Optimisation of Formulation for Starch Modified Natural Rubber Composites by Using Response Surface Methodology

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Abstract. Starch modified natural rubber vulcanisates were prepared by the melt compounding method using a two-roll mill at a constant starch loading of 20 phr. Four formulation parameters consisted of black filler, white filler, silane coupling agent (SCA) and glycerol content in the composites which were optimised using two-level factorial design via response surface methodology (RSM). The cure characteristics and rebound resilience were selected as the responses. The significance of the factors and interaction were analysed using ANOVA and the model’s ability to represent the system was confirmed using the constant of determination, R² for a value above 0.90. The R² values for all responses were obtained in the range between 0.96 and 0.99 which are close to the union (R² = 1). The final combination of factors used to achieve the highest rebound resilience and cure characteristics were with a high black filler loading of 60 phr and high glycerol of 5 % loading. These findings were further supported by morphological characteristics observed under scanning electron microscopy (SEM). Therefore, the chemical modification using both glycerol and SCA was proven to improve the cure characteristics and rebound resilience value through the enhancement of the interfacial interaction between the starch and natural rubber (NR) particles. It is expected that the findings in this study will be useful for rubber product manufacturers to explore the possibility of producing biodegradable products in the future.

1. Introduction

Recently, the use of organic fillers has attracted much interest given their low costs and relatively lightweight. Aside from being environmentally friendly, the composites produced display several mechanical property enhancements [1, 2]. Several cellulosic materials such as nut shells, bamboo, ground wood waste, cereal straw and white rice husk have been used as fillers for plastics [3] and
elastomers [4]. Starch is one of the biopolymer substances that is naturally found in grains and vegetables and mostly consists of amylose and amylopectin. Further, starch is highly hydrophilic, and under strong inter and intramolecular hydrogen bond networks, and is therefore insoluble in most solvents. Several previous studies have explored starch reinforced elastomers [5-6]. In some studies, the incorporation of starch into polymer matrices has mainly focussed on phase separation. Notwithstanding, it has been widely acknowledged that good interfacial interaction between natural rubber (NR) matrices and starch, uniform particle distribution, and dispersion state of starch in the NR matrix are three vital parameters that strongly affect the mechanical properties of NR composites [7]. As a feasible solution, the modification of starch using a silane coupling agent (SCA) to enhance the interfacial interaction, and glycerol to assist in the plasticisation of starch-based NR compound appears to be a promising approach for further study.

The performance of NR composites is highly dependent on the formulation of the compound. Indeed, experimental work to optimise the formulation can be designed using suitable mathematical and statistical tools. The design of experiments (DOE) is a useful technique employed for multifactor experiments as it is less time-consuming and can detect the true optimum values of factors [8]. According to Mohamad et al. [9], it is possible to obtain quantitative relations for the effects of multi-process parameters on the properties of the NR composites via response surface methodology (RSM) in a minimum number of experiments. In this present study, RSM using a full factorial design was used to develop a mathematical correlation between formulations (effect of chemical modification) to produce NR composites with smaller sample size [10]. The mathematical models were applied in order to determine the feasible region of filler loading and the chemical modification of starch using SCA and the glycerol level to give NR composites with the desired cure characteristics and rebound resilience.

2. Experimental study

2.1 Materials

Table 1 displays the formulation used in this study. NR was purchased from Felda Global Ventures Holdings Bhd (FGV). Both white filler and black filler were purchased from Malaysian Rubber Board. The starch was purchased from Polyscientific Enterprise Sdn Bhd and other compounding ingredients such as sulphur, zinc oxide, stearic acid, were purchased from Systerm Classic Chemical Sdn. Bhd. The TMTD, SCA and glycerol were purchased from Aldrich Chemistry Sdn. Bhd., while Flexsys America, USA supplied 6PPD.

| Table 1. Typical formulation |
|-----------------------------|
| **Materials**               | **Compound (phr)*** |
| Natural rubber (SMR 20)     | 100                  |
| Filler (white and black)    | 0,30,60              |
| Zinc oxide                 | 5.0                  |
| Stearic acid               | 2.0                  |
| Tetramethylthiuram disulfide (TMTD) | 1.0 |
| (1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD) | 1.0 |
| Sulfur                     | 2.5                  |
| Tapioca starch             | 20                   |
| Silane coupling agent (%)  | 0,2,5,5              |
| Glycerol (%)               | 0,2,5,5              |

* Parts per hundred
2.2 Preparation and testing of NR composites

The compounding process was performed according to ASTM D 3184 [2] and carried out using a two-roll mill at a temperature of 50 °C. The NR was first masticated before adding all ingredients sequentially. Lastly, sulphur was added and mixed for around 1 min before dumped and left to cool to room temperature. The cure characteristics of the compound were obtained using a Monsanto moving die rheometer (MDR 2000) test at 150 °C. The rubber compounds were subsequently compression moulded at 150 °C using a hot press based on the respective cure time, \( t_{90} \) which is in accordance with ASTM D 2084.

2.2.1. Rebound Resilience Testing. The disk-shaped samples with a thickness of 12.5 ± 0.5 mm and diameter of 29 ± 0.5 mm were prepared according to the BS 903 PT A8 standard and tested using a DUNLOP Tripsometer at room temperature. At least seven samples were tested for every set of experiments to ensure a high confidence level of the results. The angle of rebound was recorded, and the average rebound resilience (%) was calculated using Eq. (1):

\[
\text{Resilience, } R = \frac{1 - \cos(\text{angle of rebound})}{1 - \cos(\text{angle of fall})} \times 100 \quad \text{(Eq. 1)}
\]

2.2.2. Scanning Electron Microscopy. Scanning electron microscopy (SEM), model EVO-50 from Zeiss, USA, was used to analyse the fracture surface regarding the morphological properties and distribution of starch granules in the NR composites. Next, the samples were placed onto an aluminium stub and sputter coated with a thin layer of gold, of about 20 mm thickness before the scanning process in order to avoid the occurrence of electrostatic charging and poor resolution during the examination. The fracture surface was observed under secondary electrons at the magnification of 500x and 1000x. The quadratic method applied against the micrographs to analyse starch distribution in the NR composites and the skewness value was calculated applying Eq. (2):

\[
\beta = \frac{q}{(q-1)(q-2)} \sum \left( \frac{N_{i} - N_{\text{min}}}{\sigma} \right)^{3} \quad \text{(Eq. 2)}
\]

2.3 Experimental design and analysis

The design of experiments (DOE) were carried out using Design Expert software (Statistics Made Easy, version 6.0.8, Stat-Ease, Inc., and Minneapolis, MN).

2.3.1. Two-level factorial design experiment. Independent variables in this study were black filler (X1), white filler (X2), glycerol (X3), and SCA (X4) with levels of variables as shown in Table 2. According to this design, there were 19 experiments with three replications at the centre point.

| Table 2. Levels of Variables |
|-----------------------------|
| Black filler (X1; Phr) | White filler (X2; Phr) | Glycerol (X3; %) | SCA (X4; %) |
| 0 (-1) | 0 (-1) | 0 (-1) | 0 (-1) |
| 30 (0) | 30 (0) | 2.5 (0) | 2.5 (0) |
| 60 (+1) | 60 (+1) | 5 (+1) | 5 (+1) |

2.3.2. Analysis of variance (ANOVA). An appropriate polynomial relationship for the dependent variables (response) was obtained. The result of this design was used to fit a first-order polynomial as given in Eq. (3):

\[
Y = \beta_{0} + \beta_{1}X_{1} + \beta_{2}X_{2} + \beta_{3}X_{3} + \ldots + \beta_{k}X_{k} + \varepsilon \quad \text{(Eq. 3)}
\]
where \( Y \) is the predicted response, \( \beta \) are the coefficient values, \( X \) is the independent variables, and \( \epsilon \) is a random error. In this study, \( k = 4 \) was used as there were four independent variables involved. From the RSM, a regression equation for the selected model for the response, \( Y \) was derived.

3. Results and discussion

In Table 3, the cure characteristics and rebound resilience results for each experiment are presented. In Table 4, the regression models for each response are presented. Accordingly, this mathematical relationship represents the quantitative effects of the independent variables and their interaction effects on the response. The positive values reflect the effects that lead to optimisation whereas negative values are the factors which provide an opposite effect on the response [11]. The \( R^2 \) values indicate the degree of agreement between the experimental results with those predicted by the model. The \( R^2 \) values for all responses are obtained in the range of 0.96–0.99 which are very close to the union \( (R^2 = 1) \). The model presented almost 100% of the variation in the overall system. Therefore, this indicates that the regression model is accurate in describing and predicting the pattern of significance for each factor studied [9, 12].

**Table 3. Cure Characteristics and Rebound Resilience**

| Experiment | Scorch time \( (t_{sc}) \) | Cure time \( (t_{90}) \) | Rebound resilience (%) |
|------------|---------------------------|---------------------------|------------------------|
| 1          | 0.57                      | 1.17                      | 36                     |
| 2          | 0.78                      | 1.19                      | 34.15                  |
| 3          | 0.57                      | 1.11                      | 37.54                  |
| 4          | 0.86                      | 1.36                      | 32.18                  |
| 5          | 0.37                      | 0.96                      | 11.6                   |
| 6          | 0.69                      | 1.44                      | 51.46                  |
| 7          | 0.49                      | 1.08                      | 27.72                  |
| 8          | 0.57                      | 1.17                      | 54.68                  |
| 9          | 1.02                      | 1.65                      | 49.46                  |
| 10         | 0.62                      | 1.04                      | 51.06                  |
| 11         | 0.71                      | 1.5                       | 29.24                  |
| 12         | 0.4                       | 1.05                      | 46.92                  |
| 13         | 0.5                       | 0.91                      | 23.52                  |
| 14         | 1.46                      | 2.25                      | 48.5                   |
| 15         | 0.54                      | 1                         | 31.2                   |
| 16         | 0.49                      | 1.15                      | 53.2                   |
| 17         | 0.69                      | 1.12                      | 37.92                  |
| 18         | 1.25                      | 2                         | 39                     |
| 19         | 0.46                      | 1                         | 39.1                   |

**Table 4. Regression Equation for different responses**

| Responses          | \( R^2 \) | Adjusted \( R^2 \) | Equation of the models                                                                 |
|--------------------|-----------|--------------------|---------------------------------------------------------------------------------------|
| Scorch time \( (t_{sc}) \) | 0.9979    | 0.9953             | \( Y_1 = 0.67 + 0.069 X_1 - 0.086 X_2 - 0.026 X_3 + 0.052 X_4 - 0.067 X_1 X_2 + 0.095 X_1 X_3 - 0.044 X_1 X_4 - 0.03 X_2 X_3 - 0.096 X_2 X_4 + 0.056 X_3 X_4 - 0.089 X_1 X_2 X_3 + 0.11 X_1 X_2 X_4 \) |
| Cure time \( (t_{90}) \)     | 0.9971    | 0.9757             | \( Y_2 = 0.74 + 0.57 X_1 - 0.03 X_2 - 0.1 X_3 + 0.014 X_4 + 7.5 \times 10^{-3} X_1 X_4 - 0.057 X_1 X_3 + 0.014 X_1 X_4 + 0.25 X_2 X_4 - 0.106 X_2 X_1 + 0.047 X_2 X_4 + 0.18 X_1 X_2 X_3 + 0.076 X_2 X_3 X_4 + 0.058 X_1 X_2 X_3 X_4 \) |
| Rebound resilience    | 0.9644    | 0.9244             | \( Y_3 = 37.09 + 9.43 X_1 + 2 X_2 + 0.65 X_3 + 1.42 X_4 - 1.77 X_1 X_2 + 4.79 X_1 X_3 + 1.98 X_1 X_4 - 0.052 X_2 X_4 - 4.46 X_3 X_4 \) |
3.1 Interaction between the variables for Cure Characteristics and Rebound Resilience Properties

Scorch time ($t_s$) is the time offset during which a rubber compound is workable at a given temperature before 2% of curing [13]. Figure 1(a) depicts the response surface for the variation in scorching time as a function of glycerol and black filler. According to the response surface plot, the $t_s$ increased as the black filler content increased from 0 to 60 phr, whereas, the $t_s$ value decreased as the glycerol content increased. This might be the suitable ratio between the fillers and glycerol which considerably delayed the scorch time, and improved the processing safety towards an efficient vulcanisation system [11]. Figure 1(b) demonstrates the cure time versus black filler and glycerol in the 3D surface plot. The response surface plot shows a similar pattern to $t_s$. Figure 1(c) demonstrates the rebound resilience versus black filler and glycerol in the 3D surface plot. Accordingly, it illustrates an almost identical pattern with the effect of both black filler and glycerol to $t_s$. According to the response surface plot, the rebound resilience of the NR composites increases up to 51.96% by an increase in the carbon black from 0 to 60 phr; as well as the increase in glycerol content. Therefore, according to these results, the maximum value of the rebound resilience is obtained at high black filler loading (60 phr) and high glycerol (5%) loading.

![Figure 1](image1.png)

Figure 1. Response surface plot in (a) scorch time ($t_s$), (b) cure time ($t_{90}$) and (c) rebound resilience

3.2 Morphological analysis

Figure 2 illustrates the SEM micrographs taken from the tensile fracture surfaces of the samples from Experiment 1 and Experiment 16. The starch particles appeared lighter and dispersed as spherical granules in the darker NR matrices. The granules were found to be uniformly distributed and dispersed in the range of 5 to 10 µm. At higher magnification (Figure 2(b)), the sample for Experiment 1 displayed larger starch granules with apparent interfacial gaps between the starch and natural rubber matrix. If compared with Figures 2(c) and (d) for Experiment 16, the starch granules appeared smaller and almost wholly embedded within the natural rubber matrices. Therefore, this represents that good compatibility, and good interaction between all components occurred in Experiment 16 composites. The dimension of the starch granules was strongly influenced by the treatment with 5% glycerol and 5% SCA. The reduction in particle size and improvement in the distribution of the starch particles in the NR matrices caused a remarkable development in the rebound resilience value. This is supported by the skewness value ($\beta$) obtained for a sample from Experiment 1 which was as high as 0.77 compared to ~ 0 for Experiment 16 thereby indicating the normal distribution of the starch particles [14].
4. Conclusion
The interaction between the formulation parameters established by the RSM is consistent with the morphological characteristics of the composites. The introduced chemical modification using both glycerol and SCA enhances the matrix-filler interfacial interaction and improves the cure characteristics as well as the rebound resilience value of the composites. In this study, the coefficient of determination ($R^2$) is sufficient to represent the model’s fit between the experimental and predicted value obtained from the software. Hence, the generated regression model can be utilised to optimise the chemical modification contents as well as suitable filler loading for producing the starch modified NR composites with maximum rebound resilience and safe curing during processing. The final combination of factors used to achieve the highest rebound resilience and cure characteristics are at the highest black filler loading of 60 phr and the highest glycerol of 5% loading.

![Figure 2](image)

**Figure 2.** SEM micrographs of NR composites (a) Experiment 1 at 500x, (b) Experiment 1 at 1000x, (c) Experiment 16 at 500x and (d) Experiment 16 at 1000x magnification

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