Experimental Design and Modeling for Propylene Oxide - CO_2– Poly (Propylene Carbonate) Solutions

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Abstract

In this research, experimental design was used to formulate the empirical models of viscosity and density of poly(propylene carbonate) (PPC), propylene oxide (PO), and carbon dioxide (CO_2) solutions by designing experiments at key values of the process variables; concentration of PPC between 0 to 34% (% w/w), temperature in the reactor between 50 to 75°C, and gas phase manometric CO_2 pressure between 20 to 40 bar. A bench scale reactor (2000 ml) comprising an external circulation loop equipped with in-line viscosity and density measurement devices was used to carry out the tests. The results show that the equilibrium viscosity and density of the solution increased with the concentration of PPC and decreased with the pressure and temperature in the reactor. The density model has $R^2_{adjusted}$ value close to unity indicating that the model can predict the variation in the density with very high accuracy. In comparison, the viscosity model has a lower $R^2_{adjusted}$ value indicating a need for additional experiments to improve the model. However, both empirical models predict the general trends of the density and viscosity characteristics in the selected range and can be used as a viable alternative to thermodynamic models.

Keywords: Carbon dioxide polymers, poly(propylene carbonate), experimental design, statistical modeling

1 Introduction

1.1 Background

With recent development in the field of polymer science, CO_2 as a feedstock in a synthesis of the biopolymer, poly(propylene carbonate) (PPC), has been viewed as an attractive alternative. The research community is further motivated to explore and optimise the copolymerization of CO_2 and propylene oxide (PO) to produce PPC, as, CO_2 is relatively cheaper, abundant, and environmentally friendly in comparison to petroleum-based feedstocks (Arakawa *et al.*, 2001). Till date, the studies have specifically focused on understanding the effect of catalyst on the selectivity of the copolymer product and optimizing copolymerization in a batch reactor (Narang *et al.*, 2016; Meng *et al.*, 2016; Pan *et al.*, 2014; Wang *et al., 2012;* Qin *et al.*, 2003). However, understanding of flow characteristics (density and viscosity) of product streams with the variation in process parameters (pressure, temperature, and concentrations) is crucial for optimal product yield and economic opportunity for industrial synthesis of PPC. Prior attempts of formulating analytical models of the density and viscosity based on the thermodynamic theories by this research group at Norner Research were unsuccessful due to the complexity of polymer characteristics thereby causing difficulties in obtaining precise measurements of the concentration of the phases involved. In this research, the design of experiments (DOE) was used to plan, conduct and analyse the experiments and then formulate a statistical model of viscosity and density of PO-CO_2-PPC solutions.

1.2 Experimental Design

Experimental design is a systematic approach to perform experiments and discover the effect of controllable factors on the response variables. Experimental factors are variables which have a direct impact on the response variables. They assume a set of discrete values known as levels of the factors. There are diverse types of experimental design based on the objective, levels, resolution, and the total number of runs. The general full factorial design is one of the key design where tests are performed at all the possible combinations of levels of experimental factors. It is a suitable approach to discover the general behaviour of the processes, formulate an empirical model and validate analytical models (Davim, 2016; Montgomery, 2001; Montgomery *et al.*, 2007).

In this study, a general full factorial design of experiments with three factors (initial concentration of PPC, the temperature in the reactor and gas phase CO_2 pressure in the reactor) at three levels is used to study the viscosity and the density of the solution and formulate second-order empirical models with 9 parameters.

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2 Experimental

2.1 Chemicals

Table 1 is a list of the chemicals used in the tests. PPC was purchased from Empower Materials with the product name QPAC® 40 and a range of molecular weights between 100-300 kmol/g. PO with a purity of 99.5% w/w was supplied by Acros Organics. Acetone and heptane from Sigma Aldrich were used to wash up the set-up.

Table 1. List of chemicals.

Chemical	*Symbol*
Propylene oxide	PO
Heptane	C_7H_{16}
Acetone	$(CH_3)_2CO$
Carbon dioxide	CO_2
Poly (propylene carbonate)	PPC

2.2 Set-up

Figure 1 shows a bench-scale batch reactor set-up used in the tests. The reactor was equipped with temperature control, stirrer to maintain homogenity of the chemical mixture and inlet for pressure controlled CO_2 feeding. A pump was used to ensure continuous flow in the circulation unit (CU). The unit was equipped with inline viscometer to measure viscosity and density of the solution. Furthermore, the unit was equipped with a flow meter to measure flow in the circulation unit.

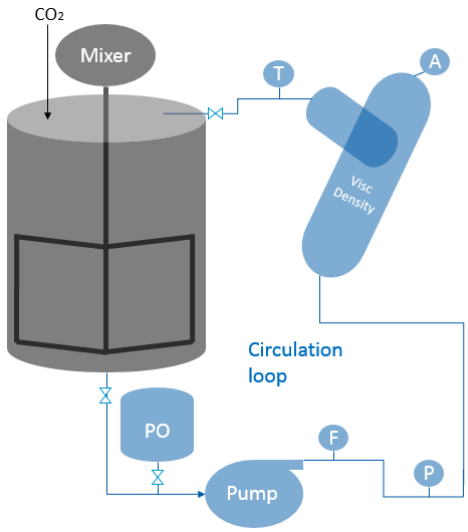

Figure 1. A bench scale reactor equipped with in-line measurement devices for density and viscosity characterisation of the reactor solution.

2.3 Design Space

Table 2 shows the design space of factorial experimental design. The design space includes the relevant operating window for the polymer synthesis.

Table 2. Design space for the experimental design

Factors	*Max*	*Min*
Initial concentration of PPC (C) (% w/w)	34.0	0.0
Temperature in the reactor (T) (°C)	75.0	50.0
Gas phase CO_2 pressure (P) (bar)	45.0	20.0

2.4 Factorial Experimental Design

Table 3 is a full factorial design implemented to study the flow characteristics of the PO-CO_2-PPC solutions.

Table 3. Full factorial experimental design.

Test runs	*C [% w/w]*	*T [°C]*	*P [bar]*
1	0	50.0	20.0
2	0	50.0	32.5 (30.0)
3	0	50.0	45.0 (40.0)
4	0	62.5	20.0
5	0	62.5	32.5
6	0	62.5	45.0
7	0	75.0	20.0
8	0	75.0	32.5
9	0	75.0	45.0
10	17	50.0	20.0
11	17	50.0	32.5
12	17	50.0	45.0
13	17	62.5	20.0
14	17	62.5	32.5
15	17	62.5	45.0
16	17	75.0	20.0
17	17	75.0	32.5
18	17	75.0	45.0
19	34	50.0	20.0
20	34	50.0	32.5
21	34	50.0	45.0
22	34	62.5	20.0
23	34	62.5	32.5
24	34	62.5	45.0
25	34	75.0	20.0
26	34	75.0	32.5
27	34	75.0	45.0

2.5 Procedures

The test runs were separated into three distinct groups based on the concentration of PPC (0 %w/w, 17 %w/w, 34 %w/w). Before performing tests of each group, the set-up was cleaned with heptane/acetone and dried with N_2 gas/ vacuum.

After the equipment was washed and dried, the reactor was loaded with the required amount of PPC.

The reactor was then assembled, and N_2 was purged out followed by feeding of PO into the reactor, stirring and increasing the reactor temperature to the set-point. Viscosity and density responses were measured at equilibrium (steady state) in distinct combinations of gas-phase CO_2 pressure and temperature. At the end of tests of each group, the set-up was cleaned and prepared as described above for the next loading of PPC with the accompanying group of tests.

3 Results and Discussions

3.1 Summary of Experimental Observations

Table 4 shows an overview of viscosity (μ) and density (ρ) responses of the solution after the complete test runs (according to full factorial design, test runs 1-27), preliminary tests at 0% PPC concentrations (test runs 28-30) and the replication tests at 17% PPC concentration (test 31-38). The experimental factor values were controlled according to the factorial design, but there were minor deviations between design values and experimental values due to random noise.

Table 4. Viscosity (μ) and density (ρ) responses.

Test runs	*C* % w/w	*T* °C	*P* bar	ρ kg/m^3	μ cP
1	0.0	50.0	19.7	811.0	0.6
2	0.0	50.0	29.6	816.0	0.6
3	0.0	50.0	40.0	822.0	0.8
4	0.0	62.5	20.0	791.0	0.7
5	0.0	62.5	32.5	797.0	0.6
6	0.0	62.5	40.0	799.0	0.7
7	0.0	75.0	20.0	772.0	0.7
8	0.0	75.0	32.5	774.0	0.4
9	0.0	75.0	40.0	776.0	0.8
10	17.0	50.0	20.0	862.0	4.5
11	17.0	50.7	32.5	858.0	2.0
12	17.0	50.0	38.5	883.0	2.0
13	17.0	62.5	20.0	846.0	4.5
14	17.0	62.5	30.0	845.0	3.1
15	17.0	62.5	40.0	846.0	1.2
16	17.0	75.0	20.0	830.0	4.7
17	17.0	75.0	30.0	828.0	3.3
18	17.0	75.0	40.0	827.0	2.3
19	34.0	50.0	20.3	916.0	80.5
20	34.0	50.0	32.5	918.0	44.0
21	34.0	50.0	45.0	923.0	180.0
22	34.0	62.5	20.7	900.0	80.0
23	34.0	62.5	32.5	899.0	48.0
24	34.0	62.0	45.6	888.0	35.0
25	34.0	75.0	20.0	882.0	76.0
26	34.0	75.0	32.5	883.0	50.0
27	34.0	75.0	45.0	881.0	34.0
28	0	50.0	20.0	810.0	0.6
29	0	50.0	32.5	817.0	0.6
30	0	50.0	40.0	820.0	0.72
31	17%	50	20	856	3.4
32	17%	50	19	858	4.6
33	17%	50	29.3	860	5
34	17%	62.5	19.6	840	4.5
35	17%	62.5	29.6	845	3.3
36	17%	62.5	39.3	856	3.4
37	17%	75	19.5	825	4.5
38	17%	75	31	829	3.3

As regression coefficients of statistical model formulated using coded factors can be directly compared to determine the relative significance of coefficients, factors values were transformed to coded value using Equation (1).

$$X_{Coded} = 2\frac{X_{Actual} - X_{Min}}{X_{Max} - X_{Min}} - 1 \qquad (1)$$

Where,

X_{Coded}	Factor values in the coded form
X_{Actual}	Actual factor values in Table 4
X_{Min}	Minimum factor values in Table 2
X_{Max}	Maximum factor values in Table 2

3.2 Density Model

Equation (2) is a density model formulated using coded factor values.

$$\rho = 846.5 + 51.5C - 19.6T + 2.8P + 0.62C^2 + 1.2T^2 + 0.9P^2 + 1.6TC + 3.3TP + 2.6PC \qquad (2)$$

In statistical modelling, analysis of variance (ANOVA) and goodness of fit is used to test the significance of a model. The goodness of fit (R^2) measures the error in fitting experimental data in the regression model. Its values are between 0 and 1, and higher values mean better fit and vice versa. However, for a certain set of data used in the formulation of a regression model, R^2 value is entirely model dependent and increases with the inclusion of additional parameters even if the parameters are insignificant (overestimation). To deal with this problem, $R^2_{adjusted}$ is used. It measures the percentage of variation due to the significant parameters and decreases with the inclusion of additional insignificant model parameters. Together with the determination of R^2 value, ANOVA

is performed to test that the selected parameters in the model are jointly responsible for the variation in response variable (Montgomery, 2001; Montgomery *et al.*, 2007).

Table 5 presents the analysis of variance (ANOVA) and summary of statistics in the formulation of density model. As Significance F-test value (P value of F test) is 0.0, it can be concluded with 95% confidence that the model parameters in the density model are the primary cause of variation in density responses of the mixture. $R^2_{adjusted}$ value is closed to unity, which indicates that the error in fitting experimental density responses in the regression model is negligible and the predicted and measured density responses are statistically identical. This is also evident in the root mean squared prediction error $\sigma = 4.51\ kg/m^3$ which is merely 0.53% of the mean density response. Based on ANOVA and $R^2_{adjusted}$ value it can be statistically concluded that the model can explain most of the variations in experimental density responses and it can be used to predict the density responses in the vicinity of the design space.

Table 5. ANOVA analysis and summary of statistics of density model.

Description	*Values*
Multiple R	0.995
R-squared	0.990
Adjusted R-squared	0.987
F-value	323.9
Significance-F (P-value)	0.0
Variance (σ^2)	20.4

Figure 2 shows a plot of density residuals and Figure 3 shows the normal probability plot of density residuals. Both plot are symmetrical about X-axis except few outliers indicating that model predicted density values and measured density values are statistically identical. However, the residuals are relatively higher at higher PPC concentrations.

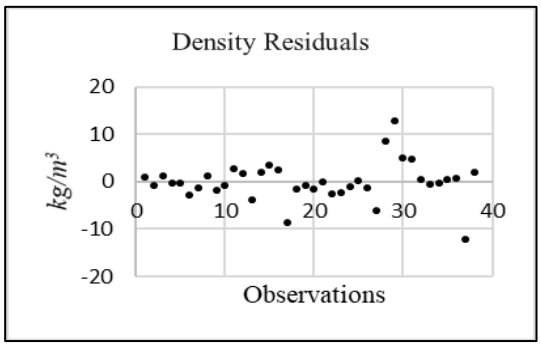

Figure 2. Residual plots of density model.

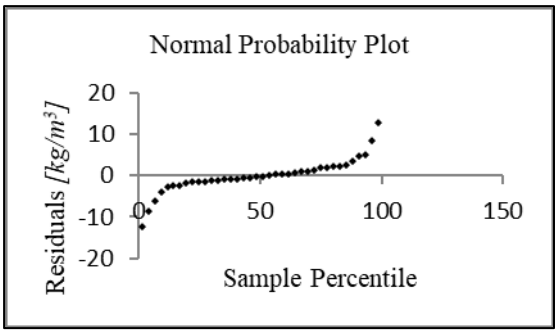

Figure 3. Normal probability plot of density model

Table 6 presents a significance test (*t-test*) of regression coefficients in the density model. P-values of regression coefficients in the *t-test* shows that linear terms (*C, T, P*) and a second-order term (*T·P*) have a significant impact on the density responses while other second-order terms do not contribute significantly in the model.

Table 6. *t-test* of coefficients in density model.

Coefficients	*t-stat*	*P-value*
C	48.4	0.0
T	-20.5	0.0
P	2.2	0.0
C^2	0.4	0.7
T^2	0.7	0.5
P^2	-0.4	0.7
T·C	1.3	0.2
T·P	-2.5	0.0
P·C	-1.8	0.1

Equation (3) is reduced density model considering only significant terms with 95% confidence (P value less than 0.05) in the model.

$$\rho = 846.5 + 51.5C - 19.6T + 2.8P - 3.3TP \quad (3)$$

The reduced density model shows that the density varies linearly with the factors. Among the factors, density increases linearly with the concentration of PPC and density decreases with an increase in the temperature. However, pressure contribution to the variation in density responses is relatively low in comparison to other factors.

3.3 Viscosity Model

Equation (4) is the viscosity regression model formulated using coded factor values.

$$\begin{aligned}\mu = {} & -5.9 + 32.5C - 9.5T + 3.67P + 29.7C^2 \\ & + 6.6T^2 + 13.3P^2 \\ & - 10.6TC - 13.8TP \\ & - 0.8PC\end{aligned} \quad (4)$$

Table 7 presents ANOVA and summary of statistics in the formulation of viscosity model. Similar to the density model, Significance F-test value is 0.0, and it can be concluded with 95% confidence that the model

parameters in the viscosity model are the primary cause in a variation of viscosity responses of the mixture. On the other hand, Adjusted R-squared value (0.710) is relatively lower, and the root mean square prediction error ($\sigma = 19.3\ cP$) is considerably high in comparison to most of the viscosity responses (all viscosity responses at 17% PPC and 0% PPC are equal or lower than 5.0 *cP*). In order to formulate model with better fit and lower prediction error, additional tests with smaller PPC concentration changes at higher PPC concentration is essential as the residuals are substantially higher at higher PPC concentrations. However, the model can still sufficiently explain and predict the general trends of the viscosity responses of the mixture in the selected operating range.

Table 7. ANOVA and summary of statistics of viscosity model.

Description	*Values*
Multiple R	0.884
R-squared	0.781
Adjusted R-squared	0.710
F-value	11.10
Significance-F (P-value)	0.00
Variance (σ^2)	372.8

Figure 4 shows a plot of viscosity residuals and Figure 5 shows the normal probability plot of viscosity residuals. Both plots consist of outliers with higher PPC concentration indicating that the model is unable to represent viscosity responses at higher PPC concentrations.

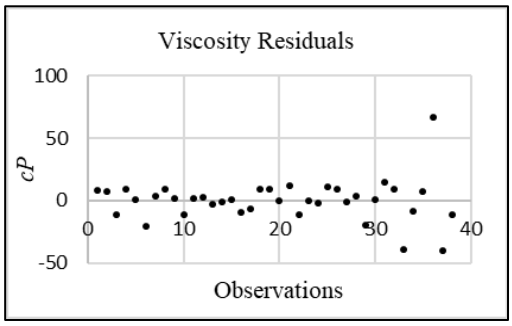

Figure 4. Residual plot of viscosity model.

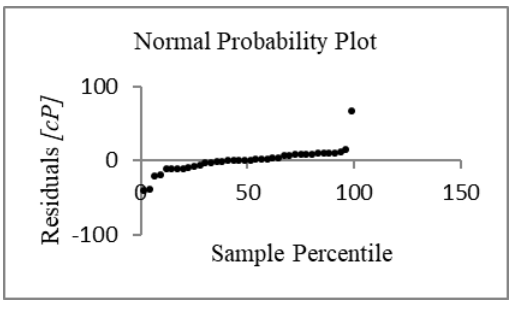

Figure 5. Normal probability plot of viscosity residuals.

Table 8 presents a significance test (t-test) of regression coefficients in the viscosity model. Linear terms (C, T), as well as second order term (C^2, T·C, T·P), have a significant impact (95% confidence) on the viscosity responses with P-value less than 0.05. The remaining terms (P, T^2, *and* P^2) do not contribute significantly to the model.

Table 8. *t-test* of coefficients in viscosity model.

Coefficients	*t-stat*	*P-value*
C	7.2	0.0
T	-2.3	0.0
P	0.7	0.5^+
C^2	4.5	0.0
T^2	1.0	0.3
P^2	1.5	0.1
T·C	-2.1	0.0
T·P	-2.5	0.0
P·C	-0.1	0.9

Equation (3) is a reduced density model excluding insignificant terms with 95% confidence in Equation (4).

$$\mu = -5.9 + 32.5C - 9.5T + 29.7C^2 + 13.3P^2 - 10.6TC - 13.8TP \quad (5)$$

The reduced viscosity model shows that the viscosity primarily depends on the concentration of PPC in the mixture. It increases quadratically with the concentration of PPC and decreases with temperature in the reactor. On the other hand, viscosity changes quadratically with the pressure at constant temperature and concentrations. Besides, the pressure-temperature combination has an inverse effect on the viscosity response of the mixture.

4 Conclusions

The full factorial design of experiments is an efficient approach to formulate empirical models of the viscosity and density of a mixture of PPC, PO and CO_2 under varying concentration of PPC, temperature in the reactor and gas phase CO_2 pressure. The reduced empirical/regression model of density obtained from statistical analysis is highly efficient in the prediction of density response of the mixture in the design space. The density decreases insignificantly with increase in the gas phase CO_2 pressure at the higher temperature and increases at low temperatures due to second order effect of (TP), and increases linearly with PPC concentrations. On the other hand, the viscosity of the mixture predominantly depends on the concentration of PPC in the mixture. The viscosity increases with an increase in the PPC concentration and decreases with an increase in the temperature of the reactor. The residual analysis of

viscosity shows that more experiments are required to predict the impact of the selected factors on the viscosity to obtain lower root mean squared prediction error ($\sigma < 19.3\ cP$). However, both models explain the impact of pressure, concentration, and temperature in the viscosity and density responses of CO_2-PO-PPC solutions in a relevant process operation window and will be useful in the process development in the future.

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