OPTIMIZATION OF PROCESS PARAMETERS FOR MASTERBATCH SULFUR DISPERSION IN CHEMICAL PLANT

BY

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A thesis submitted in fulfilment of the requirement for the degree of Master of Science (Biotechnology Engineering)

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DECEMBER 2020

ABSTRACT

One of the main factors limiting the production of a stable sulfur dispersion in masterbatch or in mass scale is finding the optimized parameters set for each of the processes employed, subject to its particle size, viscosity, pH and TSC. Instable sulfur could affect the final product’s quality, for example, “sulfur bloom” on the produced rubber film. In this study, the experimental design follows Taguchi’s L_9 orthogonal array to determine the optimum parameters for sulfur dispersion prepared via masterbatch mixing in 4 MT mixing tank; to determine the optimum parameters for sulfur dispersion grinded in 60-Litre grinding mill; and finally, to analyze the morphology of sulfur dispersed in rubber film from selected sulfur dispersion sets. The study involved mixing of sulfur with water and surfactant of a fixed dosage in 4 MT mixing tank with various mixing speed and mixing time. The sulfur dispersion with optimized mixing parameter set was chosen for the grinding mill optimization which involved various grinding mill’s motor speed and pump rate. The plot of means and tabulated ANOVA based on respective S/N ratio show that particle size and viscosity were mostly affected with both processes’ parameter changes. At higher mixing speed of 800 rpm and longer mixing time of 30 minutes, an optimized sulfur dispersion was able to be obtained according to the viscosity and particles size responses. It was also found that higher motor speed and lower pump rate of the grinding mill at 800 rpm and 350 L/min respectively produces smaller particle size of sulfur dispersion which also hinders severe formation of sulfur crystals observed on the casted rubber film. Severe sulfur crystals were observed on the rubber film’s casted with larger sulfur particle size or ‘less stable’ sulfur dispersion. Overall, higher mixing speed and longer mixing time, followed by higher grinding mill’s motor speed and lower pump rate favors the production of smaller particle size of sulfur dispersion that is optimized and is more stable especially when applied in rubber products.

خلاصة البحث

أحد العوامل الرئيسية التي تحد من إنتاج الكبريت الثابت المنتشر في الماستر باتش أو على نطاق واسع هو العثور على المتغيرات المحسنة المحددة لكل من العمليات المستخدمة، وفقًا لحجم الجسيم واللزوجة ودرجة الحموضة وTSC. يمكن أن يؤثر عدم استقرار الكبريت على جودة المنتج النهائي، على سبيل المثال، دمج الكبريت على الفيلم المطاطي الذي يتم إنتاجه. تطبق هذه الدراسة تصميمًا تجريبيًا يتضمن مصفوفة تاجوشي المتعامدة L_9 لتحديد المتغيرات المثلى لانتشار الكبريت والذي سيتم تحضيره من خلال خلط الماستر باتش في خزان خلط سعته 4MT؛ ولتحديد المتغيرات المثلى لانتشار الكبريت الذي تم طحنه في مطحنة تسع 60 لترًا؛ وأخيرًا، لتحليل شكل الكبريت المنتشر في الفيلم المطاطي من مجموعات مختارة من الكبريت المنتشر. تضمنت الدراسة خلط الكبريت بالماء وخافض التوتر السطحي بجرعة ثابتة في خزان خلط 4MT مع سرعة خلط ووقت مختلفين. تم اختيار الكبريت المنتشر ذو المجموعة المثلى من متغيرات الخلط لتحسين الطحن والتي تضمنت سرعات طحن ومعدلات ضخ مختلفة. تُظهر مجموعة الوسائل وANOVA المجدولة بناءً على نسبة S / N ذات الصلة أن حجم الجسيمات واللزوجة تأثرتا بشكل كبير بتغير عوامل العمليتين. عند سرعة خلط عالية (تبلغ 800 دورة في الدقيقة) ووقت خلط أطول (يبلغ 30 دقيقة) يمكن الحصول على انتشار كبريت أمثل وفقًا لاستجابات اللزوجة وحجم الجسيمات. أظهرت النتائج أيضًا أن سرعة المحرك العالية ومعدل الضخ المنخفض للطاحونة واللذان يبلغان 800 دورة في الدقيقة و350 لتر/ دقيقة على التوالي ينتجان حجم جزيئات أصغر للكبريت المنتشر مما يعيق التكوين المكثف لبلورات الكبريت التي تم رؤيتها على فيلم المطاط. تم ملاحظة وجود بلورات كبريتية مكثفة على الفيلم المطاطي بجسيمات كبريت ذات حجم أكبر أو انتشار كبريت "أقل استقرارًا". بشكل عام، فإن سرعة الخلط الأعلى ووقت الخلط الأطول، تليها سرعة الطحن الأعلى ومعدل الضخ المنخفض تتسبب في إنتاج حجم جزيئات أصغر من الكبريت االمنتشر الذي يتم تحسينه ويكون أكثر استقرارًا خاصة عند استخدامه في المنتجات المطاطية.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Biotechnology Engineering).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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ACKNOWLEDGEMENTS

Assalamualaikum w.b.t.,

In the name of Allah, The Most Gracious, The Most Merciful. All glories and praises are to Allah the Almighty, Lord of the Universe, the Merciful and Beneficent to Prophet Muhammad S.A.W, His Companion and the people who follow His path. Allah's Blessings and Mercies on me ease the herculean task of accomplishing this thesis.

I hereby would like to thank everyone who had contributed to the successful completion of this thesis for my Master programme. I would like express my upmost gratitude towards especially **Dr. Fathilah Ali** as my supervisor who had supervised me with useful comments, invaluable advices, guidance, motivations and enormous patience for me to complete this thesis. Also, I would like to thank to my co-supervisor, **Dr. Azlin Suhaida** for her guidance and patience as well, and also my Field supervisor, **Dr. Nuriah Mohamad** as Manager for R&D Department at Top Glove Sdn. Bhd. who had given me countless advices, guidelines and motivations throughout my project. Enormous helps from biotechnology engineering department team were also greatly appreciated.

Plus, I would as well like to express my gratitude towards my **parents, Mr. Omar** and **Mdm. Noor Leha** who had given me motivational supports in completing the research, enormous advices by my **siblings** as well. Also towards other **lecturers** and **friends** who eventually helped me out with encouragement, support and comments useful for my development throughout the whole this Master programme period. Special thanks to the lecturers and staffs that have been part of the postgraduate thesis workshop – that consequently helps a lot in my skills especially in writing, management and so on.

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LIST OF ABBREVIATIONS

TSC	Total Solids Content
S	Sulfur (element)
H_2S	Hydrogen Sulfide
SO_2	Sulfur Dioxide
CMC	Critical micelle concentration
MT (unit)	Metric-tonne
rpm (unit)	Revolutions per minute
cP (unit)	centi-Poise
µm (unit)	micro-meter
L/min (unit)	Litre per minute
Eq.	Equation
S/N ratio	Signal-to-noise ratio
DOE	Design of experiments
ANOVA	Analysis of variance
DF	Degree of freedom
Adj MS	Adjusted mean squares
Adj SS	Adjusted sum of squares
LED	Light-emitting diode
SEM/EDX	Scanning Electron Microscopy / Energy Dispersive X-Ray Analyzer

LIST OF SYMBOLS

$^+$	positive charge
$^-$	negative charge
$\sum$	summation
º	degree
%	percent
μ	micro

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Sulfur production over the world is considerably increasing over the past years to date, reflecting its high demand by different industrial applications. The sulfur element may undergo many distinguish processes to yield different forms of sulfur that are deemed suitable for the end-user's respective usage objective.

Additionally, tackling issues with sulfur especially on the sulfur bloom as in rubber vulcanization is crucial in order to maintain the quality of their end-products. Key industries such as rubber has been considerably consuming a large amount of sulfur (in dispersion form) for their production, particularly during their latex compounding procedure (blending of latex, sulfur dispersion, and other additives which are typically in dispersion form). Promising studies such as optimizing sulfur dispersion's manufacturing parameters are possible to be done so as to highly utilize the exceptionally precious sulfur without wastages (Omar, Ali, Mohamad, & Azmi, 2019).

The Taguchi approach is greatly used in any manufacturing unit or industries to determine the optimal combination of process' parameters and responses for better performance (Chen, Li, & Cox, 2009). Since this approach offers a great focus on process enhancement strategy on continuous improvement and innovation, it is best employed for the improvement of existing technology of any industries (Jirasukprasert, Garza-Reyes, Kumar, & Lim, 2015). Additionally, Taguchi's parameter design is an experiment-based process that covers the following scopes or steps to identify settings of design parameters that optimizes performance characteristics or response(s):

i. Identify initial and competing settings of design parameters, as well as important noise factors and their ranges.
ii. Construct the design and noise matrices, and plan the parameter design experiments.
iii. Conduct the parameter design experiments and evaluate the performance statistic for each test run of the design matrix.
iv. Use the values of the performance statistic to predict new settings of the design matrix.

Thus, this study proposed the empirical application of Taguchi's approach to optimize the process steps that in turn can improve quality of sulfur dispersion product in a chemical dispersion manufacturing plant in Malaysia. The DOE and response analysis for the process validation will be done with Taguchi's DOE and ANOVA.

1.2 PROBLEM STATEMENT

Producing high quality sulfur dispersion is a challenging process for chemical manufacturers, where a lot of rubber goods performance mostly depends on sulfur dispersion's quality characteristics' compliance. Sulfur is usually prepared as colloid or dispersion state via mixing and/or chemical grinding process that will produce fine sulfur particle size that rarely settles or sediments. This sulfur dispersion in turn will be suitable to be used in latex compounds. Several studies have been done with different sulfur types and optimal ball-milling process conditions that is proven could comparatively give obvious changes in rubber vulcanizate's mechanical properties (Pangamol et al., 2016b). Thus, it is suggested that improper optimization of process conditions such as ball-milling to effectively reduce the particle size and/or their distributional behavior could remarkably affect its stability or dispersibility in the rubber matrix.

Quality issue often associated with sulfur includes faster rate of particles sedimentation or chemical instability where separations of chemical phases occurred due to inhomogeneity. This consequently affects the final goods produced from them. A poor sulfur dispersion quality may affect vulcanization and crosslinking performance that will subsequently alter the final rubber goods performance in turn. Stable particle dispersions are often formed by adjusting the suspension's ionic strength and pH or by surface modification themselves by mechanical means (Inkyo et al., 2006). Thus, process selection and parameters play a great role in producing homogenous chemical dispersions such as sulfur. According to Wręczycki, Bieliński, & Anyszka (2018), crosslinks in the rubber network are distributed rather randomly and their inhomogeneity may be the result of poor dispersion of curatives such as sulfur during the preparation of rubber mixes. This significantly related to the process parameters for the preparation of sulfur dispersion from the raw material mixes to the subsequent processes that follow, or rather issues related to latex compounding process.

Thus, sulfur dispersion's mixing and grinding processes have been selected in this research, and these two processes' parameters optimization for sulfur dispersion were performed in order to revise and create a milestone for the full utilization and fine-tuning the optimized way in improving the quality and performance of the sulfur itself. Besides that, it will benefit the chemical dispersion manufacturing industry as the product defects can be minimized and as such, the sulfur consumer can manufacture rubber goods at relatively better performance. Additionally, no study has been conducted in optimizing the process conditions of sulfur dispersion in mixing and grinding processes in large scale. Ideally, this study will also benefit the end users of the rubber products to gain confidence from them and avoid the usage of second grade, rejected, or damaged rubber goods.

1.3 IMPORTANCE OF STUDY

The importance of this study is to enhance the raw chemicals mixing and grinding process of sulfur dispersion in a chemical plant by optimization study for both the processes. Sulfur in its dispersion form mainly acts as one of the contributing agents especially in rubber production, during the latex compounding procedure by introducing vulcanization.

Continuous advancements and researches were done in order to develop good rubber end-products. Thus, this study was done to contribute in improvements not only for the rubber products, but as well towards other industrial applications that uses sulfur as their main consumable or major raw material. Originating from the sulfur dispersion itself, this process enhancement study is hoped to benefit most sulfur-user industries, especially the producer/manufacturer which is the chemical dispersion plant itself in terms of quality improvement, process enhancement as well as waste elimination.

1.4 OBJECTIVES

The present study is mainly to develop to achieve the objectives as mentioned below:

1. To determine the optimum parameters for sulfur dispersion prepared via masterbatch mixing in 4 MT mixing tank in terms of its particle size distribution, viscosity, pH, and TSC.
2. To determine the optimum parameters for sulfur dispersion grinded in 60-Litre grinding mill in terms of its particle size distribution, viscosity, pH, and TSC.
3. To analyze the morphology of sulfur dispersed in rubber film using SEM/EDX from selected sulfur dispersion sets of Objective 2.

1.5 SCOPES OF STUDY

For this research, the scopes as mentioned below have been identified:

1. Design of Taguchi's L_9 orthogonal array for sulfur dispersion's mixing tank optimization with 2 factors (mixing speed and mixing time) and 3 levels for each factors (800, 600 and 400 rpm for mixing speed; with 30, 20 and 10 minutes for mixing time).
2. Design of Taguchi's L_9 orthogonal array for sulfur dispersion's grinding mill optimization with 2 factors (motor speed and pump rate) and 3 levels for each factors (800, 700 and 600 rpm for motor speed; with 750, 550 and 350 L/min for pump rate).
3. The output of the mixing process was measured in terms of sulfur dispersion's chemical specifications as follows:
    i. particle size distribution, D90,

   ii. viscosity,
   iii. pH, and
   iv. TSC.

4. The optimized sulfur dispersion mixing process was next chosen for its grinding mill optimization.
5. Similarly, the output of the grinding process was measured in terms of sulfur dispersion’s chemical specifications as follows:
   v. particle size distribution, D90,
   vi. viscosity,
   vii. pH, and
   viii. TSC.
6. After the grinding mill step, evaluation on instability index of various selected sulfur dispersions sets (after grinding mill) with index value results close to “0” as most stable and close to “1” as least stable sulfur dispersion; was performed.
7. Apart from that, rubber films were casted using sulfur dispersions obtained from the steps above and characterized for its morphology using SEM/EDX to analyze the elemental compositions on the rubber films’ surface.

1.6 THESIS ORGANIZATION

This thesis mainly consists of five chapters. Firstly, Chapter One was initiated with a brief description of the research's background which include descriptions on goal of organizations or manufacturers to produce good quality products with optimizations. Separately, description of the product chosen (sulfur dispersion) was also briefed to connect with optimization. Apart from that, details on problem statement, research objectives together with their scopes and importance of the research were also listed and described for readers' attention.

Subsequently, Chapter Two further thoroughly detailed on the elements presented in the research. As such, each detail on sulfur and its dispersion form were reviewed and detailed in the subsequent sub-chapter. Taguchi's approach as the optimization tool was also detailed in this chapter to provide a clear basis for a better understanding of the readers before proceed to the main focus of the research, which is optimizing process parameters of sulfur dispersion product.

Chapter Three presented the flowchart of the research methodology that fulfills the three objectives as mentioned in Chapter One. The flowchart would be helpful to provide the idea on the flow of the research in general. This chapter also revealed on the chosen materials, formulation, and parameters in terms of the design of Taguchi's L_9 orthogonal array for mixing process and grinding mill process of the sulfur dispersion, with chosen sulfur dispersion's specifications (factors, levels and responses).

Chapter Four in this thesis discussed thoroughly on the compiled, tabulated, and analyzed results for both optimization studies (mixing process parameters and grinding mill parameters). Generally, the selected or optimized sulfur dispersion's mixing process was chosen for optimization of the next process step – grinding mill parameter optimization. Consequently, means and S/N ratios were calculated for each run and the results were analyzed using ANOVA table that measures *p*-value to indicate the significance of each of the factors chosen. Additionally, morphology of the sulfur sets on the surface of rubber film casted was also observed, analyzed and discussed in this chapter.

Lastly, Chapter Five summarized and concluded the overall research and the results' significance. Apart from that, recommendations on further improvements on the research work were also outlined.

CHAPTER 2

LITERATURE REVIEW

2.1 BACKGROUND OF SULFUR

The Earth is richly equipped with various chemical elements in different regions in land and in the sea. As the elements naturally exist, their usage is exceptionally important for living things. Examples of elements include carbon, oxygen, zinc, magnesium, calcium and so much more. Sulfur (S) is one of the elements abundantly present in bulk on the Earth, both naturally and by chemical means. Its usage is exceptionally important as well especially in different industrial applications.

Today, in some regions of the world, sulfur (S) (in its powder or derived form) or interchangeably spelled as sulphur, has been widely manufactured and used in many industrial applications (Blight, Currell, Nash, Scott, & Stillo, 1978; Nehb & Vydra, 2012). U.S was the largest producer of elemental sulfur in the world, followed by Canada, in 2013. Apparently, China shot up its sulfur production until the year 2015, then continued throughout until 2018 and became the world's largest manufacturer of sulfur (Kutney, 2013). Figure 2.1 by the U.S. Geological Survey, (2019) shows the graph of sulfur production from the year 2013 to 2018, by country.