

Prediction of Mechanical Properties of Compatibilized Styrene/Natural-Rubber Blend by Using Reaction Conditions: Central Composite Design vs. Artificial Neural Networks

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ABSTRACT: A polystyrene (PS)/rubber blend compatibilized with PS-*g*-rubber copolymer, prepared via emulsion polymerization using redox initiator system, is used to investigate the utilization of central composite design (CCD) and artificial neural network (ANN) approaches in correlating polymerization conditions to mechanical properties (tensile strength and abrasion loss) of unfilled compound vulcanizates. The conditions were manipulated by changing four factors: reaction temperature and time, percentage of deproteinized rubber in the mixture containing natural rubber, and amount of chain transfer agent. The results show that the relationships between the conditions and the mechanical properties for compatibilized PS/rubber blend are too complex to be explained by polynomials, but are well described by the ANN models, developed for each response. In addition, simulation results for the tensile strength response as a function of those factors using the obtained ANN are in agreement with literature, whereas those results for the abrasion loss do not quite agree with literature due to the interference of the large measurement error. This suggests that only experimental data with high precision should be used to train an ANN to achieve a model with not only best performance but also high reliability. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Natural rubber from *Hevea brasiliensis* is an elastomer of interest herein due to its abundance in Thailand. One effective way to increase its value-added price is to improve its mechanical properties. It is commonly known that this can be done by blending with a small quantity of thermoplastic polymer possessing superior mechanical properties and/or by vulcanization that induces the crosslink density of the rubber phase.^{1–3}

In blending thermoplastic and elastomer that are immiscible, a two-phase system normally occurs. The lack of interpenetration at the phase boundaries causes a reduction in the useful mechanical properties. Thus, it is often necessary to improve the compatibility between the two phases by the addition of compatibilizers, such as graft or block copolymers, prepared from the thermoplastic and the elastomer themselves or from different polymer pairs with similar chemical structures to them. Such a compatibilizer can penetrate into both phases at the interface, thus improving interfacial adhesion between two phases in polymer/rubber blends and acting as an emulsifier that reduces the

size of the dispersed domains.^{4–9} For instance, polystyrene–natural rubber graft copolymer (PS-*g*-NR) and polystyrene–polybutadiene block copolymer (PS-block-PB) enhance the compatibility of PS/NR blend and PS/PB blend, respectively.^{8,10–12} A copolymer can be either directly added into polymer blends or made during the polymerization of thermoplastic monomers in the presence of rubber particles (some of monomers are grafted onto rubber particles to form graft/block copolymer and some become homopolymers).^{8,10–12}

In addition to the crosslink density of the rubber phase due to vulcanization, the improvement of mechanical properties of the compatibilized polymer/rubber blends reportedly depends on the amount of graft copolymer and its composition. The positive effect of grafting amount on mechanical properties of peroxide vulcanizates of polymer/rubber blend is observed and explained by the graft copolymer being able to reduce interfacial energy between two phases and the domain size.¹³ The inverse effect reportedly exists when grafting amount is excessive, which is attributed to the formation of a thick layer of excessive

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grafting molecules around dispersed phases, destabilizing the phase morphology, and lowering the mechanical properties.¹⁴ It should also be noted that when saturation of graft copolymer on the domain surface is reached, the further reduction of dispersed domain size with increasing the graft copolymer concentration is not discerned.^{15,16} Moreover, Chuayjuljit et al.¹⁷ attributed an increase in the tensile strength of the 30/70 PS/NR blend film containing PS-NR graft copolymer to the higher PS level in the graft copolymer and the hard brittle nature of PS.

It is reported that proteins in the rubber can compete for free radical species, resulting in lower amount of chain grafted onto natural rubber, and lower monomer conversion.^{18–20} In addition, the proteins, being hydrophilic by nature, in unvulcanized natural rubber can absorb moisture from the atmosphere, leading to the deterioration in degree of crosslinking and other cure characteristics of some vulcanizing systems, and thus causing variation in the modulus of vulcanized rubber.²¹ Accordingly, the amount of deproteinized natural rubber (DPNR) in polymer blends may potentially affect mechanical properties.

Literature data indicated that the amount of graft copolymer and its composition can be controlled by polymerization conditions—e.g., reaction time and temperature, amount of chain transfer agent (CTA), type of natural rubber latex (deproteinized or fresh natural rubber latex).^{20,22–27} This implies a correlation between the polymerization conditions and the mechanical properties. In consequence, it is interesting to develop a model that correlates the conditions to the properties of polymer/rubber blends because the model will assist researchers in designing new polymer/rubber blends with desired properties by simply changing model inputs (i.e., reaction conditions) without actually conducting experiments. Response surface methodology (RSM) and artificial neural networks (ANNs) are tools that have potential to fulfill this requirement without understanding the underlying mechanisms.

Central composite design (CCD), one of the most important response surface methods, utilizes available data and an interpolation method to form a polynomial function.²⁸ It can be used not only to optimize process variables in order to obtain the maximum or minimum response, but also to study the influences of those variables and their interactions on the process response. Several studies reported the use of CCD in studying the optimization, interactions, and influences of conditions of graft polymerization on response values, such as degree of grafting, grafting efficiency, and processing torque.^{29,30} Nevertheless, none of these focused on the correlation between mechanical properties and polymerization conditions of polymer/rubber blends.

An ANN, in a metaphorical sense, is composed of a biological brain having two sets of nervous systems acting as input and output streams. Through the nervous system, experimental data input and output values are given to the “brain.” The brain scrutinizes the relationship between the input and output data and finally obtains parameters that are hidden in the brain and cannot be extracted. Though a mathematical model cannot be obtained from the approach, the ANN approach is known for its reliability in predicting response values, high resistance to

noisy or missing data, and capability to handle a number of variables with unknown interactions.³¹ Many researchers successfully used this approach to investigate many polymer-related systems that possess nonlinear or complex relationship between the independent and dependent variables, including polymer blends/composites and graft polymerizations.^{32–38} Most of independent and dependent variables in those reports are curing conditions (or fractions of polymers) and corresponding mechanical properties or polymerization conditions and corresponding monomer conversion. As with the RSM application, no one has ever attempted to establish an ANN that maps the graft polymerization conditions to mechanical properties of polymer/rubber blends.

In this work, the compatibilized PS/rubber blend was prepared by allowing styrene monomers to react with themselves and with the NR-DPNR mixture using emulsion polymerization under various reaction conditions by changing four factors: reaction temperature and time, weight percent of DPNR in the rubber mixture, and amount of CTA. This article is the first work that attempts to use CCD and ANN with the back-propagation algorithm approaches to correlate the polymerization conditions to the corresponding mechanical properties (i.e., tensile strength and abrasion resistance). Additionally, we present the results of our studies on the unfilled vulcanized system. Later, the models with better performance were used to simulate the properties as a function of each factor.

EXPERIMENTAL

Materials

Fresh NR latex with a solid content of 60% was purchased from Thailand Natural Rubber Research Institute. DPNR with a nominal nitrogen content of 0.02% was prepared by allowing NR latex to react with 0.1% urea in sodium dodecyl sulfate solution (SDS; Fluka, purity ~ 90%) for 15 min in an ultrasonic bath, followed by centrifugation to rinse latex particles in the 1% SDS solution. The DPNR was later dissolved in an aqueous solution and immediately used in the graft polymerization.²⁷ Styrene monomer (Merck, purity ~ 99%) was purified by washing several times with an aqueous solution of 15% sodium hydroxide (NaOH). The redox initiator, cumene hydroperoxide (CHPO; Fluka, purity ~ 80%), and the activator agent, tetraethylene pentamine (TEPA; Fluka, purity ~ 85%), were used as received. Potassium hydroxide (Fluka) for pH control, SDS as an emulsifier, and other chemicals were analytical grade and used as received.

Preparation of PS-g-Rubber

Following the recipe in Table I, the NR-DPNR mixture in a certain ratio was purged with nitrogen for 30 min prior to the respective addition of styrene, *n*-dodecyl mercaptan (used as a CTA) and TEPA. The mixture, maintained at pH 10 and a certain temperature, was continuously stirred at 400 rpm for 1 h to allow rubber particles to swell in styrene. At a stirring speed of 400 rpm, upon the addition of CHPO, the reaction instantaneously began and was stopped at a certain time by dropping hydroquinone. To facilitate the milling, fresh NR latex was added into the polymer solution such that the weight ratio of fresh NR to the NR in the polymer solution was 2 : 1.

Table I. Recipe for Emulsion Copolymerization of Styrene and Rubber

Organic component (rubber : styrene = 76 : 24, g)	100.00
Deionized water (g)	305.00
Isopropanol (g)	7.60
SDS (g)	1.14
TEPA (g)	0.24
CHPO (g)	0.19
Hydroquinone (g)	0.83

Afterwards, the polymer coagulation was conducted by continuously dropping 10% formic acid into the polymerized mixture, and the obtained gross polymer was dried at 70°C for a week or until a constant weight was obtained.

Compounding and Vulcanization

A semi-efficient vulcanization system was used in this work. The compounding and vulcanization were as described in the ASTM D3182. The dried gross polymer was mixed with vulcanizing agents in a two-roll mill maintained at 70°C (Table II). The rubber compound was conditioned at room temperature for 24 h before cure assessment on a Monsanto Die Rheometer (MDR 2000) at 150°C to determine the cure times. The compound was then vulcanized in the compression molding according to the predetermined cure times.

Mechanical Properties

The vulcanizates were cut into dumbbell shape according to ASTM D412 Die, and the tensile strength was measured at room temperature using Instron (Model 1011, USA) according to ISO 37 (Type 1). Abrasion resistance of the vulcanizates in terms of DIN volume loss was conducted on an APH-40 Abrasion tester (Hampton Test Equipment) according to DIN 53516.

Modeling by Using CCD Approach

For each response, CCD was used to design experiments for the four factors: reaction temperature and time, %DPNR in the rubber mixture, and CTA amount; five level values were provided for every factor, as shown in Table III. The levels of these factors were chosen based on previous experiments and literature,²³ and there are four repeated runs at the central levels.

By using regression analysis, multiple regression equations were developed [eq. (1)], followed by statistical analyses, which include analysis of variance (ANOVA) and *F*-test for testing significance of overall models and each coefficient. All of these were carried out by a trial version Minitab 16.

$$Y = b_0 + \sum_{i=1}^{n=4} b_i X_i + \sum_{i=1}^{n=4} b_{ii} X_i^2 + \sum_{i=1}^{n=4} \sum_{j=1}^{n=4} b_{ij} X_i X_j \quad (1)$$

where *n* corresponds to the number of factors, *Y* is the response variable (tensile strength or abrasion), and *X_i* is independent variable. *b_i* is the linear coefficient, whereas *b_{ii}* and *b_{ij}* are squared and interaction coefficients for each variables *X_i* and for each pair (*X_i* and *X_j*), respectively. The mathematical model in eq. (1), comprising linear, quadratic, and interaction terms, explains the relationship between independent and dependent variables.

Modeling by Using ANN Approach

ANN is a highly simplified model of decision-making and predicting processes and is inspired by biological neural structures of the central nervous system. It imitates the function of a human brain in processing information to understand the input–output relationship and finally being able to transform inputs into meaningful outputs. The obtained knowledge is then used in the prediction of response values.

In brief, ANN has basic elements, which are three layers (so-called input, hidden, and output layers), weights, bias, and transfer functions.^{36–38} It should be noted that there can be more than one hidden layer, but usually a network containing one hidden layer and numerous neurons is enough to perform a task. Each neuron, or node, in the input layer corresponding to each independent variable sends a vector of the variable, which must be modified according to eqs. (2) and (3), to all neurons in the hidden layer. Each vector element is calculated as follows:

$$\text{net}_j = \sum_{i=1}^q w_{ji} x_i + \mu_j \quad (2)$$

$$y_j = f(\text{net}_j) = \frac{1}{1 + e^{-\text{net}_j}} \quad (3)$$

where *net_j* is the net input to the *j*th neuron in the hidden layer, *x_i* is the variable from the *i*th neuron in the input layer, *q* is the number of neurons in the input layer, *w_{ji}* is the connection weight from the *i*th neuron in the input layer to the *j*th neuron in the hidden layer, *μ_j* is the bias corresponding to the *j*th neuron in the hidden layer, and *y_j* is the output for the *j*th neuron in the hidden layer, calculated by using a transfer function, *f*(*net_j*). In addition, besides the sigmoid function shown in eq. (3), one could use other nonlinear transfer functions, such as a log function, a segment function, and a Gauss function.³⁹

Next, output vectors from every neuron in the hidden layer are modified by using eqs. (2) and (3) where currently *j* represents the *j*th neuron in the next layer, *i* denotes the *i*th neuron in the current layer, and *q* is the number of neurons in the current layer. Then, the modified output vectors will be sent to each neuron in the *j*th layer. Here there is only one hidden layer, and

Table II. Rubber Compound Formulation

Ingredient	Amount (phr)
Dried gross polymer	100.00
Zinc oxide	3.00
Stearic acid	2.00
Wingstay 29 (antioxidant)	1.00
Wingstay 100 (antioxidant)	1.25
Highly aromatic oil (lubricant)	2.00
2-Benzothiazolethiol	1.25
Methyl Tuads®	0.25
Sulfur	1.60

Table III. Central Composite Design for Emulsion Copolymerization and Experimental Responses Used in the CCD and ANN Studies

Run	A ^a (°C)	B ^b (h)	C ^c (%)	D ^d (phr)	Tensile strength (MPa)	Abrasion loss (mm ³)
1	50	4	25	0.25	19.60	76.00
2	70	4	25	0.25	21.60	64.30
3	50	6	25	0.25	18.60	57.10
4	70	6	25	0.25	21.70	76.80
5	50	4	75	0.25	19.40	35.10
6	70	4	75	0.25	20.30	21.50
7	50	6	75	0.25	20.60	62.40
8	70	6	75	0.25	22.40	72.90
9	50	4	25	0.75	19.30	68.20
10	70	4	25	0.75	20.10	72.10
11	50	6	25	0.75	17.10	86.70
12	70	6	25	0.75	20.20	79.90
13	50	4	75	0.75	15.45	51.85
14	70	4	75	0.75	21.30	50.70
15	50	6	75	0.75	19.60	59.10
16	70	6	75	0.75	21.70	53.20
17	40	5	50	0.50	17.70	63.00
18	80	5	50	0.50	18.30	66.20
19	60	3	50	0.50	12.40	82.70
20	60	7	50	0.50	18.10	72.10
21	60	5	0	0.50	18.50	74.10
22	60	5	100	0.50	14.20	44.80
23	60	5	50	0.00	20.70	51.50
24	60	5	50	1.00	14.25	56.55
25	60	5	50	0.50	20.30	64.30
26	60	5	50	0.50	19.90	72.90
27	60	5	50	0.50	21.20	91.60
28	60	5	50	0.50	18.30	82.70

^aA = reaction temperature, ^bB = reaction time, ^cC = %DPNR in the rubber mixture, ^dD = CTA amount and its unit is phr (part per hundred of organic component).

thus the next layer is the output layer. Each neuron in the output layer corresponds to each dependent variable.

To train a network, a back-propagation feed-forward algorithm is used. Weight and bias values between each layer pair must be corrected to minimize the root mean square error (RMSE) between the output elements from the output layer (y_{pre}) and experimental (y_{exp}) values of a dependent variable [eq. (4)]:

$$RMSE = \sqrt{\frac{\sum_{m=1}^p (y_{pre,m} - y_{exp,m})^2}{p}} \quad (4)$$

where p denotes the total number of data points. The correction is first made to the weight and bias before the output layer and then propagates backward to the first ones. After finishing the correction in the backward direction, the whole process is repeated (i.e., starting from the transmission of input vectors from the input layer to the hidden layer and that output vectors from the hidden layer to the output layer) until an acceptable error (i.e., lower than the property measurement error) is reached.

After the training, the obtained network is validated and tested using different data sets. Obtaining the best network may require changes in the transfer function, training function, learning rate, and the number of neurons in the hidden layer.

In this report, an ANN model, correlating the polymerization conditions and a mechanical-property response, was developed by using the same data sets used in the CCD studies, which were normalized in the range 0.05–0.95. However, for the replication at the center point, a single number (being the average of those four replicates) is used; that is, there are 25 runs instead of 28 runs (see Table III). The whole process of training, validating, and testing a model was conducted by using NNTOL box in MATLAB. The performance quality of the network is determined by RMSE, a plot of predicted versus observed normalized values, and the value of determination coefficient (R^2).

RESULTS AND DISCUSSION

Regression Modeling by Using CCD Approach

The regression analysis of the experimental data in Table III gives estimated regression coefficients [b_i , b_{ij} , b_{ij} as in eq. (1)],

Table IV. Results of Regression Analysis and Corresponding *T*- and *P*-Values of Quadratic Polynomials for Tensile Strength and Abrasion Loss

Model term	Tensile strength			Abrasion loss		
	Coefficient ^a	<i>T</i> -value	<i>P</i> -value	Coefficient ^a	<i>T</i> -value	<i>P</i> -value
Constant	19.9250	14.918	0.000	77.8750	12.577	0.000
A	0.4344	1.593	0.135	0.0281	0.022	0.983
B	0.3385	1.242	0.236	1.8156	1.437	0.174
C	-0.1260	-0.462	0.651	-4.8531	-3.840	0.002
D	-0.4656	-1.708	0.111	1.3698	1.084	0.298
A × A	0.0116	0.085	0.934	-0.9184	-1.453	0.170
B × B	-0.1603	-1.176	0.261	-0.1184	-0.187	0.854
C × C	-0.0915	-0.672	0.514	-1.2402	-1.963	0.071
D × D	-0.0212	-0.156	0.879	-1.5793	-2.499	0.027
A × B	0.0086	0.051	0.960	0.6258	0.809	0.433
A × C	0.0258	0.154	0.880	-0.2383	-0.308	0.763
A × D	0.0633	0.379	0.711	-0.2320	-0.300	0.769
B × C	0.1695	1.015	0.328	1.0711	1.384	0.190
B × D	0.0008	0.005	0.996	-0.5664	-0.732	0.477
C × D	0.0023	0.014	0.989	-0.1523	-0.197	0.847
Adjusted <i>R</i> ²		0.00			0.38	
<i>R</i> ²		0.44			0.70	

^aEstimated regression coefficients are for input data in uncoded units (values are in the same ranges shown in Table 3).

as listed in Table IV. The *P*-value corresponds to the *T*-value, which is the ratio of a coefficient and its corresponding standard error (results not shown). When the *P*-value is less than 0.05, this indicates 95% confidence that the variation does not occur by chance. As a result, a model term with $P < 0.05$ is considered significant and has a significant effect on the response.⁴⁰

In Table IV, since $P > 0.05$, none of these model terms are significant to the first response (tensile strength), whereas only *C* and *D*² are significant to the second response (abrasion loss). The results of the former response are consistent with ANOVA results in Table V, which shows $P > 0.05$ for all terms. For the latter response, the results are slightly different; that is, only the linear term is considered significant in the ANOVA Table ($P < 0.05$). Nonetheless, low values of both *R*² and adjusted *R*² of both responses' models imply a poor fit, which is in agreement with the insignificance of the regression terms in Table V (*P*-value > 0.05). Furthermore, Figure 1(a,b) show the scatter around the lines with slopes of one, confirming poor fitting models for both responses. As a result, it can be said that the relationships between the reaction conditions and each property are too complicated and cannot be simply described by quadratic polynomial equations developed from CCD approach.

Modeling by Using ANN Approach

We first tried to build only one model for two responses, but the model performance was unsatisfactory. Instead, better performance is attained when developing one model for each response, the topology details of which are shown in Table VI. This approach has similarities to a network with one neuron in an output layer for experiments having multiple responses,

which is also found in polymer-related literatures.^{36–38} For instance, Delfa et al.³⁶ tried to develop one model for three responses in order to optimize conditions for styrene-butadiene rubber emulsion polymerization and eventually found out that one model for each response shows better performance.

In Table VI, for each response, four neurons in the input layer correspond to the four factors (reaction temperature and time, %DPNR, and CTA amount). Only one hidden layer was found to be enough for the tasks, and the number of neurons was increased from a small number to a number yielding the model with the best performance. Both optimum networks for each response use a sigmoid function as the transfer function and the gradient descent approach (GDA) with adaptive learning rate as the training function. Small values of RMSE that are lower than the measurement errors calculated from repeated experiments (0.094 and 0.132 for respective normalized tensile strength and abrasion loss values) justify the best performance of both models. Furthermore, the quality of fit can be visualized in Figure 2(a,b) for tensile strength and abrasion loss,

Table V. ANOVA for the Fitted Quadratic Polynomials for Tensile Strength and Abrasion Loss

Source	Tensile strength		Abrasion loss	
	<i>F</i>	<i>P</i> -value	<i>F</i>	<i>P</i> -value
Regression	0.73	0.718	2.18	0.084
Linear	1.80	0.189	4.50	0.017
Quadratic	0.45	0.773	2.31	0.113
Interaction	0.20	0.971	0.55	0.759

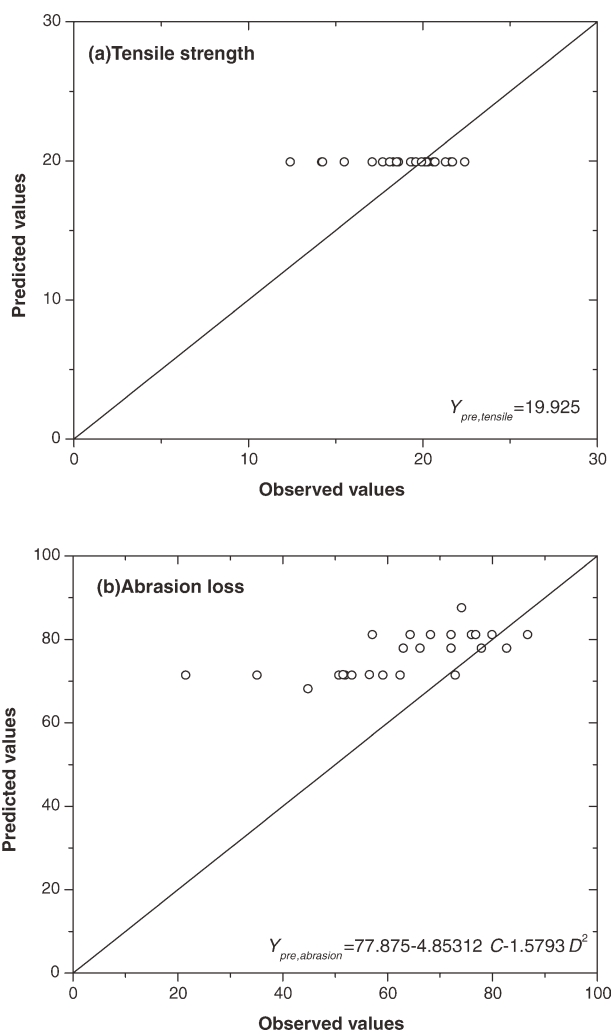


Figure 1. Predicted versus observed values from the CCD models for (a) tensile strength and (b) abrasion loss. Polynomial equations used for the prediction are listed in corresponding figures.

respectively. Most data are clustered around the lines with slopes of one, which is in agreement with high R^2 values.

A comparison between models obtained from CCD and ANN approaches is made by comparing R^2 and RMSE values. For both responses, it is clear that the ANN models give higher R^2 (Table VI) and lower RMSE than the CCD models (0.386 and 0.23 for respective normalized tensile strength and abrasion loss), which signifies the suitability of the ANN models over the CCD models in explaining the relationships between the reaction conditions and mechanical properties.

It should be noted that the total number of data to establish a network depends on the complex of the input–output relationship.³⁷ In addition, some results in the literature acquire good-fitting ANN models using the total number of data between 10 and 35 for polymer systems. Vijayabaskar et al.³⁷ shows that a data set with more than 20 observations is sufficient to suppress error growth in the attempt to correlate the mechanical properties to the volume fraction of crosslinked nitrile rubber. Delfa et al.³⁶ successfully uses about 15–30 data to establish three

Table VI. Details of ANN Models for Predicting Tensile Strength and Abrasion Loss

	Tensile strength	Abrasion loss
Number of neurons (input : hidden : output)	4 : 5 : 1	4 : 5 : 1
Transfer function	Sigmoid	Sigmoid
Training function	GDA	GDA
Learning rate	0.01	0.01
Epochs	15,000	50,000
RMSE ^a	0.0899	0.0919
R^2 ^a	0.84	0.74

^aBoth RMSE and R^2 presented here were calculated by using dimensionless (normalized) data. It should be noted that R^2 from dimensionless (normalized) and dimensional data are equal to each other.

models for solid content, Mooney viscosity, and polydispersity of styrene–butadiene rubber. Dhib and Hyson even used a number of data as low as 10 to develop models predicting

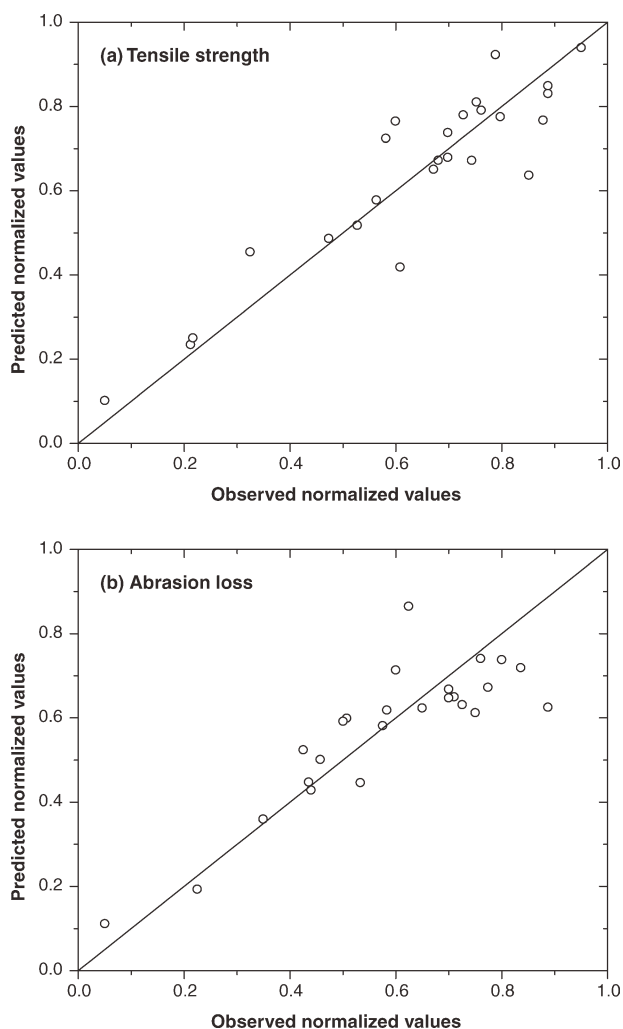


Figure 2. Predicted versus observed normalized (dimensionless) values from the ANN approach for (a) tensile strength and (b) abrasion loss.

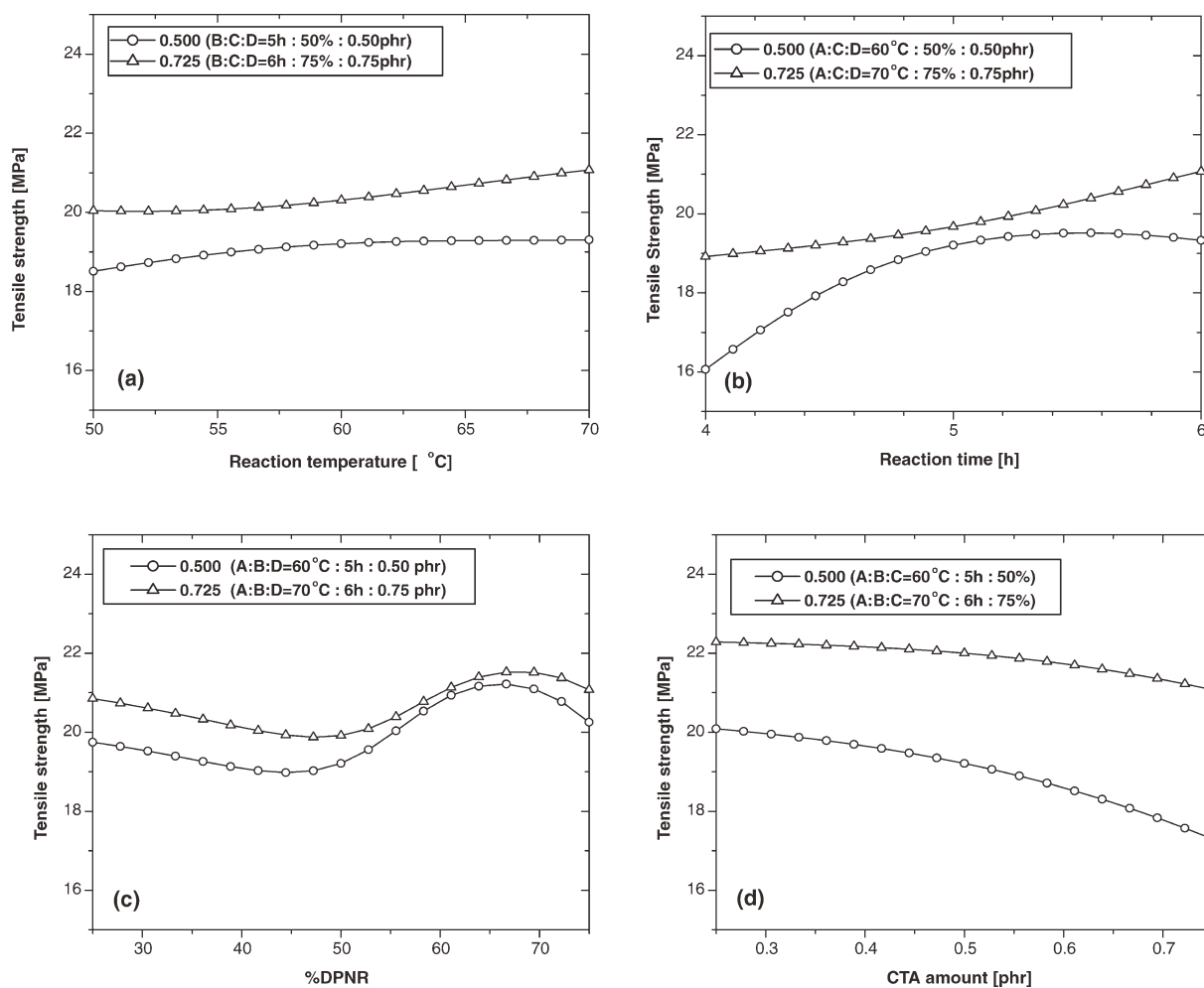


Figure 3. ANN-simulated values of tensile strength as a function of (a) reaction temperature, *A*, (b) reaction time, *B*, (c) %DPNR, *C*, and (d) CTA amount, *D*. Levels of the other factors are fixed and denoted in each figure, in both normalized and unnormalized forms.

conversion and molecular weight of polystyrene as a function of time.³⁵

Simulation Results of Mechanical Properties

To perceive how these mechanical properties change over the factors' ranges of interest, values of tensile strength and abrasion loss as a function of each factor were simulated using the attained ANN models; results are displayed in Figures 3 and 4. The values of the simulation inputs and of simulation outputs were in the normalized form (between 0.05 and 0.95), which were afterward converted to values with units for easy presentation. Also, for each effect studied, the normalized values of other factors were fixed at 0.5 and 0.725.

Tensile Strength

Effect of Reaction Temperature [Figure 3(a)]. When the three other factors (reaction time, %DPNR, and CTA amount) are fixed at levels of 0.5, the tensile strength slightly increases with temperature; a similar trend is also observed at the higher levels (0.725). In this temperature range, the increment is only 1 MPa, which is equal to the measurement error. Hence, the tensile strength may be considered constant with temperature. For emulsion polymerization using redox initiator system, Kohut-

Svelko et al.⁴¹ observed that temperatures in this range (50–70°C) for reactions conducting with enough initiator concentration do not notably affect monomer conversion, resulting in constant grafting amount. Similarly, Juntuek et al.²² reported that the amount of glycidyl methacrylate-g-natural rubber copolymer obtained in an emulsion polymerization using redox initiator is rather constant in the range of 30–70°C. As a result, the contribution of grafting amount which improves the interfacial adhesion between the polymer domains and rubber matrix is nearly the same in this temperature range, leading to nearly unchanged tensile strength of products.

Although at fixed levels of all other three factors (i.e., reaction time, % DPNR, and CTA amount) tensile strength is nearly constant over the entire temperature range, increasing levels of those three factors at the same time can raise the tensile strength of 18.5–19.3 to 20–21 MPa over the entire temperature range.

Effect of Reaction Time [Figure 3(b)]. The tensile strength remarkably increases with reaction time and the values of three fixed factors (reaction temperature, %DPNR, and CTA amount). Only when the three fixed factors are at the lower levels and reaction time is itself large, a small decrease in tensile strength is

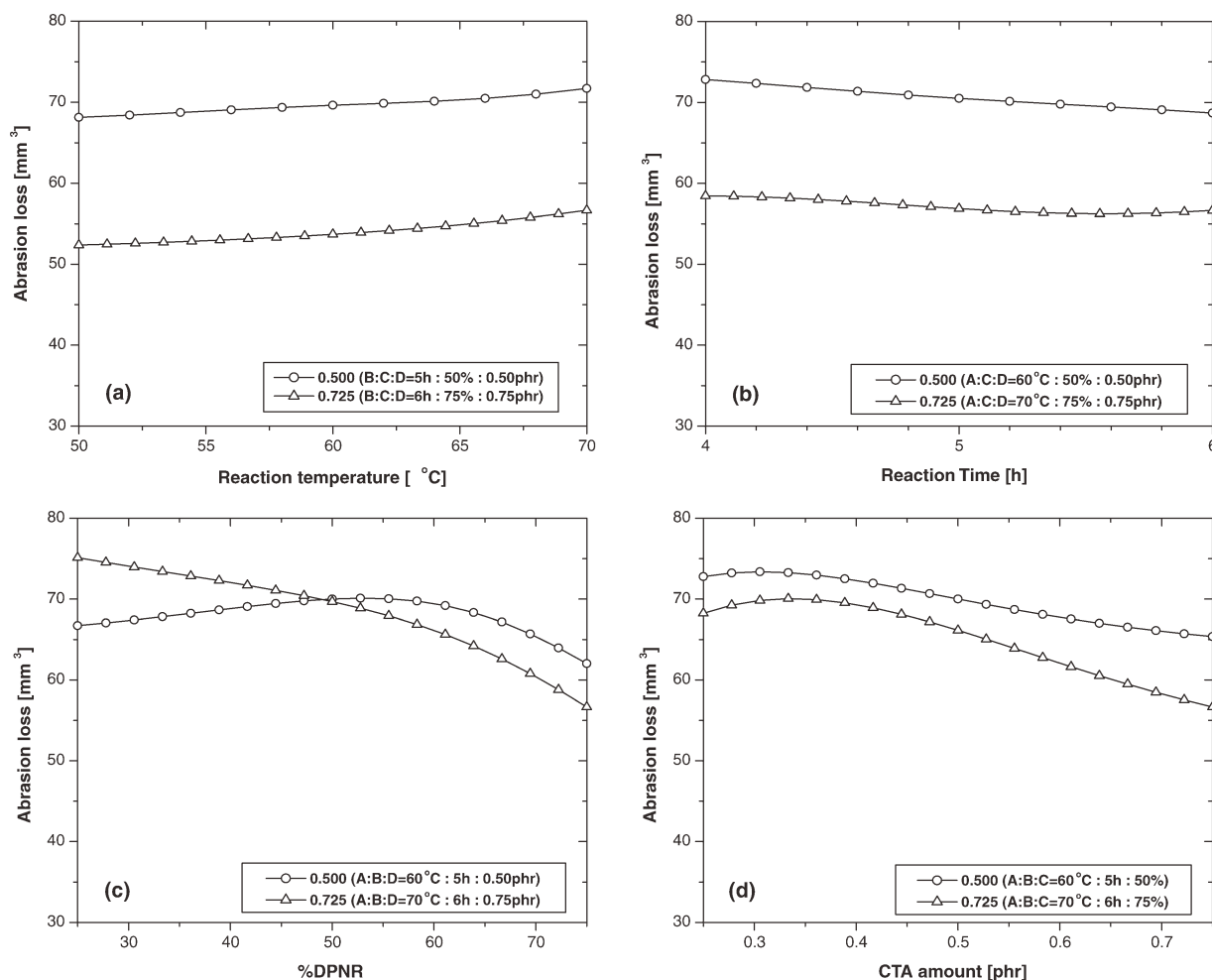


Figure 4. ANN-simulated values of abrasion loss as a function of (a) reaction temperature, A, (b) reaction time, B, (c) %DPNR, C, and (d) CTA amount, D. Levels of the other factors are fixed and denoted in each figure, in both normalized and unnormalized forms.

detected as the reaction time is increased. The small drop is, however, less than the measurement error of 1 MPa and thus deemed negligible.

For emulsion polymerization, the reaction rate increases at the early stage of the reaction due to abundant amount of available micelles, later becomes unvarying when the number of particles is constant and monomer supply is still excessive, and finally decreases when the monomer droplets outside particles disappear.⁴² Accordingly, the noticeable rise of tensile strength with time can be justified by the substantial reaction rate, and the leveling-off in tensile strength can be ascribed to the diminishing reaction rate at larger time, where the grafting amount is barely increased. It should be noted that we observed the decay of the reaction rate beyond 2 h and the reaction rate equal to zero beyond 5 h (data not shown). In addition, a few researchers attribute the time influence to free radicals having more time in the reaction, resulting in increases in both conversion and grafting amount.^{43,44}

The leveling-off in tensile strength at longer time does not occur when reaction temperature, %DPNR, and CTA amount are increased to the higher levels.

Effect of %DPNR [Figure 3(c)]. The influence of %DPNR on tensile strength is not apparent—both at the lower and higher levels of the three fixed factors (reaction temperature and time and CTA amount). Furthermore, the tensile strength weakly increases with the levels of those three fixed factors. The small influence of %DPNR may be explained by the work of Nakason et al.,¹⁸ which reported an increase of 0.1% in monomer conversion and an increase of 3% in grafting efficiency when grafting methyl-methacrylate onto DPNR, rather than NR, using redox initiators. However, the percent increases in monomer conversion and grafting efficiency when grafting styrene onto DPNR, rather than NR, are stated in the report of Tho et al.²⁰ (45% in styrene conversion and 230% in grafting efficiency). However, the latter report used ammonium peroxy disulfate as the initiator, which has a different mechanism from the redox initiator system, used by Nakason et al.¹⁸ and the current work.

Effect of CTA amount [Figure 3(d)]. An inverse relationship between CTA amount and tensile strength is discerned, both at the lower and higher levels of the three fixed factors (reaction temperature and time and %DPNR). This phenomenon occurs because the addition of CTA amount raises the probability of

reactions between free radical species and CTA, leading to reactions that prematurely terminate polymer chain length and reducing the grafting and polymerization rates, as well as polymer molecular weight, but not altering the number of grafting sites.^{18,20,25,45} Consequently, the grafting amount, which is the weight of the graft copolymer, is lower due to a shorter grafted chain length, and this results in poor interfacial adhesion between polymer and rubber phases.⁴⁵

Similar to Figure 3(a–c), there occurs elevated tensile strength when levels of the three fixed factors are high.

Although individual effects display quite different influences on tensile strength (monotonic increase or decrease or fluctuation), it is discernible in Figure 3(a–d) that increasing values of three of four factors noticeably improve the tensile strength.

Abrasion loss

Effects of Reaction Temperature and Time [Figure 4(a,b)]. At both lower and higher levels of the three fixed factors, the changes in abrasion loss as a function of reaction temperature and of time are less than the property measurement error of 10.3 mm³, suggesting very weak influences of these two factors. The measurement error reported herein is not large and uncommon when compared with those reported in the literature. Using the same standard (DIN 53516), Rattanasom et al.¹ reported abrasion loss DIN measurement error values between 5 and 12.5 mm³ for their filled natural-rubber vulcanizates (their abrasion loss values are 90–200 mm³), whereas Tabson et al.⁴⁶ reported a measurement error of 30 mm³ for Montmorillonite (MMT)-filled natural-rubber vulcanizates (their abrasion loss values are 150–500 mm³).

Though the alteration of reaction temperature or time alone does not significantly affect the abrasion loss, increasing the levels of the three fixed factors can appreciably reduce the abrasion loss (i.e., improve the abrasion resistance). Presumably, this is effected by the presence of graft copolymer, which plays an important role in increasing the interfacial adhesion between phases and thus enhances both tensile strength and abrasion resistance.^{13,46}

Effects of %DPNR and CTA Amount [Figure 4(c,d)]. Effects of %DPNR and CTA amount on abrasion loss are unclear at the lower levels of the fixed factors owing to the large measurement error of 10.3 mm³. However, upon fixing the other factors at their higher levels, abrasion loss is markedly reduced with increases in %DPNR and CTA amount. The former observation can be explained by the formation of a larger amount of graft copolymer when substituting DPNR for NR.¹⁸ However, the latter observation seems inexplicable because published evidence demonstrates the diminishment of grafting amount with CTA content, leading to agglomeration of the dispersed phase in order to maintain its stability in the rubber phase.⁴⁷ As a result, the size of the dispersed phase becomes bigger, implying large interfacial tension (small interfacial adhesion) and leading to poorer abrasion resistance. Therefore, these results, which indicate the opposite trend, may need to be confirmed. Since measurement error plays a relatively large role in this system (due to the comparatively small abrasion loss values measured), thus

interfering with the interpretation, the experimental procedure or equipment may need to be refined in order to confirm the obtained results.

Despite this problem, it is important to note that the ANN approach can be used to model even a system with large measurement error, like the current results for abrasion loss. However, to avoid the problem and to achieve a model with best performance and reliability, researchers should use only experimental data with high precision.

CONCLUSIONS

In this work, CCD and ANN approaches were used to correlate the graft polymerization conditions for compatibilized PS/rubber blend (reaction temperature and time, the weight percent of DPNR in the NR-DPNR mixture, and CTA amount) to mechanical properties (tensile strength and abrasion loss). However, correlations for each response are obtained with sufficient accuracy by the ANN approach with a back-propagation feed-forward algorithm, rather than the CCD approach, which is confirmed by low RSME values, R^2 , and graph visualization. It thus suggests that the correlations are nonlinear and complex such that they cannot be simply explained by quadratic polynomial models (i.e., in the CCD approach). In addition, when attempting to develop only one ANN model for the prediction of both properties, poor-fitting models with RMSE values higher than the property measurement errors were attained.

Simulation results of tensile-strength at various reaction conditions by using the ANN model with the best performance are in agreement with literature, whereas those simulation results of the abrasion loss are not quite consistent with literature due to large experimental error and thus need to be reconfirmed. This, however, suggests that only experimental data with high precision should be used to train an ANN in order to achieve a model with not only best performance but also high reliability.

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