Journal of Mechanical Engineering and Sciences
ISSN (Print): 2289-4659; e-ISSN: 2231-8380
Volume 13, Issue 2, pp. 4989-5005, June 2019

DOI: https://doi.org/10.15282/jmes.13.2.2019.16.0413

Optimization of physical and mechanical properties of glycerol - modified natural rubber/starch - filled carbon black composites using two level factorial design

M. Mazliah[1], N. Mohamad[1]*, H.E. Ab Maulod[2], A.R. Jeefferie[1], M.A.A. Mohd Abid[1], K.I. Karim[1], M.A. Mahamood[1] and M.M. Hamdan[3]

[1]Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka,
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
Phone: +606-270 2571; Fax: +606 -270 1047
*Email: noraiham@utem.edu.my
[2]Fakulti Teknologi Kejuruteraan Mekanikal & Pembuatan, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[3]Sindutch Cable Manufacturer Sdn. Bhd. Lot 38, Alor Gajah Industrial Estate, 78000 Alor Gajah, Melaka, Malaysia

ABSTRACT

This study was carried out to develop statistical models of formulation parameters for physical and mechanical properties of natural rubber/starch composites using a 2^2 full factorial central composite design via a response surface methodology. It was to measure the significance and interaction of two identified formulation variables, namely, carbon black (X_1) as the filler and glycerol (X_2) as the processing oil. The factors are optimized to achieve maximum cure characteristics, rebound resilience and tensile strength. The composites were prepared by melt compounding process using a Haake internal mixer at a constant temperature and rotor speed of 60 °C and 60 rpm. Through the use of regression models that were developed for the quadratic model, a maximum rebound resilience of 71% and tensile strength of 22.57 MPa was obtained for a carbon black loading of 50 phr and a glycerol loading of 7%.

Keywords: Response surface methodology; natural rubber; starch; dynamic mechanical analysis; desirability.

INTRODUCTION

Natural rubber (NR) is the most important elastomer and it is used extensively in many applications due to its high elasticity (reversible deformability) [1-9]. Natural rubber is extracted in the form of latex from the Hevea brasiliensis tree. It is almost 100% cis-1,4 polyisoprene with a high molecular weight ranging from 1 to 2.5 x 106 (Figure 1) [10]. It is very elastic and can be stretched to at least 200% of its original length [11]. Natural rubber tends to crystallize when stretched, and spontaneously crystallizes at low temperatures as a result of its high structural regularity. The stiffening effect due to low-temperature crystallization can be easily reversed by warming. High-crystalline natural rubber exhibits a high tensile strength and an improved resistance towards abrasion, cutting, as well as wear and tear [12, 13].

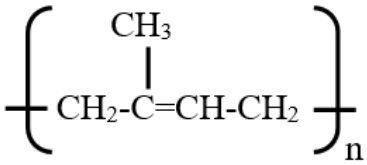


Figure 1. Natural rubber structure.

The elastic and flexible network of stretched rubber is a combination of both its crystallization-induced strength and toughness. The network is also responsible for the remarkable resilience of vulcanized rubber products. This resilience accounts for the lower loss of kinetic energy from hysteresis during deformation. The rubber polymer network is highly dependent on the processing of the rubber. It is necessary to compound the rubber with several ingredients for easier processability as well as to achieve the desired final properties and durable products [11]. In a rubber recipe, fillers, reinforcing materials, and other chemicals are usually added to enhance the final properties of the rubber. The incorporation of fillers is critical in rubber compounding as it modifies the processing and properties of natural rubber composites as well as reduces the cost of the products.

Carbon black (CB) is the most commonly used reinforcing agent in natural rubber. It is routinely employed in the rubber based product industry to enhance specific properties such as the tensile strength, facilitate the processing and reduce the cost [1, 3, 4, 14-18]. Carbon black has been widely used to produce various kinds of rubber engineering products. The physico-mechanical of the filled rubber are mostly the attributes of its multiphase system, which is defined by the mobility of the rubber molecules. This system depends highly on the dimensional and structural criteria of the carbon black; the structure of aggregates, surface characteristics, dimension of particles, and its distribution and dispersion in a rubber matrix [17]. The chemical bonding or physical interlocking between them defines the nature of the rubber-filler interaction.

Vulcanization involves the chemical reaction of rubber with curing agents in the presence of an accelerator and activator as well as other chemicals such as antioxidants and antiozonants [10]. Many chemical substances are involved in the process such as sulphur, zinc oxide, stearic acid, benzothiazyl-2-cyclohexylbenthiazyl sulphenamide and tetramethylthiuram disulphide. The ratio between the ingredients is crucial to determine the type of crosslinking. To gain a vulcanizate with mostly polysulphidic crosslinks and a relatively high level of chain modification, a conventional system (CV) is used. The CV system has a high sulphur level of 2 to 3.5 phr and a low level of accelerator of 0.5 to 1 phr. On the other hand, an efficient system (EV) of low sulphur levels of 0.25 to 0.7 phr with high accelerator levels of 2.5 to 5 phr produces mainly monosulphidic crosslinks with low chain modifications. The crosslinks act as a bridge between the chains to prevent chain slippage. Effective crosslinks will result in rubber vulcanizates with improved physical and mechanical properties. The combination of useful properties for the vulcanizates can be changed or improved by modifying the compounding formulation and processing techniques.

The performance of natural rubber based products depends highly on the formulation of the compound. The evaluation of optimum parameters for multifactor experiments can be eased by utilizing an appropriate statistical and mathematical tools as well as careful selection of suitable design of experiment [18]. It is capable to identify the true optimum of various variables and is less time-consuming. Some researchers claimed that minimum number of

experiments through response surface methodology (RSM) is possible to acquire quantitative relations for the effects of various process parameters with regard to the properties of NR composites [1, 19-23]. In this work, RSM was utilized to develop mathematical relationships between the single formulation factor and its interaction factor contributions to identify the best combination of carbon black loading and glycerol loading to generate the NR/starch composites with the desired cure characteristics, rebound resilience and tensile strength [20].

METHODS AND MATERIALS

Materials

Table 1 shows the formulations that were investigated in this study. The natural rubber (NR) SMR20 was supplied by Felda Global Ventures Holdings Bhd. The black filler, carbon black N330 was procured from the Malaysian Rubber Board. Meanwhile, Polyscientific Enterprise Sdn. Bhd. supplied starch for the compound modifier. Other compounding ingredients such as stearic acid, zinc oxide and sulphur were purchased from Systerm Classic Chemical Sdn. Bhd. The rubber accelerator, TMTD was purchased from Aldrich Chemistry, while the antioxidant, 6PPD, was supplied by Flexys America, USA. All the chemicals were used as received without further purification steps. Glycerol, purchased from Sigma-Aldrich, was introduced to study its effect on the optimum cure characteristics, rebound resilience and tensile strength.

Table 1. Formulation of natural rubber/starch composites.

Materials	Compound (phr)[a]
Natural rubber (SMR 20)	100
Carbon black (N330)	0-60
Zinc oxide	5.0
Stearic acid	2.0
TMTD[b]	1.0
6PPD[c]	1.0
Sulfur	2.5
Tapioca starch	20
Glycerol (%)	0-5

[a] Parts per hundred

[b] Tetramethylthiuram disulfide

[c](1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

Compounding and Vulcanization Process

The compounding of natural rubber/starch-filled carbon black was according to ASTM D3182 [20, 23]. A Haake internal mixer working at a temperature of 60°C and a rotor speed of 60 rpm. The NR was masticated for 1 minute using Banbury rotor followed by the other ingredients and continuously mixed for another 5 minutes. At the final 1 minute, the sulphur was added and the mixing continued before it was dumped for cooling and sheeting (Figure 2). After conditioning for 24 hours, a Monsanto moving die rheometer (MDR 200) was used

to obtain the rheograph of the compound for the cure characteristics. The compound was then cured under compression in a hydraulic press at 150°C for the optimum curing time according to ASTM D 2084.

Figure 2. Natural rubber mixes.

Rebound Resilience

According to the BS 903 Pt A8 standard, disk samples of the NR/starch composites with a diameter of 29 ± 0.5 mm and thickness of 12.5 ± 0.5 mm were prepared. Then, the disks were tested at room temperature using a DUNLOP Tripsometer. A set of seven samples was tested for each formulation to ensure a high confidence level. The angle of rebound in degrees was verified and the average value of the rebound resilience, R (%) was calculated by using Equation (1):

$$R = \frac{1-\cos(\theta_{rebound})}{1-\cos(\theta_{fall})} \times 100 \quad (1)$$

Tensile Strength

Hot press-moulded sheets were cut into dumbbell-shaped samples using a die cutter. Then, the NR/starch composite samples were subjected to tensile loadings using a Universal Testing Machine in accordance to the BS 6746 standard. The tests were carried out at a constant cross-head speed of 500 mm/min at room temperature. Seven samples were tested for each formulation to achieve a high confidence level.

Dynamic Mechanical Analysis

A thermal analysis was performed using a TA Instruments DMA-7 apparatus under a nitrogen purge at a frequency of 5 Hz and a heating rate of 2 °C min^{-1}.

Experimental design and analysis

A plan was drawn up for a design of experiments (DOE), data analysis and optimization utilizing a Design Expert software (Statistics Made Easy, version 6.0.8, Stat-Ease, Inc., Minneapolis, MN).

Full factorial central composite design

Laboratory experiments based on the central composite design (CCD) was conducted to optimize the formulation variables for the preparation of the NR/starch composites. The experiments were carried out according to a two factor-two level, 2^2 full factorial design. The two independent variables were carbon black (X_1) and glycerol (X_2) at low level (−1) and high level (+1). At five replications at the centre points and four star points, a total of thirteen sets of experiments were generated (Table 2). The levels of the independent variables chosen for this trial are given in Table 3. The responses (dependent variables) selected were the cure characteristic, rebound resilience and tensile strength. The levels were selected based on the results of a preliminary study.

Analysis of variance (ANOVA)

From the experimental data, the approximate polynomial relationships for the cure characteristics, rebound resilience and tensile strength were obtained. The results were used to fit a second order polynomial with all the interaction terms, as in Equation (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_{ii}^2 + \sum \sum_{i<j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the predicted response, X represents the independent variables, β represents the coefficient values, and ε is a random error. In this study, two independent variables were involved and $k = 2$. The mathematical relationship between the variables (X_1 and X_2) and the dependent variable (Y) is defined by Equation (3):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (3)$$

where β_0 is the offset term, β_1, and β_2 are the linear coefficients, β_{11} and β_{22} are the quadratic coefficients and β_{12} is the cross-product coefficients.

Table 2. Full factorial central composite design for the optimization of formulations in the preparation of NR/starch composites.

Experiment	Coded variable	
	Carbon black (X_1)	Glycerol (X_2)
1	-1	-1
2	+1	-1
3	-1	+1
4	+1	+1
5	-1.414	0
6	+1.414	0
7	0	-1.414
8	0	+1.414
9	0	0
10	0	0
11	0	0
12	0	0
13	0	0

Table 3. Level of variables chosen for trial.

Carbon black (X_1, phr)	Glycerol (X_2, %)
50 (-1)	5.0(-1)
75 (0)	6.0 (0)
100 (-1)	7.0 (+1)

RESULTS AND DISCUSSION

Regression Models of the NR/starch Composites Properties

NR/starch composites at 13 different combinations of carbon black and glycerol were prepared and tested for the cure characteristics, rebound resilience and tensile strength. The experiments were conducted as random run order suggested by the Design Expert software. The results and regression model for each experiment are presented in Table 4 and Table 5, respectively.

Table 4. Results of each experiments.

Experiment	Scorch time (t_{s2})	Cure time (t_{c90})	Rebound resilience (%)	Tensile strength (MPa)
1	0.95	2.02	71	22.73
2	0.81	5.13	47	18.15
3	1.14	2.33	68	23.19
4	0.8	4.6	48	20.91
5	1.09	2.8	76	21.48
6	0.73	5.36	43	18.75
7	0.97	2.42	57	22.17
8	0.93	2.25	58	24.75
9	0.8	1.97	59	22.61
10	0.82	2.11	59	22.42
11	0.82	2.11	59	22.54
12	0.8	2.11	59	22.45
13	0.82	2.11	59	22.56

In Table 5, the regression model represents the quantitative effects of the independent variables (filler loading and glycerol) and their interaction effects in relation to the response, both for the physical and mechanical properties (scorch time, cure time, rebound resilience and tensile strength). Positive value indicates the effect that plays a role to a maximization of the response, whereas negative value reflects the opposite effect to the response. The coefficient of determination (R^2) values indicates the level of agreement between the predicted models with those of the actual experimental results. In this study, all the R^2 values obtained were in the range of 0.90-0.99. These values were very close to unity ($R^2 = 1$), where almost all the variations were presented by the model. This indicated the accuracy of the regression models in explaining the system hence predicting the significance for the two factors involved in this study [21, 24].

Table 5. Regression models for different responses.

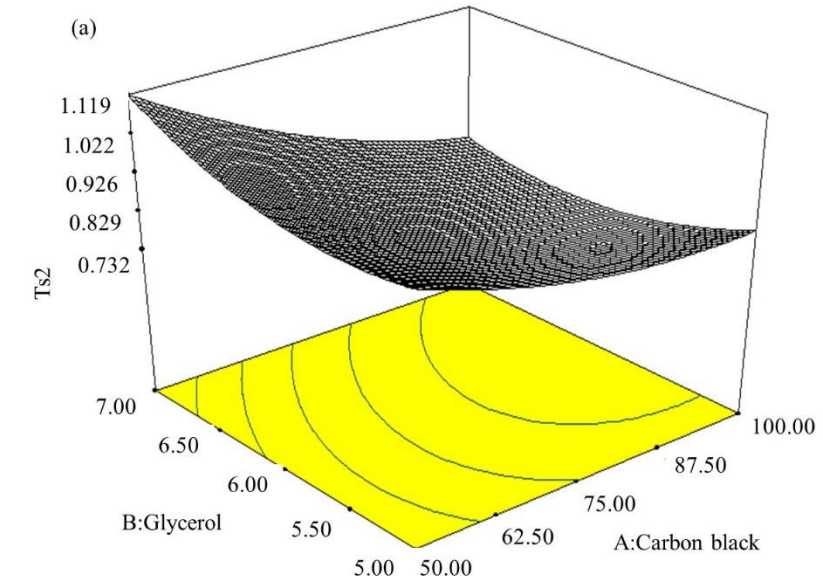
Responses	R^2	Adjusted R^2	Equation of the models
Scorch time (t_{s2})	0.9662	0.9421	$Y_1 = + 0.81 - 0.12\ X_1 + 0.018\ X_2 + 0.05\ X_1^2 + 0.07\ X_2^2 - 0.05\ X_1\ X_2$
Cure time (t_{90})	0.9703	0.9491	$Y_2 = + 2.08 + 1.13\ X_1 - 0.046\ X_2 + 1.10\ X_1^2 + 0.19\ X_2^2 - 0.21\ X_1\ X_2$
Rebound resilience	0.9976	0.9960	$Y_3 = +59.01 - 11.39\ X_1 - 0.11\ X_2 + 0.24\ X_1^2 - 0.75\ X_2^2 + 1.00\ X_1\ X_2$
Tensile strength	0.9554	0.9236	$Y_4 = +22.52 - 1.35\ X_1 + 0.86\ X_2 - 1.36\ X_1^2 + 0.35\ X_2^2 + 0.58\ X_1\ X_2$

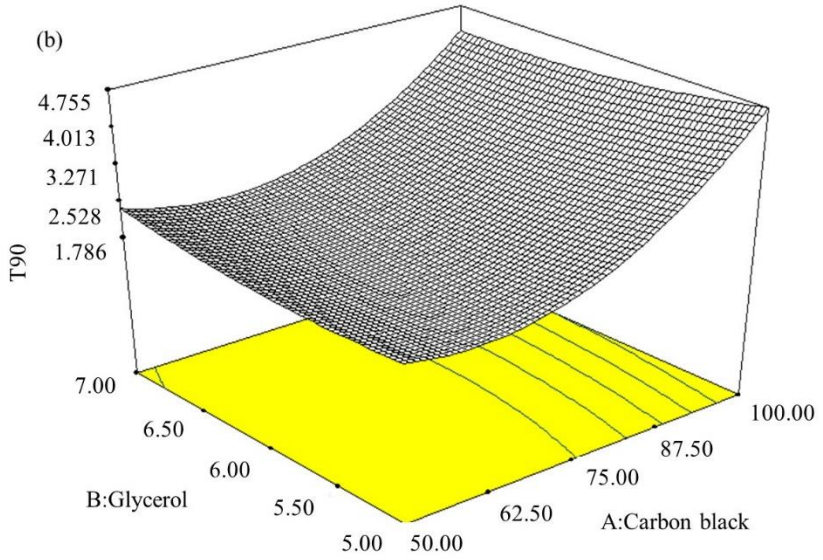
Interaction between Independent Variables of the NR/Starch Composites

The scorch time (t_{s2}) is the offset for a rubber compound to be still workable at a specific temperature before experiencing 2% curing level. In this study, an optimal t_{s2} was highly desirable to ensure a completely moulded product.

Figure 2 (a) illustrates the response surface of the scorch time as a function of the carbon black content and percentage of glycerol. From the response surface plot, t_{s2} decreased as the carbon black content was increased from 50 to 100 phr, while t_{s2} increased as the percentage of the glycerol increased. The highest t_{s2} of about 1.12 minutes was achieved at the highest glycerol content and the lowest carbon black content. This might have been due to the prolonged surface activity among the glycerol and filler, which significantly delayed the t_{s2} and improve the processing safety towards an efficient vulcanization. In contrast, according to Nor and Othman [26], a low t_{s2} indicates an improvement in the workability of a compound once it is exposed to temperature. It is correlated to the thermal energy that can be endured by a compound before it is transformed to a vulcanizate due to the formation of crosslinks [14, 25]. Some studies reported a shortening of t_{s2} once carbon black was added to the compound [14, 16]. The carbon black particles induced heat from the friction formed by the shear action during mixing. They also increased the viscosity of the compound. This was accelerated by the high molecular weight of the rubber chains, which generated high shear stresses that broke the filler aggregates and increased the uniform dispersion of the filler in the compound.

Figure 2 (b) illustrates variations in the cure time, t_{90} as a function of carbon black and glycerol. Comparing with the t_{s2}, the surface plot for t_{90} shows an opposite pattern. Meanwhile, glycerol had no substantial effect on t_{90}. This indicated that the presence of carbon black disturbed the stereo-regularity of the natural rubber chains. It slowed down the surface activity of the chemical species and simultaneously, prolonged the vulcanization action that occurred in the compound [16].


(a)
1.119
1.022
0.926
0.829
0.732
Ts2
7.00
6.50
6.00
5.50
5.00
B:Glycerol
50.00
62.50
75.00
87.50
100.00
A:Carbon black


(b)
4.755
4.013
3.271
2.528
1.786
T90
7.00
6.50
6.00
5.50
5.00
B:Glycerol
50.00
62.50
75.00
87.50
100.00
A:Carbon black

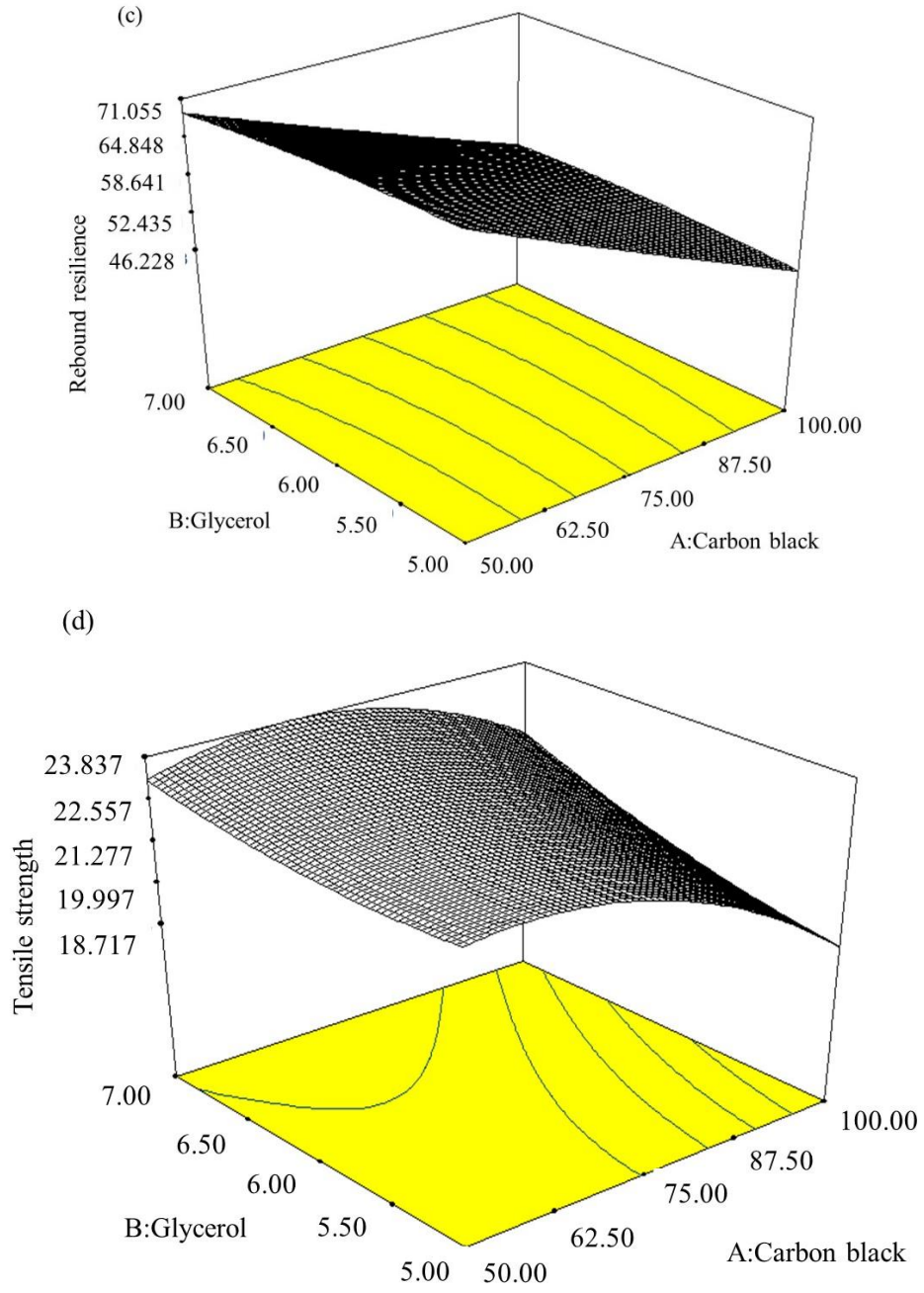


Figure 2. Response surface plot showing variations in (a) scorch time (t_{s2}), (b) cure time (t_{90}), (c) resilience, and (d) tensile strength.

Figure 2(c) depicts the 3D surface plot of rebound resilience, Y_3 of the composites versus glycerol and carbon black. It shows an almost linear response but with similar pattern as the effect of carbon black and glycerol to t_{s2}. It was observed that the rebound resilience decreased consistently with an increase in the carbon black loading. A significant number of authors have reported that the rebound resilience decreased with an increase in the filler loading [8, 20, 26-28]. This was simply attributed to the dilution effect since the rubber

portion is known to dominate the elastic response, which is later measured as the rebound resilience of a material [29, 30].

The effects of carbon black and glycerol on the tensile strength, Y_4 of the composites are depicted in Figure 2(d). The composites demonstrated the highest tensile strength when the carbon black loading was 50 phr and decreased with a higher carbon black loading. The enhanced strength was attributed to the optimum compatibility of the carbon black particles with the matrices. The good interfacial adhesion between the carbon black particles and natural rubber/starch matrices improved the mechanical properties as a result of the efficient load transfer mechanism [3, 31]. However, at higher carbon black loadings, the carbon black particles tended to aggregate due to the strong filler-filler interactions induced by the surface hydroxyl group. This led to a poorer dispersion of carbon black in the natural rubber compound.

Based on the experiment, it is postulated that a higher carbon black loading of more than 100 phr is detrimental to the rebound resilience and tensile properties of the NR/starch composites. It may result in the composites having a lower rebound resilience and tensile strength than 40 % and 18 MPa, respectively. This was due to the agglomeration of the filler particles. The effect was further depicted by a perturbation plot, as shown in Figure 3.

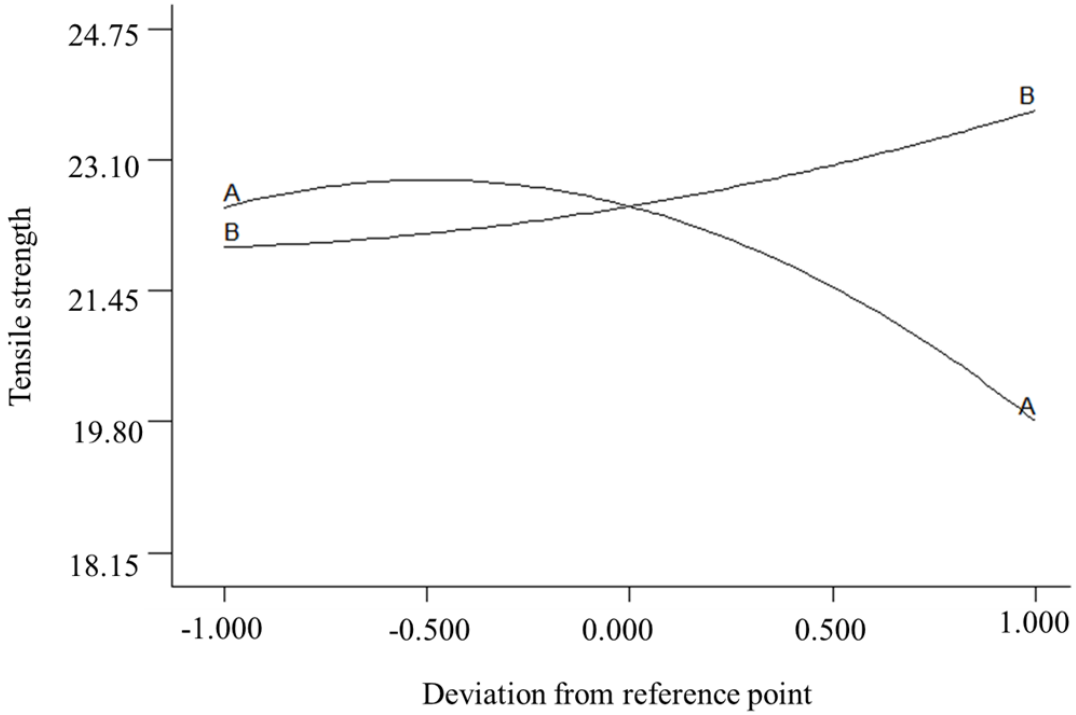


Figure 3. Perturbation of factors A (carbon black) and B (glycerol) at the reference point (carbon black =75 phr, glycerol= 6.0%).

Table 6. Comparisons of experimental and predicted tensile strength of NR/starch composites

Experiment	Experimental value (Y; %)	Predicted value (^Y;%)	Residual (Y-^Y)
1	22.73	22.57	0.16
2	18.15	18.72	-0.57
3	23.19	23.14	0.048
4	20.91	21.59	-0.68
5	21.48	21.74	-0.26
6	18.75	17.96	0.79
7	22.17	22.01	0.16
8	24.75	24.41	0.34
9	22.61	22.52	0.095
10	22.42	22.52	-0.095
11	22.54	22.52	0.025
12	22.45	22.52	-0.065
13	22.56	22.52	0.045

According to the perturbation plot in Figure 3, the carbon black loading had greater effects than the glycerol loading as it prominently changed from the reference point. However, the carbon black loading had a negative effect on the tensile strength as it exhibited a descending trend, whereas the glycerol loading showed a positive effect since the curve took an ascending trend. Consequently, the higher the loading of carbon black into the NR/starch composites, the lower was the tensile strength. In contrast, the higher the glycerol loading (>7%), the higher would be the tensile strength. This was well-supported by the regression model tabulated in Table 5.

The predicted tensile strength and experimental data at each experimental point was tabulated in Table 6. From the data, the experimental value was very close to the predicted value with a deviation of less than 3%, except for experiment 6, where the difference was about 4.2%. This was due to the carbon black loading of more than 100 phr, which further reduced the uniformity of the composites. From the data evaluation, the corresponding maximum tensile strength of around 23 MPa was obtained at 50 phr of carbon black and 7% of glycerol. Figure 4 demonstrates the histogram where the desirability of these criteria was 0.852 that close to unity [21].

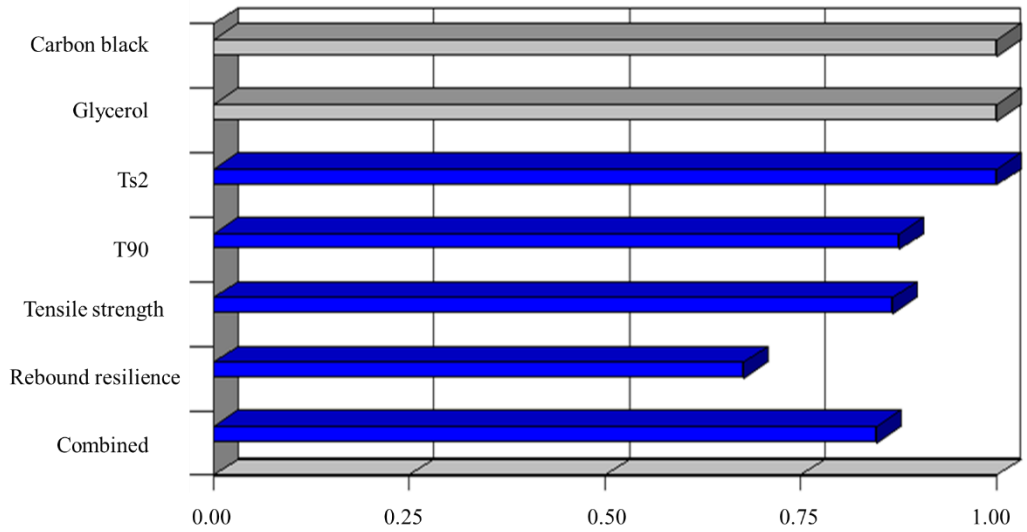


Figure 4. Effect of the independent variables, response, and their combinations for optimization desirability.

Dynamic Mechanical Thermal Analysis (DMTA)

The compatibility of the NR/starch composites was determined by DMTA, which measures the glass transition (T_g) of a material. The tan δ value decreased with an increase in the carbon black loading in the NR/starch composites. According to Utracki and Wilkie [32], a single sharp peak of tan δ indicates a miscible compound. In this study, the thermal characteristics of the NR/starch composites were examined by a DMTA within a temperature range of -100 °C to 100 °C. This methodology was used to determine the glass transition temperature (T_g), which varied from -48.58 ˚C to -50.22 ˚C as the carbon black loading was increased from 50 to 100 phr (Figure 5). According to Figure 5, all the three NR/starch composites exhibited a significant degree of miscibility, as depicted by the single and sharp peaks of tan δ. However, the tan δ value decreased as the carbon black (CB) loading increased. This was an indication that the rubber chains were restricted due to the rubber-filler interaction, as demonstrated by other researchers [31, 33].

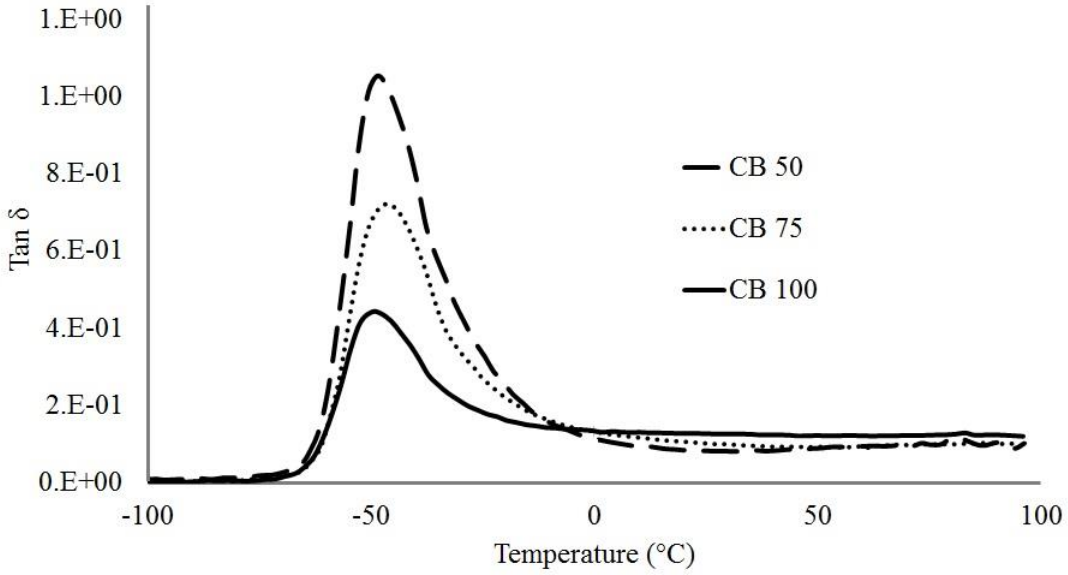


Figure 5. Tan δ values of NR/starch composites at 5.0 Hz versus temperature.

CONCLUSIONS

Response surface methodology utilizing a full factorial central composite design has proven to be a powerful and reliable tool for modelling, analyzing and optimizing the interactive effects of multiple formulations factors to produce products with desired properties. From the study, it was observed that the loading of carbon black plays a greater role than the glycerol content in altering the physical (cure characteristic) and mechanical properties (tensile strength and rebound resilience) of natural rubber/starch composites. The maximum predicted rebound resilience and tensile strength of around 70 % and 23 MPa, respectively. The parameters for optimum processability as well as the maximized rebound resilience and tensile strength were achieved at a carbon black loading of 50 phr and glycerol content of 7%. The natural rubber/starch-filled carbon black composites that were produced are promising candidates for biodegradable natural rubber-based products with appreciable processing requirements and significant mechanical properties.

ACKNOWLEDGEMENTS

The authors acknowledge Carbon Research Technology group and Universiti Teknikal Malaysia Melaka for financial support through (PJP/2016/FKP/HI6/S01484).

REFERENCES

[1] Mazliah M, Mohamad N, Maulod HEA, Jeefferie AR, Mohd Mef'at H. Rebound resilience of natural rubber composites via response surface methodology. Proceeding of Mechanical Engineering Research Day 2018, (May). 2018, 130-1

[2] Mohamad N, Yaakub J, Maulod, HEA, Jeefferie AR, Yuhazri MY, Lau KT, Ahsan Q, Shueb MI, Othman R. Vibrational damping behaviors of graphene nanoplatelets reinforced NR/EPDM nanocomposites. Journal of Mechanical Engineering and Sciences. 2017;11:3274-87.

[3] Rosszainily IRA, Salim MA, Mansor MR, Akop MZ, Putra A, Musthafah MT, Hasan MZ, Abdul Rahman MN, Sudin MN. Effect of carbon black fillers on tensile stress of unvulcanized natural rubber compound. Journal of Mechanical Engineering and Sciences. 2016;10:2043-52.

[4] Valodkar M, Thakore S. Thermal and mechanical properties of natural rubber and starch nanobiocomposites. International Journal of Polymer Analysis and Characterization. 2010;15:387-95.

[5] Khafidh M, Schipper DJ, Masen MA, Vleugels N, Noordermeer JWM. Tribological behavior of short-cut aramid fiber reinforced sbr elastomers: the effect of fiber orientation. Journal of Mechanical Engineering and Sciences. 2018;12:3700-11.

[6] Norazlina H, Firdaus RM, Hafizuddin WM. Enhanced Properties from Mixing Natural Rubber with Recycled Polyvinyl Chloride by Melt Blending. Journal of Mechanical Engineering and Sciences. 2015;8: 1440-47.

[7] Taufik RS, Nurul Farah Adibah M, Muhamad MR, Hasib H. Feasibility Study of Natural Fiber Composite Material for Engineering Application. Journal of Mechanical Engineering and Sciences. 2014;6:940-48.

[8] Jamiluddin J, Siregar JP, Sulaiman A, Jalal KAA, Tezara C. Study on Properties of Tapioca Resin Polymer. Journal of Mechanical Engineering and Sciences. 2016; 13:3178-89.

[9] Mohamad N, Nur Sharafina Z, Maulod HEA, Yuhazri MY, Jeefferie AR. Morphological and Mechanical Properties of Polypropylene/Epoxidized Natural Rubber Thermoplastic Vulcanizates Treated with Maleic Anhydride-Grafted Polypropylene. International Journal of Automotive and Mechanical Engineering. 2013;8:1305-15.

[10] Niyogi UK. Natural and Synthetic Rubber. Polymer Science. Delhi.

[11] O Aguele F, Madufor CI. Effects of Carbonised Coir on Physical Properties of Natural Rubber Composites. American Journal of Polymer Science. 2012;2:28-34.

[12] Mazliah M, Mohamad N, Jeefferie AR. Cure characteristics and tensile properties of natural rubber vulcanizates modified by tapioca starch. Proceeding of Mechanical Engineering Research Day 2016, (March). 2016;163-4.

[13] Mohamad N, Mazliah M, Jeefferie AR, Nur Sharafina Z, Amirul Asyraf M, Maulod HEA. Compressive properties of green rubber foam from reclaimed rubber glove. International Journal Materials and Product Technology. 2016;53: 252-66.

[14] Attharangsan S, Ismail H, Bakar MA, Ismail J. Carbon black (CB)/rice husk powder (RHP) hybrid filler-filled natural rubber composites: Effect of CB/RHP ratio on property of the composites. Polymer - Plastics Technology and Engineering. 2012;51:655-62.

[15] Guo C, Zhou L, Lv J. Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites. Polymers and Polymer Composites. 2013;21:449-56.
[16] Ismail H, Nordin R, Noor AM. The effect of filler loading on curing and mechanical properties of natural rubber/recycled rubber powder blends. International Journal of Polymeric Materials and Polymeric Biomaterials. 2005;54:9-20.
[17] Ramesan MT. The effects of filler content on cure and mechanical properties of dichlorocarbene modified styrene butadiene rubber/carbon black composites. Journal of Polymer Research. 2005;11:333-40.
[18] Ibrahim MS, Sapuan SM, Faieza AA. Mechanical and Thermal Properties of Composites from Unsaturated Polyester Filled with Oil Palm Ash. Journal of Mechanical Engineering and Sciences. 2012;2:133-7.
[19] Mah KH, Yussof HW, Abu Seman MN, Mohammad AW. Polyester thin film composite nanofiltration membranes via interfacial polymerization: influence of five synthesis parameters on water permeability. Journal of Mechanical Engineering and Sciences. 2018;12:3387-98.
[20] Chonkaew W, Minghvanish W, Kungliean U, Rochanawipart N, Brostow W. Vulcanization Characteristics and Dynamic Mechanical Behavior of Natural Rubber Reinforced with Silane Modified Silica. Journal of Nanoscience and Nanotechnology. 2010;10:2018-24.
[21] Mohamad N, Yaakub J, Jeefferie AR, Yuhazri MY, Shueb MI, Muchtar A. Effects of Epoxidized Natural Rubber (ENR-50) and Processing Parameters on The Properties of NR/EPDM Blends using Response Surface Methodology. Journal of Applied Polymer Science. 2014;131:40713.
[21] Mohamad N, Muchtar A, Ghazali MJ, Mohd DH, Azhari CH. Epoxidized Natural Rubber-Alumina Nanoparticle Composites: Optimization of Mixer Parameters via Response Surface Methodology. Journal of Applied Polymer Science. 2010;115:183-9.
[23] Noryani M, Sapuan SM, Mastura MT. Multi-criteria decision-making tools for material selection of natural fibre composites: A review. Journal of Mechanical Engineering and Sciences. 2018;12:3330-53.
[24] Al-Mansob RA, Ismail A, Yusoff NIM, Azhari CH, Karim MR, Alduri A, Baghini MS. Rheological Characteristics of Epdxidized Natural Rubber Modified Bitumen. Applied Mechanics and Materials. 2014;505-506:174-9.
[25] Jeefferie AR, Ahmad SH, Ratnam CT, Mahamood MA, Yaakub J, Mohamad N. Effects of EPDM- g -MAH Compatibilizer and Internal Mixer Processing Parameters on The Properties of NR / EPDM Blends : An Analysis using Response Surface Methodology. Journal of Applied Polymer SCIENCE. 2015;132:42199.
[26] Nor NAM, Othman N. Effect of Filler Loading on Curing Characteristic and Tensile Properties of Palygorskite Natural Rubber Nanocomposites. Procedia Chemistry. 2016;19:351-8.
[27] Jeefferie AR, Ahmad SH, Ratnam CT, Mahamood MA, Yaakub J, Mohamad N. NR/EPDM Elastomeric Rubber Blend Miscibility Evaluation by Two-Level Fractional Factorial Design of Experiment. AIP Conference Proceedings. 2014; 1614:82-89.

[28] Ooi ZX, Ismail H, Abu Bakar A. Synergistic Effect of Oil Palm Ash Filled Natural Rubber Compound at Low Filler Loading. Polymer Testing. 2013;32:38-44.
[29] Sae-oui P, Sirisinha C, Hatthapanit K. Effect of Blend Ratio on Aging, Oil and Ozone Resistance of Silica-Filled Chloroprene Rubber/Natural Rubber (CR/NR) Blends. 2007;1:8-14.
[30] Moonchai D, Moryadee N, Poosodsang N. Comparative properties of natural rubber vulcanisates filled with defatted rice bran, clay and calcium carbonate. Maejo International Journal of Science and Technology. 2012;6:249-58.
[31] Ooi ZX, Ismail H, Abu Bakar A. Dynamic Mechanical Properties and Tensile Behavior of Oil Palm Ash Filled Natural Rubber Vulcanizates. Advances in Rubber. 2014;844:305-8.
[32] Utracki LA, Wilkie C. Polymer Blends Handbook. 2014;2nd ed:New York: Springer.
[33] Thongsang S, Sombatsompop N, Ansarifar A. Effect of fly ash silica and precipitated silica fillers on the viscosity, cure, and viscoelastic properties of natural rubber. Polymers for Advanced Technologies. 2008;19:1296-304.