

Prediction of Styrene Conversion of Polystyrene/Natural Rubber Graft Copolymerization Using Reaction Conditions: Central Composite Design versus Artificial Neural Networks

Kittima Aroonsingkarat, Nanthiya Hansupalak

Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand

Correspondence to: N. Hansupalak (E-mail: fengnyh@ku.ac.th)

ABSTRACT: Gross copolymer or the total product of graft copolymerization of polystyrene (PS) and rubber, prepared via emulsion polymerization using a redox initiator, is used to investigate the utilization of central composite design and artificial neural network (ANN) approaches in correlating the graft copolymerization conditions to the monomer conversion. The conditions were manipulated by changing four factors: reaction temperature and time, percentage of deproteinized natural rubber (DPNR) in the rubber mixture also containing NR, and amount of chain transfer agent. For DPNR preparation, the incorporation of ultrasound energy into a deproteinizing method (i.e., urea treatment) was preexamined. A shorter reaction time, a lower total nitrogen content, and no agglomeration of rubber particles suggest the success of the incorporation. Results exhibit that the relationship between those factors and the response can be better described by the ANN model, which is further proved to be an excellent tool for the prediction of the conversion at other reaction conditions. In addition, the thermal behavior of gross copolymer is similar to its parents, the rubber and neat PS, but more to the former owing to the larger amount of rubber component. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Natural rubber (NR) from *Hevea brasiliensis* is an elastomer of interest herein due to its abundance in Thailand and easy derivation from a renewable source. Due to its high elasticity, NR is widely used in the production of, for instance, medical and household gloves.¹ In addition, owing to rubber (NR, polybutadiene, etc.) having double bonds in its backbone, rubber can graft with vinyl monomer, yielding a remarkable new polymer with a broader range of application. For instance, grafting a small amount of glycidyl methacrylate (GMA) onto NR using emulsion polymerization produces a polymer blend of GMA and NR polymers and GMA/NR graft copolymer that occur during the polymerization, exhibiting improved tensile strength and modulus with insignificant loss in elongation at break, which has led to the use of this polymer blend as seal, adhesive, and coating.² The improved properties are ascribed to the existence of vinyl polymer possessing better properties and of the graft copolymer in the polymer blend, which helps reduce the interfacial energy between the vinyl polymer and the rubber phases, and thus it can be said that that graft copolymer acts as

a compatibilizer.^{3–6} Better mechanical properties also happen for the styrene/NR blend which are compatibilized by using styrene/NR graft copolymer, of which modulus and hardness are higher than those of neat NR.⁷

To graft styrene and NR using free-radical emulsion polymerization, redox initiator is the most suitable to initiate the graft copolymerization because it not only works well at high pH (the presence of ammonia in NR latex) but also is insensitive to the existence of oxygen in the system.⁸ Literature data indicate that the styrene conversion can be controlled by the graft copolymerization conditions—e.g., reaction time and temperature, amount of chain transfer agent (CTA), type of NR (deproteinized or NR), concentrations of monomers and initiators, and monomer-to-rubber ratio.^{8–10} Reaction mechanisms are generally developed to probe relationships between monomer conversion and polymerization conditions (e.g., concentrations of monomers, initiators and CTAs).^{9,11–13} There are also other (less complicated) means to investigate the relationships without truly understanding the reaction mechanisms, such as response surface methods (RSMs) and artificial neural networks (ANNs).^{8–10,14–16}

An RSM can be applied to determine an expression (typically polynomial function) that elucidates how a dependent variable (response) is affected by those significant factors over some specified domain. Moreover, the magnitude of coefficients in the expression corresponds to the significant level of effects of both main and interaction process factors on the responses.^{17–19} In addition, the RSM can be used to optimize process variables to obtain the maximum or minimum response.^{20,21} Box–Behnken and central composite designs (CCD) are examples of RSMs that have been used in studying the optimization, interactions, and influences of conditions of graft copolymerization on response values, such as degree of grafting and graft yield and mechanical properties.^{22–25}

In case the relationship between a response and factors is very complex and cannot be described by a mere polynomial function, ANNs are considered as an alternative approach to the RSMs. 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.²⁶ Many researchers have successfully used this approach to investigate many polymeric systems that possess a nonlinear or complex relationship between the independent and dependent variables.^{14–16}

The graft copolymerization of styrene and rubber using a redox initiator and free-radical emulsion polymerization was of interest herein. We attempted to explore the relationship between the styrene conversion and the graft copolymerization conditions, that is, reaction temperature and time, weight percent of deproteinized NR (DPNR) in the rubber mixture, and amount of CTA, as they have reportedly affected the conversion of vinyl monomer, for example, styrene and methyl methacrylate.^{8,27,28} DPNR that is NR with low nitrogen content was chosen to be one of factors herein because many research studies addressed its contribution to higher monomer conversion as proteins, which are adsorbed on rubber particles, can compete with monomer for radicals.^{28–31} Thus, instead of initiating polymerization of monomer, some radicals react with proteins. Those previous works, however, conducted experiments using only pure NR or pure DPNR in the graft copolymerization.

Pukkate et al.³² claimed that the ability of urea to denature proteins accounts for the deproteinization of NR and that the reaction between NR and urea for 1 h with continuous stirring can yield a total nitrogen content as low as 0.02%, which is comparable to using proteolytic enzyme in protein removal which takes longer time (12 h). In addition, it has been documented that ultrasound energy can denature proteins in a solution through large pressure and temperature gradient and high shear forces due to the collapse of bubbles, which have been previously formed by the ultrasonic wave radiated into the solution.^{33–36} Moreover, our unpublished results indicate the unsuit-

ability of using the ultrasound energy (produced from an ultrasonic bath) alone without mechanical mixing during the reaction between urea and NR; the raised temperature of the liquid owing to the ultrasound energy and poor heat transfer give rise to the occurrence of agglomeration of NR particles. Due to the three aforementioned reasons, the present work aimed at the incorporation of the ultrasound energy and the method of Pukkate et al.³² in protein removal, which might yield more satisfying results.

As a result, this current work focused on the preparation of DPNR using ultrasound energy incorporated with the method of Pukkate et al.³² and the development of mathematical expressions that correlate the copolymerization conditions to the corresponding styrene conversion using the CCD approach and ANN approach with the back-propagation algorithm. The comparison between these two approaches was later discussed in terms of quality of fit and predictability. It should be noted that the developed model can be used to predict the conversion faster and at no additional cost, compared to running an additional experiment. The examination of thermal behavior of the gross copolymer—i.e., the total product of the graft copolymerization of styrene and rubber : PS/rubber graft copolymer, ungrafted PS, and ungrafted rubber—was also conducted in comparison with that of pure rubber and neat PS.

EXPERIMENTAL

Materials

High ammonia NR latex with a solid content of 60% was purchased from Thailand Natural Rubber Research Institute (Bangkok, Thailand). Styrene monomer (Merck, Bangkok, Thailand; purity ~99%) was purified by washing several times with an aqueous solution of 15% sodium hydroxide (NaOH). The redox initiator, cumene hydroperoxide (CHPO; purity ~80%), and the activator agent, tetraethylene pentamine (TEPA; purity ~85%), as well as potassium hydroxide for pH control and sodium dodecyl sulfate solution (SDS; purity ~90%) used as an emulsifier, were purchased from Fluka (Bangkok, Thailand). All chemicals were analytical grade and used as received. All solutions were prepared by using deionized water.

Preparation of DPNR

DPNR was prepared in a container containing NR latex, which then reacted with 0.1% urea in the presence of 1% SDS. During a 15 min long reaction, the mixture was sonicated by using a Branson 2510 E-MT ultrasonic bath (Danbury, CT) and simultaneously continuously stirred using an overhead mixer, followed by removing denatured proteins using centrifugation at 10,000 rpm in the presence of 1% SDS solution. The obtained mixture constituting DPNR was immediately used in the graft copolymerization.

The reduction in protein amount in NR latex was measured by using two methods: (1) the measurement of the total nitrogen content of rubber using the Kjeldahl method in accordance with ASTM D3533-90 (Standard Test Method for Rubber-Nitrogen Content) and (2) Fourier transform infrared Spectroscopy (FTIR) using a Perkin–Elmer Spectrum-1 FTIR Spectrometer (Bangkok, Thailand). To confirm the suitability of using ultrasound energy in combination with the method of Pukkate

Table I. Recipe for Emulsion Copolymerization of Styrene and Rubber

Organic component (rubber : styrene = 76 : 24, g)	100
Deionized water (g)	305
Isopropanol (g)	7.6
SDS (g)	1.14
TEPA (g)	0.24
CHPO (g)	0.19
Hydroquinone (g)	0.83

et al.,³² a control experiment was conducted, in which only an overhead mixer was used during the reaction between NR and urea (this is the method Pukkate et al.³² for DPNR preparation). In addition, morphology of rubber particles prepared differently was characterized by using a JEM- 2100 transmission electron microscope (Joel, Bangkok, Thailand) with specimen heating holder (up to 800°C).

Preparation of Graft copolymerization of Styrene and Rubber Latex

Following the recipe in Table I which is slightly different from literature,¹⁰ the NR-DPNR mixture in a certain ratio was purged with nitrogen for 30 min before the subsequent 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 with styrene. At a stirring speed of 400 rpm, on the addition of CHPO, the reaction instantaneously began and was stopped at a certain time by dropping hydroquinone. The gross polymer was dried in a conventional oven at 60°C for 24 h and in a vacuum oven at 60°C until no weight change was observed. Subsequently, the styrene conversion was estimated using the following equation:

$$\text{Styrene conversion (\%)} = \frac{\text{weight of monomers polymerized}}{\text{weight of monomers initially charged}} \times 100 \quad (1)$$

It should be noted that the grafting between styrene and rubber was confirmed by ¹H NMR (results not shown here) in a Varian INOVA 500 MHz NMR spectrometer (Bangkok, Thailand). Before the characterization, free polystyrene (PS) and free rubber in the gross polymer were washed out by Soxhlet extraction using methyl ethyl ketone for 24 h, followed by petroleum ether for another 24 h. Each dried sample was dissolved in CDCl₃.

Thermal Behavior of Polymers

The thermal behavior was studied by the thermogravimetric analysis (TGA) using an SDT 2960 simultaneous DSC/TGA analyzer (Perkin Elmer). Temperature was raised under a nitrogen atmosphere from room temperature to 800°C at a constant heating rate of 10°C/min. Four samples tested are neat NR, pure rubber (weight ratio of DPNR : NR = 25 : 75), neat PS, and gross copolymer (Run 1 in Table II was chosen).

Modeling the Relationship between the Styrene Conversion and Process Factors

Using CCD Approach. CCD was used to design experiments for the four process factors : reaction temperature and time, %DPNR in the rubber mixture, and CTA amount; five level values (coded as $-\alpha$, -1 , 0 , $+1$, $+\alpha$) were provided for every factor, as shown in Table III. There are four repeated runs at the central levels. The levels of these factors were chosen based on literature.¹⁰

By using regression analysis, multiple regression equations were developed [eq. (2)], 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 15.

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

where *n* corresponds to the number of factors, *Y* is the response variable (tensile strength or abrasion), and *X_i* is independent

Table II. The Experimental Design and Corresponding Values of the Response

Run	A	B	C	D	Styrene conversion (%)
1	+1	-1	-1	+1	42.27
2	+1	-1	+1	-1	10.50
3	-1	-1	-1	-1	17.53
4	+1	+1	-1	-1	41.08
5	-1	-1	+1	+1	14.48
6	-1	+1	+1	-1	17.10
7	-1	+1	-1	+1	7.52
8	+1	+1	+1	+1	29.35
9	-1	-1	-1	+1	24.40
10	-1	-1	+1	-1	16.93
11	-1	+1	-1	-1	36.53
12	-1	+1	+1	+1	22.45
13	+1	-1	-1	-1	47.82
14	+1	-1	+1	+1	19.66
15	+1	+1	-1	+1	11.43
16	+1	+1	+1	-1	28.03
17	0	0	0	0	8.01
18	0	0	0	0	18.77
19	0	0	0	0	7.27
20	0	0	0	0	4.47
21	$-\alpha$	0	0	0	3.31
22	$+\alpha$	0	0	0	24.70
23	0	$-\alpha$	0	0	1.10
24	0	$+\alpha$	0	0	27.13
25	0	0	$-\alpha$	0	14.81
26	0	0	$+\alpha$	0	12.72
27	0	0	0	$-\alpha$	33.34
28	0	0	0	$+\alpha$	12.57

Table III. Design Factor Levels for the CCD (from $-\alpha$ to $+\alpha$ levels)

Factor	Name	Coded level				
		$-\alpha$	-1	0	+1	$+\alpha$
A	Reaction temperature (°C)	40	50	60	70	80
B	Reaction time (h)	3	4	5	6	7
C	DPNR in the rubber mixture (%)	0	25	50	75	100
D	CTA (phr) ^a	0	0.25	0.50	0.75	1

^aphr is short for parts per hundred parts rubber by mass.

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. (2), comprising linear, quadratic, and interaction terms, explains the relationship between independent and dependent variables.

Using ANN Approach. In brief, ANN has basic elements, which are three layers (so-called input, hidden, and output layers), weights, bias, and transfer functions.^{37–39} 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 weighted vector of the variable to all neurons in the hidden layer. In case of one hidden layer, then the vector put through a transfer function (e.g., sigmoid function, log function, etc.) is sent to all neurons in the output layer. The number of neurons in the output layer actually equals to that of dependent variables.

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. (3)]:

$$RMSE = \sqrt{\frac{\sum_{m=1}^p (y_{pre,m} - y_{exp,m})^2}{p}} \quad (3)$$

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 datasets. 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 styrene conversion, was developed by using the same datasets used in the CCD studies, which were normalized in the range 0.05–0.95. However, for the replication at the cen-

ter 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 II). The whole process of training, validating, and testing a model was conducted by using NNTOOL box in MATLAB. The performance quality of the obtained network is determined by RMSE, a plot of predicted versus observed normalized values, and the value of determination coefficient (R^2).

RESULTS AND DISCUSSION

Characterization of the Prepared DPNR

As shown in Table IV, using both an overhead mixer and ultrasound energy during the reaction between urea and NR yields a lower total nitrogen amount of DPNR than that of the method of Pukkate et al.³² and does not induce agglomeration (see Figure 1), as occurred when we tried applying ultrasound energy more directly to the rubber mixture using an ultrasonic probe. Note that the trace of SDS added to stabilize rubber particles can be detected in Figure 1 (b,c).

It is noteworthy that the protein content in NR product cannot be exactly quantified by measuring nitrogen content using the Kjeldahl method because the value includes nitrogen derived from phospholipids and proteins adsorbed on rubber particles.⁴⁰ Consequently, FTIR spectroscopy is required to confirm the reduction in protein amount. In Figure 2, all three FTIR spectra have peaks in the range of 3290–3320 cm^{-1} , suggesting the presence of short- and long-peptide chains as assigned by Pukkate et al.^{32,41,42} Comparing three samples, the lowest peak height, indicating the lowest protein level, is from DPNR prepared by using both an overhead mixer and ultrasound energy during the reaction between urea and NR.

Thus, both the total nitrogen amount and FTIR results unanimously confirm the suitability of ultrasound energy in combination with the method of Pukkate et al.³² for NR deproteinization. Although the ultrasound is a high-energy consumption technique, evident advantages of using ultrasound energy can

Table IV. Total Nitrogen Content of NR and DPNR Prepared Differently

Sample	Total nitrogen content (wt %)
NR	0.30
DPNR (only overhead mixer)	0.04
DPNR (both overhead mixer and ultrasound energy)	0.02

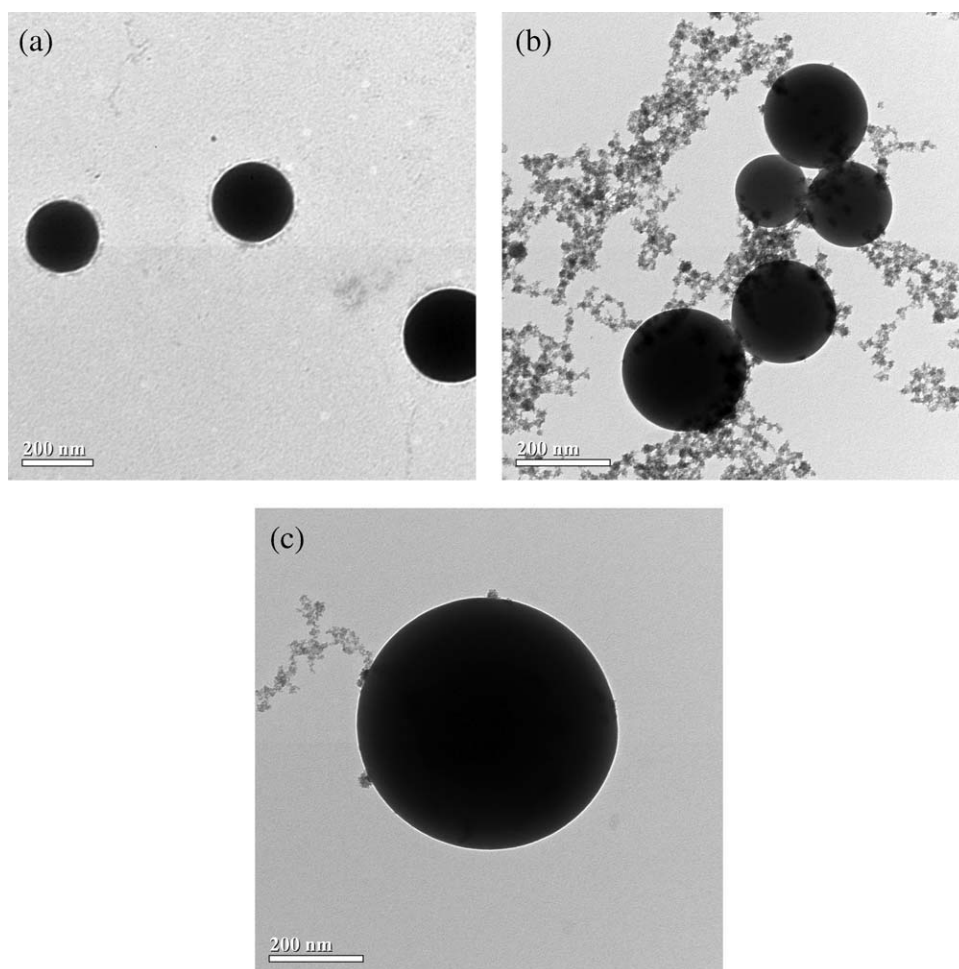


Figure 1. TEM images of rubber particles: (a) NR particles, (b) DPNR particles prepared by using an overhead mixer, and (c) DPNR particles prepared by using both an overhead mixer and ultrasound energy.

be summarized as follows: the reaction time can be reduced four times; the obtained total nitrogen content is lower; more low- and high-molecular weight proteins (i.e., the disappearance of the peak in the range of $3290\text{--}3320\text{ cm}^{-1}$ in Figure 2) can be removed, which results in less protein amount in the competition for free radicals. In addition, it should be noted that proteins with MW $\sim 5\text{--}110\text{ kDa}$ are potent allergens, causing IgE-mediated allergic reactions to human on one's exposure to NR products and possibly leading to severe anaphylactic reactions.^{43,44} In consequence, the technique, which has the potential to remove potent allergens, may be applied to applications where the allergen elimination is of concern.

Regression Modeling by Using CCD Approach

The regression analysis of the experimental data in Table II gives estimated regression coefficients [b_i , b_{ii} , b_{ij} as in eq. (2)], as listed in Table V. 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.⁴⁵

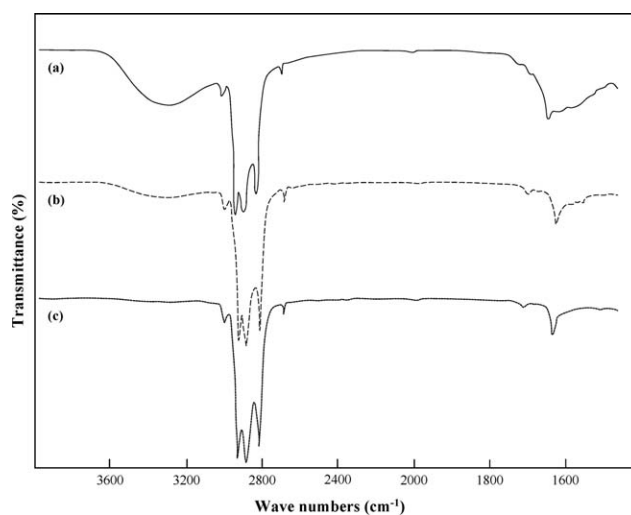


Figure 2. FTIR spectra for (a) NR, (b) DPNR prepared by using an overhead mixer, and (c) DPNR prepared by using both an overhead mixer and ultrasound energy.

Table V. Results of Regression Analysis and Corresponding *T*- and *P*-values of the Quadratic Polynomial for Styrene Conversion from the CCD Approach

Model term	Coefficient ^a	<i>T</i> -value	<i>P</i> -value
Constant	111.474	1.916	0.078
<i>A</i>	-1.213	2.355	0.035
<i>B</i>	-15.975	1.055	0.311
<i>C</i>	-1.141	-1.508	0.155
<i>D</i>	-40.975	-1.736	0.106
<i>A</i> × <i>A</i>	0.024	1.181	0.259
<i>B</i> × <i>B</i>	2.452	1.195	0.254
<i>C</i> × <i>C</i>	0.004	1.152	0.270
<i>D</i> × <i>D</i>	74.600	2.272	0.041
<i>A</i> × <i>B</i>	-0.129	-0.513	0.617
<i>A</i> × <i>C</i>	-0.010	-0.995	0.338
<i>A</i> × <i>D</i>	-0.137	-0.136	0.894
<i>B</i> × <i>C</i>	0.177	1.761	0.102
<i>B</i> × <i>D</i>	-15.005	-1.493	0.159
<i>C</i> × <i>D</i>	0.707	1.758	0.102
Adjusted <i>R</i> ²	0.336		
<i>R</i> ²	0.680		

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

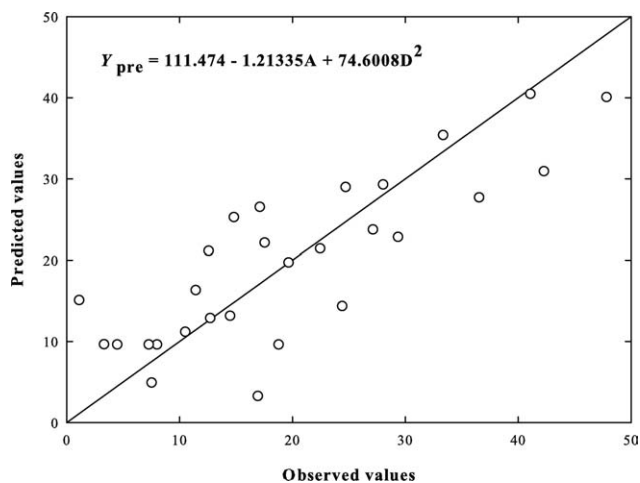
In Table V, only *A* and *D*² have *P* < 0.05 and, hence, both terms are considered significant to the response. However, the results are different from the ANOVA results in Table VI, in which linear and quadratic terms, as well as interaction terms, are considered insignificant (*P* > 0.05). Also, both *R*² and adjusted *R*² values of the response model are low, confirming a poor fit. Furthermore, Figure 3 shows the scatter around the line with a slope of one, implying the poor-fitting model for the response. As a result, it can be said that the relationship between the monomer conversion and the reaction conditions is too complicated and cannot be simply described by the quadratic polynomial equation developed from the CCD approach. Similar results were reported in Sresungsuwan and Hansupalak,⁴⁶ in which the CCD approach cannot sufficiently model the relationship between mechanical properties of gross copolymer and the reaction conditions.

Modeling by Using ANN Approach

The topology details of the model that gives the best performance are shown in Table VII. Four neurons in the input layer

Table VI. ANOVA for the Fitted Quadratic Polynomial for Styrene Conversion

Source	<i>F</i>	<i>P</i> -value
Regression	1.98	0.114
Linear	2.99	0.059
Quadratic	1.50	0.258
Interaction	1.62	0.220

**Figure 3.** Predicted versus observed values of styrene conversion (%) obtained from the CCD approach. The quadratic polynomial model used for the prediction is listed in the figure.

correspond to the four factors (reaction temperature and time, %DPNR, and amount of CTA), and one neuron in the output layer matches one response, the monomer conversion. Only one hidden layer containing five neurons was found to be enough to yield a model with the best performance. The optimum network uses a log-sigmoid function as the transfer function and the gradient descent approach (GDA) with adaptive learning rate as the training function. Small value of RMSE that is lower than the measurement error calculated from repeated experiments (0.104 for normalized styrene conversion) justifies the best performance of the model. Furthermore, the quality of fit can be visualized in Figure 4. Most data are clustered around the line with a slope of one, which is in agreement with the high *R*² value.

A comparison between models obtained from the CCD and ANN approaches is made by comparing *R*² and RMSE values. It is clear that the ANN model gives a higher *R*² value (see Table V and the footnote to Table VII for the CCD and ANN approaches, respectively) and a lower RMSE value than the CCD model (0.338 for normalized styrene conversion), which signifies the suitability of the ANN model over the CCD model in explaining the relationship between the styrene conversion and the reaction conditions.

Table VII. Details of the ANN Model for Predicting Styrene Conversion

Number of neurons (input : hidden : output)	4 : 5 : 1
Transfer function	Log-Sigmoid
Training function	GDA
Learning rate	0.01
Epochs	15,000
RMSE ^a	0.0548
<i>R</i> ² , ^a	0.944

^aBoth RMSE and *R*² presented here were calculated by using dimensionless (or normalized) data. By using dimensional data, *R*² is 0.99997.

As stated previously, the total number of data to establish a network depends on the complex of the input–output relationship.^{38,46} Some results in the literature acquiring good-fitting ANN models use the total number of data between 10 and 35 for polymer systems. Delfa et al.¹⁵ successfully used about 15–30 data to establish three models for solid content, Mooney viscosity, and polydispersity of styrene–butadiene rubber. Dhib and Hyson¹⁴ even used a number of data as low as 10 to develop models predicting monomer conversion and molecular weight of PS as a function of time. Sresungsuan and Hansupalak⁴⁶ used 25 data to correlate the tensile strength values of styrene/NR blend compatibilized by PS-g-rubber copolymer to reaction conditions.

Due to the optimal reaction conditions—giving the highest monomer conversion—corresponding to Run 13 in Table II, it is not necessary to optimize the monomer conversion. Hence, we decided to test the obtained ANN model by carrying out five repeated experiments at reaction conditions that are not listed in Table II, which are reaction temperature of 70°C, reaction time of 4.5 h, %DPNR of 25, and CTA amount of 0.4 phr. Accordingly, the obtained ANN model gives the target value of styrene conversion equal to 45.22%, whereas the polynomial equation from the CCD approach gives that of 30.56%. The percentage of monomer conversion value from confirmed experiments is 45.16 ± 0.97 , which is in agreement with the target value obtained from the ANN model, suggesting the excellent quality of the model in prediction of conversion.

Thermal Behavior of Polymers

TGA was performed to compare the thermal behavior of Run 1 to its parents, that is, the rubber (a mixture of 25% DPNR and 75% NR) and PS. It is important to note that, in the inset in Figure 5, the TGA curves of the pure rubber and the NR superpose well and are in good agreement with literature, which conducted TGA for neat NR.⁴⁷ Same results can still be observed when increasing DPNR content to 100% (data not shown). The identical thermal stability is due to polyisoprene being the most dominant component in these samples.

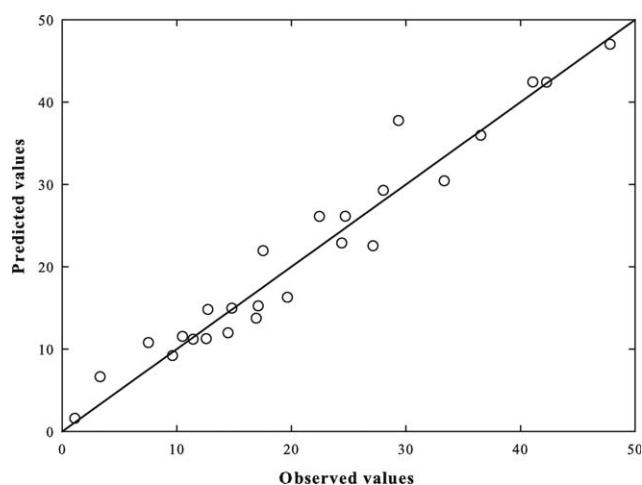


Figure 4. Predicted versus observed values of styrene conversion (%) obtained from the ANN approach.

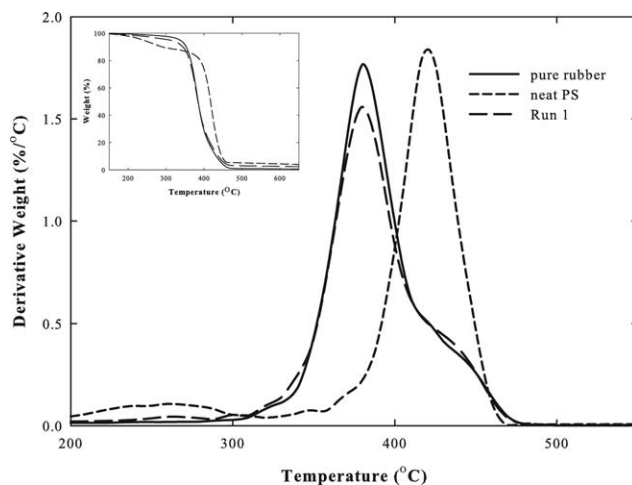


Figure 5. DTGA curves for pure rubber, neat PS, and PS/rubber blend compatibilized with PS/rubber graft copolymer (Run 1 in Table II). Note that DTGA curve of neat NR is identical to that of pure rubber. TGA weight losses for all samples are given in the inset.

The inset in Figure 5 clearly exhibits different thermal behaviors for the pure rubber and neat PS. The pure rubber decomposes one time during the temperature range 300–400°C, whereas neat PS decomposes twice: the first stage of weight loss due to the loss of benzene rings occurs during the range 200–350°C, and the second stage due to the decomposition of the polymer’s backbone occurs during the range 400–450°C. These observations for neat PS were also noted by Mathew et al.⁴⁷

In the same inset (Figure 5), the thermal behavior of Run 1 looks more similar to that of the pure rubber. However, the DTGA curve of Run 1 in Figure 5 reveals three distinct peaks, which can clearly be ascribed to thermal behavior of rubber and PS components. As a result of the addition principle for polymer blends, the similar thermal behavior between Run 1 and the pure rubber may be explained by the large quantity of rubber component in Run 1.^{47–49}

CONCLUSIONS

This work mainly focuses on (1) the incorporation of ultrasound energy into the method of Pukkate et al. for DPNR preparation and (2) the development of a mathematical expression that describes the relationship between the styrene conversion and the graft copolymerization conditions, that is, reaction temperature and time, weight percent of DPNR in the rubber mixture, and amount of CTA.

In the first part, with the application of urea, continuous stirring using an overhead mixer, and ultrasound energy, the deproteinization of NR can be achieved four times faster than the method of Pukkate et al., in addition to lower total nitrogen content and no agglomeration occurrence, suggesting that the ultrasound energy from an ultrasonic bath cooperates well with urea in eliminating proteins.

In the second part, the relationship between the response and these four factors was studied through two different

approaches: CCD and ANN. The latter approach, with lower RMSE value, high R^2 value, and less scattering in the predicted-against-observed-values plot, is proved to be able to predict the response much better than the former, thus suggesting that the relationship is nonlinear and complex such that it cannot be simply explained by a quadratic polynomial model derived from the CCD approach. Furthermore, when predicting the monomer conversion at other reaction conditions, it was found that the ANN model gives results in better agreement with experimental values, and thus the better model. In addition, the thermal behavior of gross copolymer follows the addition principle for polymer blends: its behavior is similar to both parents, but more to the larger rubber component.

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