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Modification of Common Starch into Resistant Starch in Cassava through Optimisation of Physical and Chemical Treatments

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Abstract. This study found an optimised condition in modifying common starch into resistant starch content by conducting crystallinity index analysis using X-Ray Diffraction (XRD). The methodology involved the preparation of cassava sample, optimisation of parameters using Response Surface Methodology (RSM) and crystallinity index analysis using X-Ray Diffractometers. The results obtained from the analysis were recorded in RSM to observe the suggested and optimised parameters to modify the resistant starch content. RSM proved that the addition of oil had given the most significant effect to achieve the optimised crystallinity index, followed by the autoclave duration and the cooling duration, which gave the least significant effect towards the treatment.

1. Introduction

There are three types of starch modification, i.e., slowly digestible starch, rapidly digestible starch and resistant starch, which depends on the structure that influences the digestibility [1]. Resistant starch is a starch that resists digestion in the small intestine and acts like dietary fibre [2]. It is divided into four categories, i.e., Resistant Starch Type 1 - Resistant Starch Type 4 [3-4]. Resistant Starch Type 1 is dominant in legumes and whole grain that is capsulated in a non-digestible matrix, which is physically inaccessible to digestion. Resistant Starch Type 2 is found in ungelatinised starch granule with B-type starch crystallinity. Foods that have undergone retrogradation, i.e., when foods containing starches are cooked and cooled are categorised in Resistant Starch Type 3. Resistant Starch Type 4 includes a chemical modification that is modified with the addition of ether or ester group and crosslinking amylose strand.

Cassava consists of two main parts that consumed by human, i.e., the leaves and the roots. Mature roots have a wide range of starch content from 15% to 33% depending on the soil nutrients and climate [5]. A study stated that cassava roots have 9.69% resistant starch content, which is the highest after yam and followed by other starchy foods, e.g., corns, bananas and legumes. A modification to improve resistant starch can improve the possibility of starch being converted into short-chain fatty acids by intestinal bacteria in the large intestine [6].

Response Surface Methodology (RSM) is a statistical procedure used to determine the optimisation of experimental parameters for the combined effect to distinguish unknown parameters influencing resistant starch modification [7]. Central Composite Design (CCD) is an experimental design for the



second-order response model as it gives excellent statistical properties by determining the regression equations and conditions of operation from experiments [8]. CCD involves three steps: 1) Perform the designed experiments with reliable response measurement, 2) Estimate mathematical model coefficients of the second order with the best fit, and 3) Predict the optimum parameters that produce maximum value for the response [9].

2. Materials and Methods

2.1. Preparation of Cassava

The cassava was dried and ground until it reached the desired size, i.e., in powder form.

2.2. Experimental Design using RSM

The variables and its low (-1) and high (+1) level, which are the addition of oil [1 and 10 % (w/w)], the autoclave duration (10 and 60 min) and cooling duration (18 and 28 hours). The variables were inserted in the CCD model of RSM.

2.3. X-Ray Diffraction

A Siemens D5000 (Bruker-AXS, Karlsruhe, Germany) x-ray diffractometer was used. The samples were scanned with Cu-K α . The scanning duration of 16.5 s for each sample was generated at the conditions of 30 kV and 10mA—the diffraction angle range from 10° to 50° (2 θ -range).

2.4. Crystallinity Index Analysis using XRD

In order to calculate the crystallinity index, Formula 2.1 was used. The results obtained from the calculation were recorded.

$$\text{Crystallinity Index} = \frac{\text{The crystalline area}}{\text{The area under the diffractogram}} \times 100\% \quad (2.1)$$

2.5. Optimisation Studies

The optimisation studies were applied by using Design Expert Software Version 11 that generated interaction plot, 2D contour plot and 3D surface plot.

3. Results and Discussion

3.1. Crystallinity Index using XRD

According to Formula 2.1, the area under diffractogram is all the area below the graph from the diffraction angle of 10° to 50°, as shown in Figure 1. The data in Table 1 found that the crystallinity index calculated from the XRD patterns ranged from 33.48% to 51.58%, which showed an increment from the crystallinity of typical native starch granules at 14% to 45% [10] and raw cassava with circa 13% crystallinity index [11].

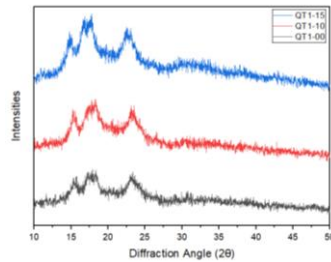


Figure 1. X-ray diffraction pattern of the control sample (QT1-00), the sample with the highest crystallinity index (QT1-10) and lowest crystallinity index (QT1-15)

Based on Table 1, the highest crystallinity index was QT1-10; meanwhile, the lowest was QT1-15 in the range of 51.58% to 33.48% of crystallinity index. The high crystallinity index was contributed by 10% (w/w) of the addition of oil with a further 10 minutes of autoclave and cooling for 28 hours. The low crystallinity index of QT1-15 was contributed by 1% (w/w) of the addition of oil with 60 minutes of autoclave duration and 28 hours of cooling duration.

Table 1. Runs generated by Central Composite Design.

Run	Code	A Addition of Oil [%(w/w)]	B Autoclave Duration (min)	C Cooling Duration (hour)	Crystallinity Index
1	QT1-01	10	60	28	46.86
2	QT1-02	5.5	35	23	44.26
3	QT1-03	5.5	60	23	45.90
4	QT1-04	5.5	35	23	44.70
5	QT1-05	1	10	18	40.73
6	QT1-06	1	10	28	39.30
7	QT1-07	5.5	35	23	44.54
8	QT1-08	5.5	35	23	44.26
9	QT1-09	5.5	10	23	41.03
10	QT1-10	10	10	28	51.58
11	QT1-11	5.5	35	23	42.53
12	QT1-12	1	35	23	42.26
13	QT1-13	1	60	18	33.87
14	QT1-14	10	35	23	48.69
15	QT1-15	1	60	28	33.48
16	QT1-16	10	10	18	37.66
17	QT1-17	5.5	35	28	43.08
18	QT1-18	5.5	35	18	38.57
19	QT1-19	5.5	35	23	43.08
20	QT1-20	10	60	18	49.89
Control	QT1-00	-	-	-	31.44

3.2. RSM Analysis

3.2.1. Development of Regression Model Equation for Crystallinity Index.

According to Table 2, the 2-factorial interaction was suggested by the model because it complies with most of the three aspects. 1) Low standard deviation, 2) High R-squared values, and 3) Low PRESS.

Table 2. Model Summary Statistics of Crystallinity Index

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	3.61	0.5145	0.4235	-0.0258	441.21	
<u>2FI</u>	<u>2.86</u>	<u>0.7535</u>	<u>0.6397</u>	<u>-0.8516</u>	<u>796.41</u>	<u>Suggested</u>
Quadratic	2.56	0.8471	0.7094	-1.5964	1116.80	
Cubic	0.8133	0.9908	0.9708	0.8629	58.95	Aliased

As shown in Table 3, the correlation coefficient, R^2 value was 0.7535, which indicates that the model can explain 75.35% of response variability. The higher the R^2 represents a better model [12]. The adjusted R^2 is moderately high, represents a moderately high significance of the model. The predicted R^2 measures how good the model is predicting a response value, and it should be within 0.20 with the adjusted R^2 for both to be reasonable [13]. In this study, it falls out of 0.20. The coefficient of variation (CV) is the degree of precision measuring the reliability of the experiment. The low CV represents a highly reliable model [14].

Table 3. The Standard Deviation and 2FI Model R^2 for Crystallinity Index

Std. Dev.	2.86	R^2	0.7535
Mean	11.38	Adjusted R^2	0.6397
C.V. %	25.10	Predicted R^2	-0.8516
PRESS	796.41	Adeq. Precision	10.1918

3.2.2. Statistical Analysis for Crystallinity Index.

Table 4 shows the degree of freedom, i.e., the number of the parameter used. The degree of freedom of the model was 6, including A-Addition of Oil, B- Autoclave Duration, C-Cooling Duration, AB, AC and BC. The model F -value was 6.62. The smaller value of F shows a lesser variation in the response that can be explained by the regression equation [12]. The p -value less than 0.05 implies that model term is significant and has a real effect on the response.

Table 4. ANOVA table for response surface 2FI model of Crystallinity Index

Source	Sum of Squares	df	Mean Square	F Value	p -value Prob > F	
Model	323.10	6	54.02	6.62	0.0022	significant
A- Addition of Oil	202.86	1	202.86	24.87	0.0002	
B- Autoclave Duration	0.0090	1	0.0090	0.0011	0.9740	
C- Cooling Duration	18.44	1	18.44	2.26	0.1566	
AB	50.95	1	50.95	6.25	0.0266	
AC	20.19	1	20.19	2.48	0.1396	
BC	31.64	1	31.64	3.88	0.0706	

3.2.3. Optimisation of the Effect of All Treatments on Crystallinity Index.

For each variable, a two-dimension (2D) contour plot and three-dimensional (3D) response graph were obtained to analyse the potential effect of two variables on the CI_{XRD} . In contrast, another variable was remained constant at one time.

Based on Figures 2 and 3, the CI_{XRD} was 45% when the addition of oil was around 7 to 8% (w/w), decrease to 40% when the addition of oil was around 2 to 3% (w/w) and the autoclave duration remains in a range of 30 to 40 minutes at constant cooling duration. The autoclave duration did not give any significant changes related to the addition of oil. However, there was less effect on the CI_{XRD} of the autoclave duration as the colour changes from blue to green upon decreasing the autoclave duration. However, there was less effect on the CI_{XRD} of the autoclave duration as the colour changes from blue to green upon decreasing the autoclave duration. The less effect indicates the retrogradation occurred in starch molecules had re-associated by the hydrogen bonds, which resulted in a difference of CI_{XRD} [15].

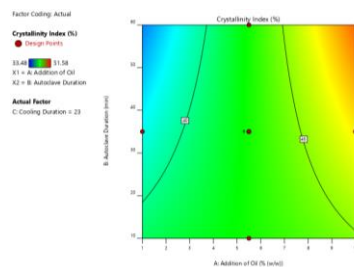


Figure 2. 2D contour plot of interaction between Addition of Oil and Autoclave Duration on Crystallinity Index

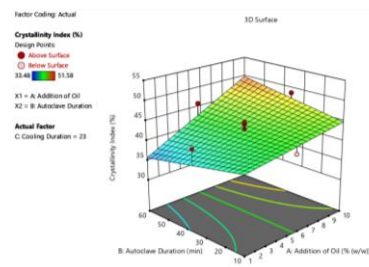


Figure 3. 3D response surface graph of interaction between Addition of Oil and Autoclave Duration on Crystallinity Index

Figures 4 and 5 show the effect of the addition of oil and cooling duration when the autoclave duration was kept constant at 35 minutes. These figures show the addition of oil around 8 to 10% (w/w) and cooling duration around 26 hours, which obtained CI_{XRD} at 48% and decrease to 40% when the addition of oil was around 2 to 3% (w/w) upon 22 to 24 hours of cooling duration. This outcome indicates that the reduction in temperature could reduce the restoration of the hydrogen bond between amylose and amylopectin of the cassava starch that further adjusted the CI_{XRD} value [16].

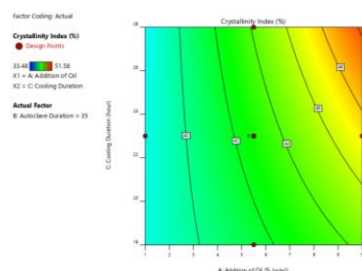


Figure 4. 2D contour plot of interaction between Addition of Oil and Cooling Duration on Crystallinity Index

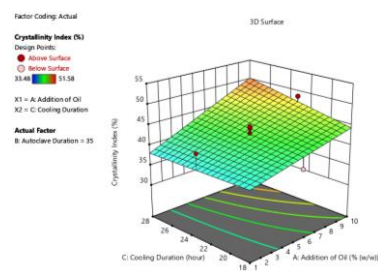


Figure 5. 3D response surface graph of interaction between Addition of Oil and Cooling Duration on Crystallinity Index

Figures 6 and 7 show the effect of autoclave duration and cooling duration on CI_{XRD} when the addition of oil was a constant, i.e., 5.5% (w/w). These figures show a slight difference in the CI_{XRD} , 44% when the cooling duration was at 25 to 27 hours and autoclave duration at 20 to 30 minutes. The CI_{XRD} decreased to 40% when the cooling duration was around 18 to 20 hours, and the autoclave

duration around 10 to 20 minutes. This result proves that the CI_{XRD} changes upon the variation of temperature due to the weakening of intra-granular forces, which causes modification in granule structure. These results comply with the relation between CI_{XRD} and resistant starch that forms starch granule, which prevents digestion in the intestinal tract [17].

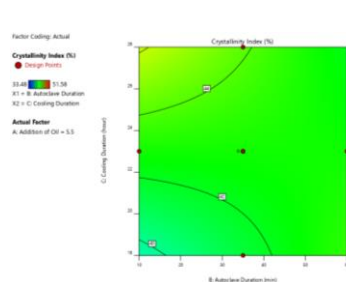


Figure 6. 2D contour plot of interaction between Autoclave Duration and Cooling Duration on Crystallinity Index

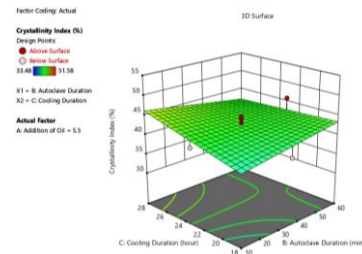


Figure 7. 3D response surface graph of interaction between Autoclave Duration and Cooling Duration on Crystallinity Index

4. Conclusion

As for the conclusion, the response surface methodology (RSM) managed to generate an optimised parameter for the factors to achieve the optimise crystallinity index. According to this study, amongst these three parameters, the addition of oil had given the most significant effect towards the resistant starch content followed by the autoclave duration and the cooling duration, which gave the least significant effect towards the treatment.

5. Acknowledgement

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