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OPTIMAL DISSOLUTION AND VISCOELASTIC BEHAVIOR OF POLYAMIDE-66 IN FORMIC ACID FOR MEMBRANE FABRICATION

Article Highlights

- High-performance polymeric membrane fabrication
- Response surface methodology based techniques for the modeling and optimization
- RSM modeling is employed to evaluate linear, quadratic, and interactive effects
- Process parameters optimized to minimize viscosity

Abstract

High-performance polymeric membrane technology is rapidly developing worldwide with the introduction of new materials and processes. Considerable research efforts are being made to establish a polymer membrane that can be used for ultrafiltration (UF) or nanofiltration (NF) applications. The development of modified polyamide-66 polymer and its compatibility in wastewater are essential elements in the quest for advances and improvements in membrane technology. The optimized conditions for membrane synthesis are critical in making it commercially viable. Response Surface Methodology (RSM) was used to find the optimum dissolution of polyamide-66 in formic acid. A model was developed and validated with experimental data, and it showed good agreement with R^2 0.9984. The optimized condition for minimizing viscosity was determined. For minimum viscosity (3.64 cp), the optimum temperature and wt.% were 20 °C and 0.6, respectively.

Keywords: optimization, polyamide-66, polymeric membrane, RSM, viscosity.

Aliphatic polyamide (PA, nylon) films are one of the most popular materials for membrane synthesis due to their permeability qualities for ultrafiltration (UF) and nanofiltration (NF) applications [1]. Different kinds of nylon, including nylon 66, show excellent permeability characteristics to smaller urea, water, and sodium chloride molecules. In contrast, higher molecular weight molecules and the non-ionized and less polar species display less diffusion through nylon films [2].

Polyamide thin-film composite (TFC) membranes dominate the RO membrane market. It consists polyester web, a microporous interlayer, and an ultra-thin barrier layer [3]. Aromatic polyamide is the most common material used in barrier layers. The process is done mainly via interfacial polymerization of 1,3-phenylenediamine and the tri-acid chloride of benzene [4]. Enhanced resistance to chemical attack and structural stability allows it to tolerate impurities, last longer, and clean more efficiently [5, 6]. Different studies are available in the literature for preparing polyamide 6. Peng *et al.* [7] produced semi-aromatic modified PA6 through a green and efficient in situ polymerization method. They used caprolactam, purified terephthalic acid (PTA) without adding a conventional polymerization initiator. As a result of the polymerization process, the possible path is that a random distribution of PTA might occur in the copolymer once the amide is exchanged.[7]. In another study, Polyamide 6-based copolymer with a molecular structure comparable to polyamide 6 was prepared using amide exchange [8]. Polyamide spiral wound membranes dominate the RO/Nanofiltration (NF) market with a 91 percent share because of its higher

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salt rejection ability and net pressure as the driving force [9]. However, in another study [10], compared to alcohol/salts, the dissolution of PA solution in different organic and acid solvents differs from solvent to solvent, which profoundly influences the PA dope solution viscosity [11]. Concerning the dissolved state of the PA in acid solvents, the PA molecular chain reveals polyelectrolyte nature in an aqueous acid solution and an aqueous concentrated sulfuric acid solution due to the protonation of the polymer amide group, which strongly interacts with the polymer chains [12].

The casting solution is one of the essential factors for the high-performance membrane. The membrane structure and skin properties mainly depend upon the type of solvent, the viscosity of the solution, and the concentration of the polymer [13]. Nevertheless, polyamide glassy nature and crystalline structure are resistant to many polar, dipolar, and nonpolar solvents. However, multiple researchers reported that the dissolved state of polyamide in the alkyl solvents cooperated with inorganic salts such as methanol with LiCl, $CaCl_2$, $SnCl_4$, and $TiCl_4$, respectively, can be used to enhance properties [12].

Idris and Ahmed [14] highlighted that the polymer and viscosity concentration are the main parameters that influence the structure and performance of the membranes. They also highlight the effect of viscosity and concentration on the membrane's performance, along with the fact that too high or too low viscosities significantly impact the performance of the membrane. The present study includes an optimization study of the experimental data available in the literature [15]. Research studies have been conducted to determine the best techniques for determining maximum and minimum response for attributes [16, 17]. It is possible to determine the optimum parameter values using various optimization methods. Using the VIKOR method, complex systems with many criteria may be optimized efficiently. This approach is based on rating and picking from a collection of presented options [18]. A second method TOPSIS is based on the idea that the selected choice should be the one that comes closest to the ideal solution and remains far from the negative-ideal option.

In contrast, the mathematics-based Promethee may solve issues involving several criteria and have various applications in picking acceptable alternatives, prioritizing tasks, and predicting [19]. The present study's data is optimized using Response Surface Methodology (RSM), a relatively advanced and more reliable technique. RSM is a practical and valuable tool for evaluating the relationship between process input and response for experimental design. Multiple runs are usually done by varying the values of parameters [20]. Once the data is collected, statistical analysis is conducted to find the inaccuracies in the measured data. The interaction between the factors is also considered for studying the multiple factors and individual factors' impact [21]. This study finds the two main factors, i.e., concentration and temperature, to optimize viscosity, leading to an excellent membrane fabrication for water application.

MATERIALS AND METHODS

The input parameters studied in this work are polyamide-66 polymer weight percent (wt. %) and temperature. In addition, the effect of polyamide-66 concentration and temperature on the viscosity of the solution was examined. Face-centered ventral composite design (CCD) was used to evaluate parameters. The face-centered CCD consists of six face-centered, eight corner points, and six center points. The input values of the parameters are provided in Table 1. The experimental data are taken from the research presented by Alghoraibi [15]. Polyamide-66 (PA66) polymer (Mw 262,35 g/mol) was received from Sigma Aldrich Co. Statistically, the analysis of RSM was used to form an empirical relationship between the temperature, concentration, and viscosity (response).

The RSM is considered authentic and consistent in the research investigation. The most important part of this technique is examining the effect of the least and most significant factors on the final response. The capability of RSM to analyze multiple inputs to produce a single output makes it very attractive for researchers in modeling and optimization. The present work includes developing an empirical model to predict the change in viscosity of polyamide-66 mixture with the change in wt.% and temperature. In the next step, an optimization was conducted using a developed model. The work was started by creating a second-order polynomial equation to show the relationship between parameters and output. The general correlation is given in Eq. (1):

$$\text{Response} = \beta_0 + \sum_{i=1}^{p}\beta_i X_i + \sum_{i=1}^{p}\beta_{ii} X_i^2 + \sum_{i=1}^{p-1}\sum_{j=1}^{p}\beta_{ij} X_i X_j \quad (1)$$

where β_0 is a constant, the coefficients β_1, β_2…., β_p and β_{11}, β_{22}…., β_{pp} are the linear and quadratic terms, respectively while β_{12}, β_{13}…., β_{p1} are the interacting terms.

RESULTS AND DISCUSSION

Considering that the reaction is dependent on a single component, it is essential and rational to find out the influence of both parameters concurrently [22]. The results of the design of experiment (DoE) with face-centered CCD method using the Polyamide-66 wt. % and the temperature (°C) as the input factors and the corresponding response, viscosity, are provided in Table 1.

Table 1. DoE according to face-centered CCD

Sr. No	Temperature (℃)	(wt. %)	Viscosity
	A	B	cp
1	30	0	0.84
2	30	1.5	6.65
3	30	1.5	6.57
4	30	3	12.8
5	10	0	1.0
6	50	0	0.5
7	30	1.5	6.4
8	30	1.5	6.5
9	10	1.5	9.9
10	10	3	17.6
11	50	1.5	4.6
12	30	1.5	6.45
13	50	3	8.5

An empirical relationship using RSM is developed and tested between polyamide-66 wt. % and temperature, considering the mixture's viscosity as output in the form of a quadratic polynomial. The development of an empirical equation was followed by optimization using the analysis of variance (ANOVA). The results provide a relationship among the parameters, their interactions, and the squares of the inputs (Table 2). The model is highly significant as the table has an overall *F*-value of 853.09 for the viscosity and a low probability value (p-value = <0.0001), considering that the resulting p-value is less than 0.05 [23,24]. These results highlight that prediction and optimization are possible using the developed model. The results in Table 2 also show that the developed model has five significant terms, namely A, B, A^2, B^2, and AB. Eq. 2 represents the developed model.

The model can be improved by removing non-significant terms using the backward elimination process. The terms with minimal effect can be omitted without affecting the required ones in the developed model. R^2 values and the ANOVA table were further used to compare and examine the model. This comparison can help enhance the model efficiency. The new and reduced model is further processed using a backward elimination process; the ANOVA values are provided in Table 3. With a p-value less than 0.05, it is clear from this table that the *F*-value for the reduced model is greater than the *F*-value for the original model. These results show the improvements in the analysis by using the reduced model.

Table 2. ANOVA results for the viscosity

Source	Sum of Squares	Degree of freedom	Mean Squares	*F* values	p values
Model	278.82	5	55.76	853.09	< 0.0001
A	37	1	37	566.06	< 0.0001
B	222.77	1	222.77	3408.02	< 0.0001
A^2	0.49	1	0.49	7.43	0.0295
B^2	3.16E-04	1	3.16E-04	4.83E-03	0.9465
AB	18.49	1	18.49	282.86	< 0.0001
Residual	0.46	7	0.065	-	-
Lack of Fit	0.42	3	0.14	14.34	0.0132
Pure Error	0.039	4	9.73E-03	-	-
Cor Total	279.28	12	-	-	-

$$\text{Viscosity} = -0.0795A + 6.226B + 0.001048A^2 - 0.00475B^2 - 0.0176AB + 1.9439 \quad (2)$$

The R^2-values for the original and reduced model are compared in Table 4. Both models show high-efficiency prediction as to the R^2-value is almost approaching 1. However, after backward elimination (reduced model), the model shows an enhancement in Adeq. Precision value. The new amount of Adeq. Precision is 116 compared to the previous value of 99.25, which means the new model is improved. In this way, the final viscosity model that may be utilized for further analysis, prediction, and optimization has been presented by Eq. 3.

Table 3. ANOVA results of viscosity by using the reduced model

Source	Sum of Squares	Degree of freedom	Mean Squares	*F* values	p values
Model	278.82	4	69.71	1217.86	< 0.0001
A	37	1	37	646.48	< 0.0001
B	222.77	1	222.77	3892.19	< 0.0001
A^2	0.56	1	0.56	9.73	0.0142
AB	18.49	1	18.49	323.05	< 0.0001
Residual	0.46	8	0.057	-	-
Lack of Fit	0.42	4	0.1	10.76	0.0204
Pure Error	0.039	4	9.73E-03	-	-
Cor Total	279.28	12	-	-	-

Table 4. R-squared values the model

Terms	Before backward elimination	After backward elimination
R^2 (overall)	0.998	1
Adjusted R^2	0.997	1
Predicted R^2	0.988	0.99
Adeq. Precision	99.25	116

$$\text{Viscosity} = -0.07895A + 6.212B + 0.001038A^2 - 0.0716AB + 1.9423 \quad (3)$$

Adequacy tests of the developed models

It is essential to test the developed model by plotting the residues curves. Points in the residual plot should be near a straight line and not follow a pattern. The residual plot for the viscosity model is presented in Figure 1. It is evident from the figure that there is no sequence exists between the points, and a fall of residual to the straight line confirms the normal distribution of errors reaffirming the least square fit [25]. The graphical representation means that the results are satisfactory, and the model can be used for prediction and optimization.

Further, the externally studentized residual versus predicted plot is presented in Figure 2. No evident and unusual pattern was found. Therefore, an acceptable range of ± 4.5 has been selected for the good points in this study. The randomly scattered plot within acceptable range exhibited the absence of lurking variables and shows that the model is credible and adequate. The results also confirm the validity of the model and the effectiveness of the randomization process [26]. Generally, negative residual values mean an over prediction, a positive residual point to a low prediction. Any plot closer to the estimated regression line at zero (0) highlights the exactness of model prediction [27]. The data points which do not come in this range are considered unreliable. Figure 2 shows that all the data points fall in the given range.

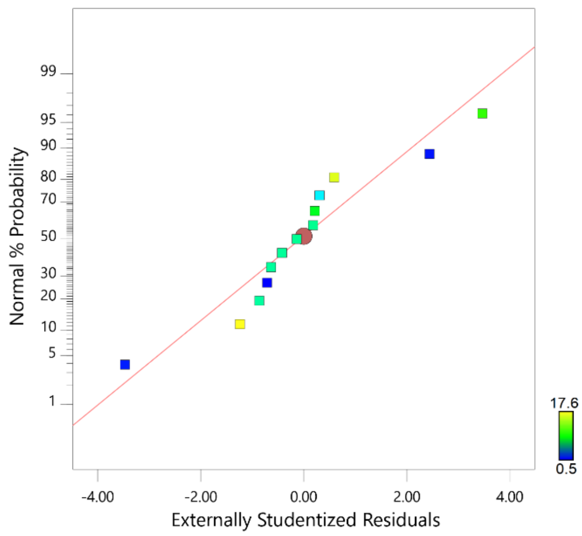

Figure 1. Normal plot of residual.

Verification tests of the models

The results were verified by selecting a random set of data and then comparing it with results obtained in the model using Eq. (3). Figure 3 shows the results of the comparison. It is evident from the figure that the developed model's predicted results show excellent

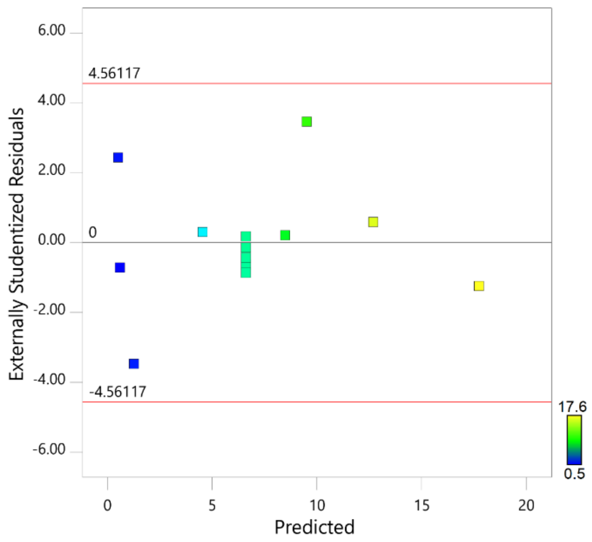

Figure 2. Externally Studentized Residual versus predicted plot for the viscosity model.

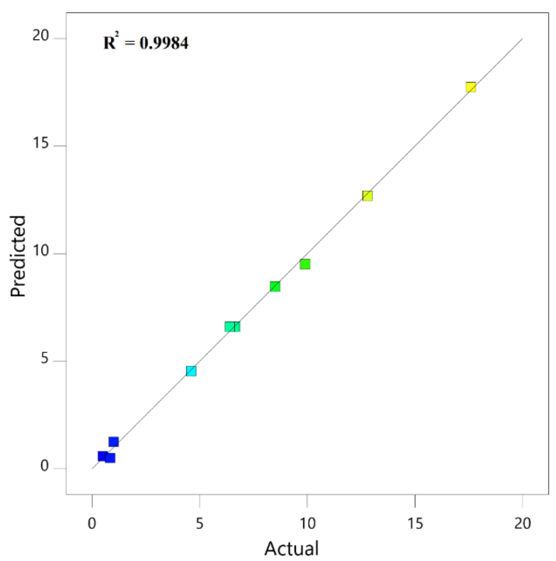

Figure 3. Validation of the model.

aagreement with the experimental values with an R^2 of 0.998.

It showed that data points were near the diagonal line and revealed that the observed response showed an excellent analogy to the predicted one. It is clear from the validation that the proposed model can be applied to the present system. To better understand the model results, a contour plot with a 3D surface plot has been drawn in Figure 4. Polyamide 66 wt.%, temperature, and viscosity have been plotted on the surface plot. Figure 4 highlights the fact that lower temperature leads to higher concentration viscous polyamide-66 mixture.

All the data required for fulfilling the primary goal of minimizing viscosity, including optimization cases, their ranges, their objectives, and factors, are provided in Table 5. The present results were achieved by combining the input parameters using multi-objective optimization. The advantage is that it arranges the input parameters so that the final response provides the best results. The solutions to the optimization case are summarized in Table 5 and Figure 5. Finding the best solution with minimum viscosity with the highest desirability (0.934) is essential. Table 6 shows that in the case of minimum viscosity (3.64 cp), temperature and weight percent, 20 °C and 0.6 were the optimal values.

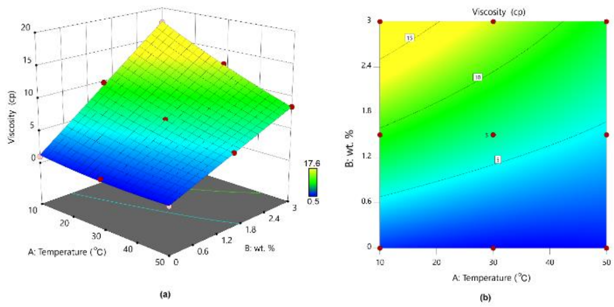

Figure 4. 3D response surface plot (a) and contour plot (b).

Table 5. All the optimization cases, their objectives, factors, and ranges

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Temperature	is in range	10	50	1	1	3
wt. %	is in range	0	3	1	1	3
Viscosity	Minimize	0.5	17.6	1	1	3

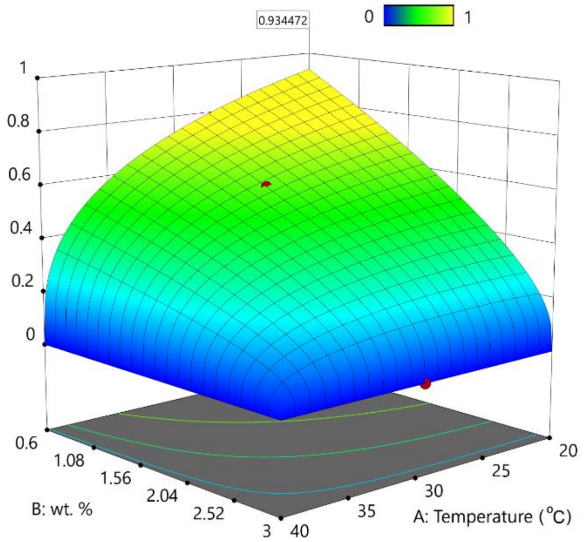

Figure 5. 3D surface plot for the input parameters and desirability.

Table 6. Optimization solutions for minimize viscosity

Number	Temperature (°C)	wt. %	Viscosity (cp)	Desirability
1	20.0	0.60	3.64	0.934
2	20.0	0.712	4.18	0.907
3	23.18	0.60	3.39	0.887

CONCLUSION

The present study explores the optimization of the viscosity of polyamide-66 dissolutions in formic acid. Using RSM, an empirical model was developed to predict the viscosity by considering input factors such as temperature and concentration. The model was tested and validated, which showed a good agreement with experimental results. The model's error was measured using statistical techniques, which is 0.9984. An optimization scenario was| investigated, which included the minimization of viscosity. The optimum temperature (20 °C) and concentration (0.6 wt.%) were calculated with the minimum viscosity value of 3.64 cp.

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NAUČNI RAD

OPTIMALNO RASTVARANJE I VISKOELASTIČNO PONAŠANJE POLIAMIDA-66 U MRAVLJOJ KISELINI ZA IZRADU MEMBRANA

Tehnologija polimernih membrana visokih performansi se brzo razvija širom sveta sa uvođenjem novih materijala i procesa. Ulažu se značajni istraživački napori da se napravi polimerna membrana koja se može koristiti za ultrafiltraciju (UF) ili nanofiltraciju (NF). Razvoj modifikovanog polimera na bazi poliamid-66 i njegova kompatibilnost sa otpadnim vodama su suštinski elementi u potrazi za napretkom i poboljšanjima u membranskoj tehnologiji. Optimizovani uslovi za sintezu membrane su kritični za njenu komercijalnu održivost. Metodologija površine odgovora (RSM) je korišćena da se pronađe optimalno rastvaranje poliamida-66 u mravljoj kiselini. Model je razvijen i validiran eksperimentalnim podacima, koji je pokazao dobro slaganje (R^2 = 0,998). Određen je optimizovan uslov za minimiziranje viskoznosti. Za minimalni viskozitet (3,64 cP), optimalna temperatura je 20 °C, a mas.% 0,6.

Ključne reči: optimizacija, poliamid-66, polimerna membrana, RSM, viskoznosti.