ministry of Scientific Research Ministry, Egypt ., 2018.

[18] T. Shah, S. Ritchie, Development and characterization of a microfiltration membrane catalyst containing sulfonated polystyrene grafts, Appl. Catal.A: General., **296**, 12–20, 2005

[19] N. D. Koromilas, C. Anastasopoulos, E. Oikonomou and J. Kallitsis, Preparation of Porous Polymeric Membranes Based on a Pyridine Containing Aromatic Polyether Sulfone, Polymers., **10**, 59-79, 2018.