Prediction of Properties of Rubber by Using Artificial Neural Networks

V. Vijayabaskar,[1] Rakesh Gupta,[2] P. P. Chakrabarti,[2] Anil K. Bhowmick[1]

[1]*Rubber Technology Center, Indian Institute of Technology, Kharagpur-721302, India*
[2]*Computer Science and Engineering Department, Indian Institute of Technology, Kharagpur-721302, India*

Received 28 September 2004; accepted 1 March 2005
DOI 10.1002/app.22356
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Different rubber formulations were designed using nitrile rubber and a mixed crosslinking system consisting of sulfur/accelerator and electron beam radiation. Based on the experimental results, an artificial neural network (ANN) was constructed to simulate the mechanical properties and volume fraction of rubber. The ANN could predict accurately the above properties for a series of nitrile rubber compounds. However, the number of training data played a key role in the ANN predictive quality. In addition, the more complex the nonlinear relation between input and output was, the larger was the number of training dataset required. The predicted results were further validated using another mathematical model. The constructed ANN was verified with a completely different styrene butadiene rubber system. The prediction was found to be extremely good.
© 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2227–2237, 2006

INTRODUCTION

Advanced formulation techniques for the development of different rubber compounds for specific purposes are of major strategic importance to rubber compounding industries. These industries face increasing pressure to develop a compound of particular characteristics in a stipulated period of time, while ensuring the quality or consistency of the final product. Currently, the main factors limiting the development of different rubber compounds include limited availability and incapability of different modeling techniques to predict properties, and the highly sensitive and nonlinear behavior of different parameters affecting the properties of the final product.

It is not generally easy to formulate a compound to meet specific requirements exactly. Usually a trial compound is mixed, its properties measured, and the formulations are subsequently amended according to specifications.[1,2] Often, this procedure may involve a cycle of changing the formulation and retesting until usable results are obtained. Development of compounds to meet the specifications of a product is routinely done in industries and many laboratories are using the above method. The primary focus of this article is to predict the mechanical properties and swelling of rubber vulcanizates using an artificial neural network approach (as defined later) with a minimum number of experiments. To develop and verify this concept, filled nitrile rubber (NBR) having a mixed crosslinking system and styrene butadiene rubber (SBR) vulcanizates with a mixed crosslinking system have been used. Conventional curing agents are used to improve the physical properties of rubbers. A number of curing agents are available for vulcanization that can give different properties of a base polymer depending on the requirement of the end-use. But in many cases, one type of crosslink does not satisfy all of the required properties, so mixed crosslinking systems are essential to have a compromise set of properties. The mixed crosslinking system has been widely studied by many workers.[3–9] We have introduced for the first time a mixed crosslinking system consisting of sulfur acting as the conventional curing agent and an electron beam as the additional crosslinker.[10] This has also allowed us to operate a large number of variables consisting of the nature of rubber and the type and level of crosslinking with a view to producing vulcanizates having a wide range of properties.

To meet a special application, for example, concerning one or several measurable material properties, rubber compounds can be designed by selecting the appropriate parameters and their levels in the formulation. One such application, namely development of rubber compounds based on nitrile rubber for seals, o-rings, and so forth, is targeted in this article. Modification of rubbery materials by electron beam (EB) radiation is a potential method for the development of new materials for specific applications. In the green drive, that is, to make the world pollution free, this technology takes an important position. The process is

Correspondence to: A. K. Bhowmick (anilkb@rtc.iitkgp.ernet.in).

© 2006 Wiley Periodicals, Inc.

very clean, requires less energy, permits greater processing speed, and operates at ambient temperature. Such consequences are rarely possible in the case of crosslinking by other thermo chemical means.[11,12] It has also been demonstrated that apart from crosslinking, oxidation and degradation of the network structure take place during EB radiation. The above structural changes lead to drastic changes of mechanical, dynamic mechanical, and elastic properties, and thermal stability of the materials.[13,14] The mechanical properties, an important criterion of any compound for such an application, are affected by many factors, such as the nature of the raw material, crosslinking system, nature and amount of filler, and so forth. Six significant factors, namely radiation dose, sensitizer, filler, antioxidant, accelerator, and sulfur, have been selected here. As the number of experiments increases, it becomes time consuming, with more numbers and levels of factors. So, a partial factorial design, namely the Taguchi statistical technique—L25 model—is adopted. But it is very difficult to know exactly how these factors affect the final properties of a given compound. Due to the characteristics of the compounds and the complexity of the elaboration process, it is virtually impossible to predict the mechanical properties of the compound in terms of first principles. Even the analysis and prediction of results are not possible with the usual practice of "computer compounding" with packages like E-CHIP, MAXIMISE, and JUSE-QCAS followed in industries.[15] This effected our use of Artificial Neural Networks (ANN).

ARTIFICIAL NEURAL NETWORKS

An artificial neural network (ANN) approach is a powerful mathematical tool in modeling of material properties, and therefore it has been introduced into the fields of material science recently.[16,17] Neural networks are composed of simple elements operating in parallel. These elements are inspired by biological nervous systems. As in nature, the network function is determined largely by connection between these elements, which are mostly nonlinear transfer functions in computer simulations. An ANN can be trained to perform a particular function by adjusting the values of the connection (weights) between the elements. Roughly speaking, with enough parameters, these networks are able to approximate any reasonable functions.[18]

The use of ANNs can help us to find complicated dependencies among input (formulation of the compound) and output (properties). ANNs have the ability to measure nonlinear relationships among variables, without prior information about the process.[19] Recently, ANNs have been used successfully to predict the copolymer composition as a function of reaction conditions and conversion.[20]

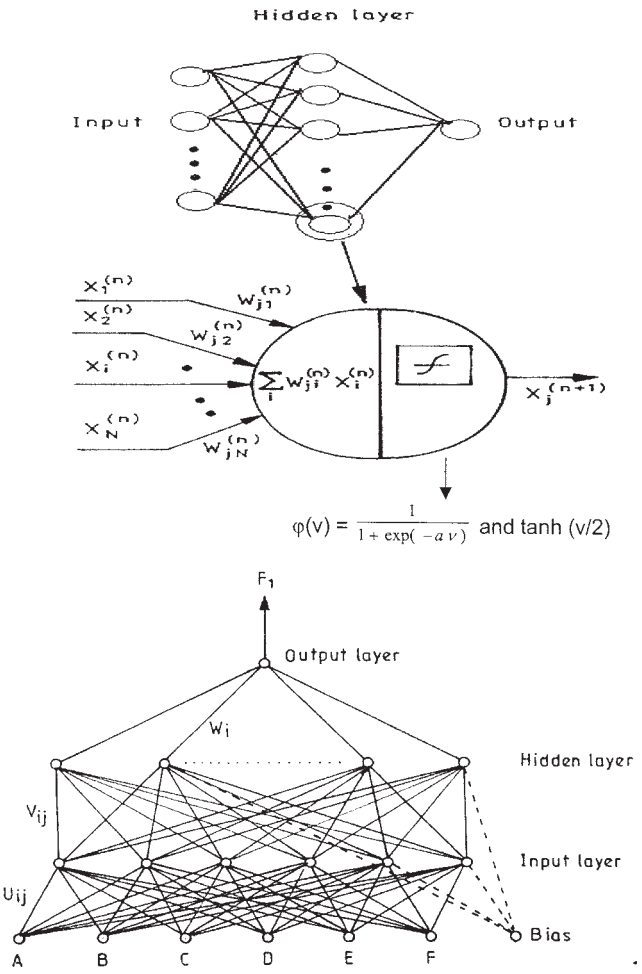

Figure 1 (a) General structure of the artificial neural network, where $X_1^{(n)} \ldots .. X_N^{(n)}$ are the inputs and $W_{j1}^{(n)} \ldots W_{jN}^{(N)}$ are the weights. (b) Structure of a constructed back propagation algorithm, where A,B. . . . . F are the six inputs, Uij is the input layer, Vij is the hidden layer, and F1 is the output.

We can consider "compounding and their relationship to properties" as a gray box and train a neural network using available experimental data. These are mathematical models that have the ability to learn the correlation between input and output values. The training of the network consists of introducing a set of correlated inputs and outputs, called examples. From these examples, the network goal is modeling the relationship between the input and the output variables, by adjusting the node connection weights. The general structure of an ANN is shown in Figure 1a. When the system converges to a stable solution, we can enter a new formulation and get its mechanical properties. The greatest advantage of an ANN is its ability to model complex nonlinear, multidimensional relationships without any prior assumptions about the nature of the relationships, and the network is built directly from experimental data by self-organizing capabilities. In this work, a neural network is imple-

TABLE I
Taguchi L25 Model

Run	Dose	Sensitizer	Filler	Antioxidant	Accelerator	Sulfur
1	I	I	I	I	I	I
2	I	II	II	II	II	II
3	I	III	III	III	III	III
4	I	IV	IV	IV	IV	IV
5	I	V	V	V	V	V
6	II	I	II	III	IV	V
7	II	II	III	IV	V	I
8	II	III	IV	V	I	II
9	II	IV	V	I	II	III
10	II	V	I	II	III	IV
11	III	I	III	V	II	IV
12	III	II	IV	I	III	V
13	III	III	V	II	IV	I
14	III	IV	I	III	V	II
15	III	V	II	IV	I	III
16	1V	I	IV	II	V	III
17	1V	II	V	III	I	IV
18	1V	III	I	IV	II	V
19	1V	IV	II	V	III	I
20	1V	V	III	I	IV	II
21	V	I	V	IV	III	II
22	V	II	I	V	IV	III
23	V	III	II	I	V	IV
24	V	IV	III	II	I	V
25	V	V	IV	III	II	I

mented and analyzed to predict the mechanical properties and swelling resistance of new compounds from their formulation. Network characteristics have been analyzed to guarantee the stability and convergence of the solutions, and some applications and possible extensions of this kind of treatment are discussed.

IMPLEMENTATION

In this work, a three-layer back propagation algorithm has been used. To simplify the model, only a subset of components and a subset of properties have been taken into account. Six relevant variables (components) of compound formulations have been considered in this analysis: radiation dose, sensitizer, sulfur, antioxidant, accelerator, and carbon black. Other ingredients in the formulation have been proven not to be important in this analysis, as shown later. Three output variables have been taken into account: 100% modulus, tensile strength, and elongation at break. Selecting 25 compounds, the formulations have been designed on the basis of Taguchi statistical technique (L25), as shown in Table I. The values have been normalized in the range 0–1. Table II shows a list of the designed compounds, and their experimental results are given in Table III.

The term back propagation refers to the process by which derivatives of network error, with respect to

TABLE II
Formulation for 25 Sets of Compounds Indicating the Levels of Six Factors by Following the Taguchi Table Mentioned in Table I

Run	Dose (kGy)	Sensitizer (phr)	Filler (phr)	Antioxidant (phr)	Accelerator (phr)	Sulfur (phr)
1	0	0	0	0	0	0.05
2	0	1	15	0.5	0.2	0.2
3	0	2	30	1	0.5	0.5
4	0	3	45	1.5	1	1
5	0	4	60	2	1.5	1.5
6	50	0	15	1	1	1.5
7	50	1	30	1.5	1.5	0.05
8	50	2	45	2.0	0	0.2
9	50	3	60	0	0.2	0.5
10	50	4	0	0.5	0.5	1
11	100	0	30	2.0	0.2	1
12	100	1	45	0	0.5	1.5
13	100	2	60	0.5	1	0.05
14	100	3	0	1	1.5	0.2
15	100	4	15	1.5	0	0.5
16	150	0	45	0.5	1.5	0.5
17	150	1	60	1	0	1
18	150	2	0	1.5	0.2	1.5
19	150	3	15	2	0.5	0.05
20	150	4	30	0	1	0.2
21	200	0	60	1.5	0.5	0.2
22	200	1	0	2	1.0	0.5
23	200	2	15	0	1.5	1
24	200	3	30	0.5	0	1.5
25	200	4	45	1	0.2	0.05

TABLE III
Mechanical Properties and Volume Fractions for the Above 25 Sets of Compounds

Run	100% modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Volume fraction
1	0.3	0.3	79	0.021
2	0.4	0.5	66	0.096
3	0.8	5.0	1300	0.042
4	1.2	9.8	883	0.073
5	2.3	11.6	443	0.112
6	1.3	7.8	574	0.127
7	1.0	12.4	1000	0.082
8	1.0	9.4	1027	0.067
9	2.8	15.5	476	0.123
10	0.8	3.5	651	0.149
11	1.5	8.2	501	0.118
12	3.3	16.2	402	0.146
13	3.3	17.5	485	0.119
14	0.8	2.4	462	0.126
15	1.2	8.6	665	0.122
16	2.9	13.5	383	0.135
17	4.4	17.5	362	0.138
18	1.0	2.1	331	0.147
19	1.4	6.7	444	0.161
20	3.0	11.5	283	0.165
21	3.7	15.1	367	0.108
22	0.9	2.4	377	0.135
23	2.1	8.0	331	0.162
24	3.3	8.6	225	0.174
25	3.8	14.9	315	0.157

network weights and biases, can be computed. The training of ANNs by back propagation involves three stages: (i) the feed forward of the input training pattern, (ii) the calculation and back propagation of the associated error, and (iii) the adjustment of weights. Training, an important procedure in the prediction, can be elaborated as follows. Training the network to learn consists of presenting it with a set of correlated inputs and outputs, called examples. The system learns by adjusting the weights w_i of the node connections in such a way as to minimize the differences between the target output d_k predicted for the kth pattern and the actual output y_k (measured). This means minimizing the mean square error given by eq. (1):

$$E_{\text{error}} = \sum_{k=1}^{k} [d_k - y_k]^2 \quad (1)$$

The most extended method of minimizing the error function is the back-propagation algorithm, a generalization of the steepest method, which adjusts each individual weight by eq. (2)[21]:

$$\Delta w_i = -\eta_{\text{learning}} \frac{\partial E_{\text{error}}}{\partial w_i} \quad (2)$$

where η_{learning} is the learning constant that influences the convergence speed and the effectiveness of the learning process. In general, the optimum value of η_{learning} depends on the problem that is being analyzed, and only small values of η_{learning} guarantee stable solutions. The learning parameter η_{learning} should be chosen small to provide minimization of the total error function E_{error}. However, for a small η_{learning}, the learning process becomes very slow. On the other hand, large values of the same correspond to fast learning, but lead to parasitic oscillations that prevent the algorithm from converging to the desired solution. Moreover, if the error function contains many local minima, the network might get trapped in some local minimum, or get stuck on a very flat plateau. The network training finishes when all the errors E_{error} (after training) are below a previously established error, E_{error}. This process can be used with a number of different optimization strategies.

In this study, a three-layer back propagation network (BP) based on C++ programming has been built, in which there are six nodes in the input layer, 8 nodes in the hidden layer, and only one node in the output layer. Figure 1(b) shows the structure of this BP network, in which w_i is the connection weight between the output layer and the ith node in the hidden layer, V_{ij} is the connection weight between the ith node in the hidden layer and jth node in the input layer, and U_{ij} is the connection weight between the ith node in the input layer and the jth input variable. In this work, radiation dose in kGy (C_1), the level of the sensitizer (C_2), and the amount of filler (C_3), antioxidant (C_4), accelerator (C_5), and sulfur (C_6) comprise the input signals. Four multilayered feed forward networks have been constructed, and the four outputs, namely 100% modulus, tensile strength, elongation at break,

TABLE IV
Details of the Materials and Their Suppliers

Material	Supplier/Manufacturer
NBR	
ACN content: 33 %	JSR Industries Ltd., Japan
SBR-1502	Synthetics and chemicals
TMPTA[a], density 1110 kg m^{-3}	UCB chemicals, Drogenbos, Belgium
Zinc oxide[a]	E-Merck, Mumbai, India
Stearic acid[b]	Local supplier
Dioctyl phthalate	Ranbaxy Ltd., Mumbai, India
MBTS[c]	ICI Ltd., Rishra, India
Carbon black	Philips carbon black, Durgapur, India
Sulfur	Qualigens, Mumbai, India
Methyl ethyl ketone	E-Merck, Mumbai, India

[a] Trimethylolpropane triacrylate.
[b] rubber grade.
[c] Mercapto benzothiazole disulphide (accelerator).

TABLE V
ANOVA Summary on Tensile Strength of Nitrile Rubber

Factors	Sum of squares SS	Degree of freedom (N)	Variance (V_f) SS/N	F Ratio V_f/V_e	Remarks on comparison with theoretical F ratio = 2.1 4,24 from tables at 90% confidence
Radiation dose	89	4	22.2	6.8	Significant
Sensitizer	55	4	13.8	4.2	Significant
Filler	616.5	4	154.1	47.4	Highly significant
Antioxidant	13	4			
Accelerator	52	4	13	4	Significant
Sulfur	72	4	18	5.5	Significant
SS (T)	897.5	N (T) = 24			
SS (e)	13	N (e) = 4	V_e = 3.25		

Where,
SS(T) = Total sum of squares.
SS(e) = Sum of squares due to pooled error.
N(T) = Total degree of freedom.
N(e) = Degree of freedom due to pooled error.
V_f = Variance due to factor.
V_e = Variance due to pooled error.
*Indicates factor considered to generate the pooled error estimate.

and volume fraction of rubber in the swollen gel, have been predicted for different formulations. All the inputs are brought down to a normalized amplitude range, and training of the network is carried out by calculating the mean squared error between the target (d_k) and measured outputs (y_k) (eq. (1)). The weights are updated and the training is performed by a back propagation algorithm.[22]

Evaluation of the ANN method

The quality of the prediction can normally be characterized by the root mean square error (RMSE) of the predicted values from the real measured data. The smaller the RMSE of the test dataset is, the higher is the predictive quality.

As an improvement, the coefficient of determination B[23] (also called R^2 coefficient in some publications[24,25]) has been introduced to evaluate the ANN's quality, as defined by eq. (3):

$$B = 1 - \frac{\sum_{i=1}^{m} (O(p^{(i)}) - O^{(i)})^2}{\sum_{i=1}^{m} (O^{(i)} - O)^2}$$

where $O(p^{(i)})$ is the predicted property characteristic, $O^{(i)}$ is the ith measured value, O is the mean value of $O^{(i)}$, and m is the number of test data. The coefficient B describes the fit of the ANN's output variable curve. Higher B coefficients indicate an ANN with better output approximation capabilities. To avoid any artificial influence in selecting the test data, a random technique can be applied in the selection, and the entire process is repeated independently many times (e.g., 50 times). Afterwards, the distribution of B values is recorded and the percentage of $B > 0.9$ is calculated. Since this value is identified as of high predictive quality, that is, less than 15% of the RMSE is between the predicted values and the measured

TABLE VI
Comparison Between Predicted Values by the ANN and Actual Values with Different Training Inputs

	Real values			Predicted values		
Trial no.	100% modulus, MPa	Tensile strength, MPa	Elongation at break, %	100% modulus, MPa	Tensile strength, MPa	Elongation at break, %
9	2.8	15.5	476	3.6	16.7	635
10	0.8	2.4	462	0.4	17.4	815
16	2.9	6.7	444	0.5	17.1	890
24	3.3	8.6	225	3.1	14.5	609

Training inputs were 21 datasets from Table II.

TABLE VII
Additional 16 Sets of Compounds Indicating the Levels of Six Factors to Improve the Efficiency of the ANN and Value of Their Mechanical Properties and Volume Fractions

Trial	Dose (kGy)	Sensitizer (phr)	Filler (phr)	Antioxidant (phr)	Accelerator (phr)	Sulfur (phr)	100% modulus (MPa)	Tensile strength (MPa)	E.B., %	Volume fraction of rubber
1	20	0	0	0	0.5	1.5	0.88	3.5	1193	0.077
2	50	0	0	0	0.5	1.5	0.98	2.9	519	0.149
3	150	0	0	0	0.5	1.5	1.11	2.6	369	0.189
4	300	0	0	0	0.5	1.5	1.4	2.7	273	0.211
5	20	0	0	0	1.5	0.5	0.73	2.4	1027	0.070
6	50	0	0	0	1.5	0.5	0.78	1.7	477	0.116
7	150	0	0	0	1.5	0.5	0.89	1.7	347	0.161
8	300	0	0	0	1.5	0.5	1.17	1.6	171	0.196
9	150	0	0	0	0.5	0.1	0.60	1.0	286	0.157
10	150	0	0	0	0.5	0.4	0.70	1.8	639	0.217
11	150	0	0	0	0.5	0.7	0.80	2.0	723	0.327
12	150	0	0	0	0.5	1.2	0.90	2.4	610	0.329
13	150	1	0	0	0.5	1.2	0.94	3.1	521	0.331
14	150	3	0	0	0.5	1.2	0.98	4.0	357	0.340
15	150	0	20	0	0.5	1.2	1.50	15.0	719	0.342
16	150	0	40	0	0.5	1.2	2.39	16.2	489	0.375

ones, it is clear that the higher the percentage of B > 0.9 is, the better is the quality.[23]

EXPERIMENTAL

Preparation of the samples, materials, and sample designation

The list of chemicals, nature and grade of rubber, and their suppliers are listed in Table IV. The samples are designated as $M_{a/b/c/d/e/f}$, where M stands for nitrile rubber, a for amount of sulfur (phr), b for accelerator (phr), c for radiation dose in kGy, d for TMPTA (phr), e for carbon black (GPF grade), and f for antioxidant (phr). For example, $M_{1.5/0.5/150/0/0/0}$ indicates a sample containing 1.5 phr of sulfur, 0.5 phr of accelerator (MBTS), irradiation dose of 150 kGy, 0 phr TMPTA, 0 phr carbon black, and 0 phr antioxidant. The nitrile rubber was mixed with sulfur, MBTS, and other ingredients using the conventional mixing procedure in an open two-roll mill (Schwabenthon, Berlin). The optimum cure time of all the compounds in the above three sets were determined from the rheometric study of the corresponding compounds in an oscillating disk rheometer (ODR, 100S Monsanto) at 150°C. The sheets were compression molded between Teflon sheets at a temperature of 150°C and at a pressure of 5 MPa in an electrically heated Moore press for optimum cure time to obtain sheets of dimension 11.5 cm $\times$ 11.5 cm $\times$ 0.1cm. The styrene butadiene rubber was mixed using the same procedure, except that the accelerator was added at the end of the mixing cycle. The detailed procedures were described in our earlier articles.[26,27]

Irradiation of samples

The molded nitrile rubber samples were irradiated in air at room temperature of 25 $\pm$ 2°C by an electron beam accelerator at the NICCO Corp. Ltd, Shyamnagar, in West Bengal, India. The specifications of the electron beam accelerator were given in our earlier articles.[10]

TABLE VIII
Comparison Between Predicted Values by the ANN and Actual Values with 30 Training Inputs

	Real values			Predicted values		
Trial no.	100% modulus MPa	Tensile strength, MPa	Elongation at break, %	100% modulus, MPa	Tensile strength, MPa	Elongation at break, %
9	2.8	15.5	476	3.2	16.4	570
10	0.8	2.4	462	0.5	3.6	583
16	2.9	6.7	444	1.4	8.1	595
24	3.3	8.6	225	3.4	9.5	312

Training inputs were 30 datasets from Table II and Table VII.

TABLE IX
Comparison Between Predicted Values by the ANN and Actual Values with 37 Training Inputs

	Real values				Predicted values			
Trial no.	100% modulus, MPa	Tensile strength, MPa	Elongation at break, %	Volume fraction of rubber	100% modulus, MPa	Tensile strength, MPa	Elongation at break, %	Volume fraction of rubber
9	2.8	15.5	476	0.126	3.1	16.1	511	0.133
10	0.8	2.4	462	0.149	0.6	2.9	534	0.154
16	2.9	6.7	444	0.161	2.6	7.1	473	0.156
24	3.3	8.6	225	0.174	3.1	9.1	270	0.182

Training inputs are 37 datasets from Table II and Table VII.

Characterization of samples

Chemical test methods

Volume fraction of the rubber in the swollen gel ν_r was calculated using the relation[28]:

$$V_r = \frac{(D_s - F_f A_w)\rho_r^{-1}}{(D_s - F_f A_w)\rho_r^{-1} + A_s \rho_s^{-1}} \quad (4)$$

where ν_r D_s, F_f, A_w, A_s, ρ_r, and ρ_s are volume fraction of rubber, deswollen weight of the sample, fraction insoluble, sample weight, weight of the absorbed solvent corrected for swelling increment, density of rubber, and density of solvent, respectively. Methyl ethyl ketone was used as the solvent for nitrile rubber and toluene for styrene butadiene rubber.

Mechanical properties

Tensile specimens were punched out from the molded sheets using ASTM Die–C. The tests were carried out as per the ASTM D 412–98 methods in a universal testing machine (Zwick 1445) at a crosshead speed of 500 mm/min at 25°C. The average of three tests is reported here.

ANOVA analysis[29]

Analysis of variance (ANOVA) is a mathematical technique that breaks total variation down to accountable sources; total variation is decomposed into its appropriate components. The significance of each factor is determined by comparing with the theoretical F ratio from statistical tables.

RESULTS AND DISCUSSION

The significance of parameters was determined by ANOVA analysis.[29] A sample calculation is shown for tensile strength in Table V for nitrile rubber, and the results are interpreted by comparing with the theoretical F ratio from statistical tables. It is found that at least five of the above selected parameters played a significant role in influencing the mechanical properties and volume fractions for the 25 sets of compounds. It is impossible to design a model by other methods, like Response Surface Methods, unless a reasonable quantity of experience is available. This created the necessity to opt for neural networks for predicting the mechanical properties. The use of neural networks can circumvent many of these limitations. It is possible to use a well-trained network to generate, by numerical simulation, any experimental design independently of the required number of experiences. Moreover, it doesn't matter if a given point of the experiment design has been measured or not; the network will predict the value from the available information.

Once the optimum parameters in the ANN, as defined in eq. (2), are determined, the network is ready to be used. To ensure that the network predicts correctly the mechanical properties of the new compounds, 25 sets of compounds given in Table II are divided into two subsets: one for training (training set, comprising 20 experiments) and the other for test (test set). The network training has been carried out with the data of the first subset. During the training process, the neurons learn the relationship between the

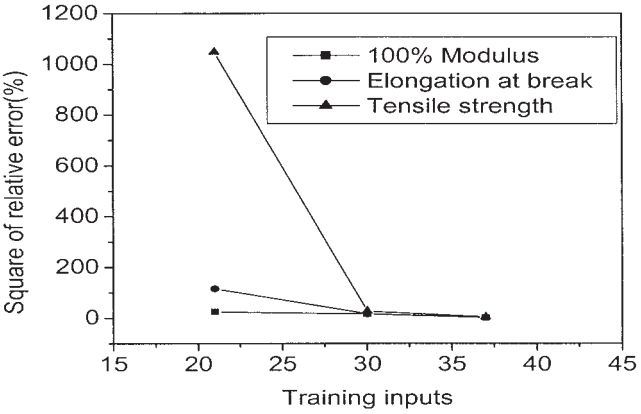

Figure 2 Percent of relative error of predicted results with the training data.

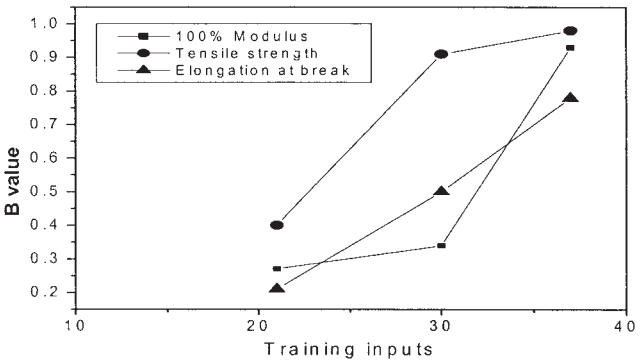

Figure 3 Dependence of test dataset B value on the number of the training dataset for 100% modulus, tensile strength, elongation at break, and volume fraction.

output variables and the input ones by adjusting the connection weights. After the ANN has been trained, it can be used to predict the compound properties of the test set. Compounds with trial numbers of 9, 10, 16, and 24 have been entered in the network for the prediction process. Table VI shows the results obtained from 20 elements for the training set and 4 for the test set. The predictions are not accurate, and it is better only for a few 100% modulus values. The greater and more representative the training set, the smaller will be the error for predicting the properties of new compounds. This fact has been utilized, and more data sets from Table VII are supplemented in the training process. The network was retrained with 30 datasets from Tables II and Table VII, and the predicted values for the same from sets 9, 10, 16, and 24 are given in Table VIII. It is found that the overall relative error is less as compared with training the network with 21 datasets. The efficiency of prediction has been further improved by increasing the number of datasets (epoch number). The network predicts very precisely with 37 datasets (21 datasets from Table II and 16 datasets from Table VII). The relative average error decreases with the increase in the number of datasets, as shown in Table IX and Figure 2. The network is able to predict even the volume fraction very precisely with same number of training datasets. Further, the quality of ANN prediction has been characterized from the coefficient of determination or B value. Figure 3 gives the B value (calculated by eq. (3)) versus the number of training datasets. It can be clearly seen that increasing the training datasets could reach very good agreement for 100% modulus, tensile strength, and volume fraction, but the required number for reaching a perfect predictive quality for elongation at break is low. These could be considered as follows: 100%modulus, tensile strength, and volume

TABLE X
Formulation and Properties of SBR

S.no.	Radiation dose (kGy)	TMPTA level (phr)	Silane level (phr)	Filler loading (phr)	Silica content	300% modulus, MPa	T.S. MPa	E.B., %	Volume fraction
1	0	0	0	20	4.7	3.1	12.4	700	0.172
2	100	0	0	20	4.7	3.4	10.8	590	0.182
3	200	0	0	20	4.7	4.2	9.4	484	0.181
4	0	3	0	20	4.7	3.0	12.8	710	0.171
5	20	3	0	20	4.7	3.0	12.5	684	0.176
6	50	3	0	20	4.7	3.0	13.2	715	0.177
7	100	3	0	20	4.7	3.1	14.8	741	0.187
8	200	3	0	20	4.7	3.3	15.2	725	0.188
9	100	1	0	20	4.7	3.8	13	659	0.224
10	100	5	0	20	4.7	3.1	14.1	734	0.178
11	100	0	1	20	4.7	3.8	12.6	598	0.183
12	0	0	3	20	4.7	3.4	12	620	0.183
13	100	0	3	20	4.7	3.9	12.3	596	0.186
14	100	0	5	20	4.7	4.0	11.1	562	0.188
15	0	0	0	10	4.7	2.2	7.6	710	0.168
16	0	0	0	60	4.7	12.3	20.9	417	0.222
17	100	3	0	10	4.7	2.2	7.0	607	0.168
18	100	3	0	40	4.7	5.7	26.8	751	0.192
19	100	3	0	60	4.7	12.3	27.7	529	0.211
20	100	0	3	10	4.7	2.1	7.5	715	0.171
21	100	0	3	60	4.7	14.2	25.5	445	0.260
22	100	3	0	20	0	3.2	12.4	704	0.169
23	100	3	0	20	2.3	3.2	12.7	719	0.182
24	100	3	0	20	5.6	3.3	14.6	696	0.182

The formulation was based on 100phr of rubber.
The results have been taken from A. M. Shanmugharaj and Anil K. Bhowmick.[26]

TABLE XI
Real Values vs. Predicted Values of Datasets in Table X.

	Real values				Predicted value			
Trial no.	300% modulus, MPa	Tensile strength, MPa	E.B. (%)	Volume fraction of rubber	300% modulus, MPa	Tensile strength, MPa	E.B. (%)	Volume fraction of rubber
5	3.0	12.5	684	0.176	3.3	12.6	711	0.185
10	3.1	14.1	734	0.178	3.4	14.4	738	0.180
15	2.2	7.6	710	0.168	2.5	7.9	713	0.171
20	2.1	7.5	715	0.171	2.4	8.1	725	0.182
24	3.4	14.6	696	0.182	3.8	15.5	709	0.186

fraction have a stronger relationship than elongation at break to those of material compositions. In other words, the nonlinear behavior of elongation at break is higher than that of the other outputs. Therefore, an ANN needs more experience in learning a complex nonlinear relationship for elongation at break than for other outputs.

The effectiveness in prediction by the constructed ANN has been further tested by a completely new dataset using styrene butadiene rubber[26] (Table X). The nature of rubber and experimental conditions were different. The parameters were entirely different. The network has been trained with 24 datasets, and the predicted results are given in Table XI. The coefficient of determination B, with a value of 0.97 and 0.82 for tensile strength and volume fraction of rubber, respectively, and low value of relative % error indicate the exactness in prediction of the network (Table XII).

It must be stated here that for all these compositions for both NBR and SBR, the relative error and B values lie in the same range even when training and test datasets are interchanged/varied, provided 35 or 37 datasets are used for training the network.

Validation of generated results

It does not matter if a given point of the experimental design was measured or not; the network will predict the value from the available information. This is discussed in this section for the $M_{1.5/0.5/0-300/0/0/0}$ and $M_{0.5/1.5/0-300/0/0/0}$ systems. The dependence of 100% modulus for two systems, namely $M_{1.5/0.5/0-300/0/0/0}$ and $M_{0.5/1.5/0-300/0/0/0}$, is shown in Figure 4(a,b).

An increase in 100% modulus is observed with an increase in radiation dose, since the degree of crosslinking involving both shorter and larger macromolecular chains is directly proportional to the integral radiation dose absorbed by the polymer. The predicted values of 100% modulus for the 70 kGy dose by ANN fall in the straight line fit with a regression

TABLE XII
Relative Error (%) Between Predicted and Real Values

300% modulus (MPa)	Tensile strength, (MPa)	Elongation at break, %	Volume fraction of rubber
Error	Error	Error	Error
	0.8	3.9	5.1
9.6	2.1	0.5	1.1
13.6	3.9	0.4	2.9
14.2	8.0	1.4	1.7
11.7	6.2	1.9	2.1
Avg. 11.8	4.2	1.6	2.6

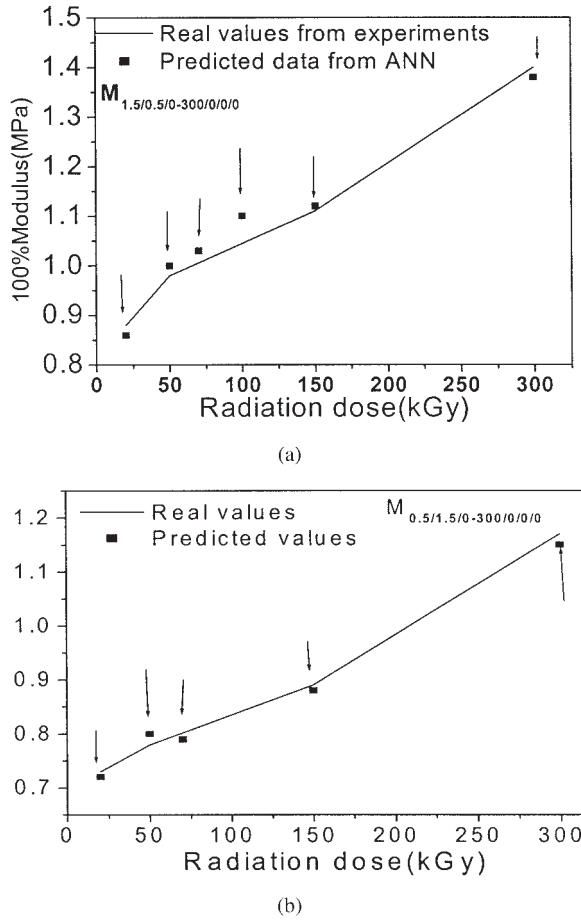

Figure 4 Validation plots for the predicted results of 100% modulus for (a) $M_{1.5/0.5/0-300/0/0/0}$ and (b) $M_{0.5/1.5/0-300/0/0/0}$.

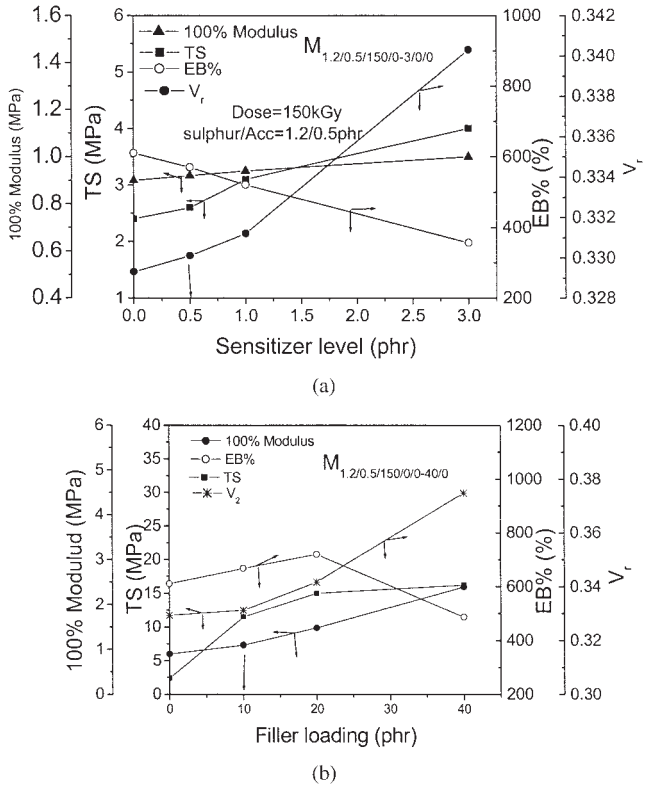

Figure 5 (a) Validation plots for the predicted results of 0.5 phr loading of TMPTA for $M_{1.5/0.5/150/0–3/0/0}$; (b) Validation plots for the predicted results of 10phr loading of carbon black (GPF grade) for $M_{1.5/0.5/150/0/0–40/0}$.

value of 0.9 for both the $M_{1.5/0.5/0–300/0/0/0}$ and $M_{0.5/1.5/0–300/0/0/0}$ systems. It is also observed that the prediction is quite accurate for 20, 50, 100, 150, and 300 irradiation doses.

There are certain chemical agents, often called prorads, that act as radiation sensitizers in an electron beam induced curing process. TMPTA is one such sensitizer that is suitable for use in NBR rubber. The predicted values for 100% modulus, tensile strength, elongation at break, and volume fraction for $M_{1.5/0.5/150/0–3/0/0}$ are in good accord with the experimental values [Fig. 5(a)]. Similarly, the predicted values of mechanical properties and volume fractions of carbon black filled NBR, that is, $M_{1.5/0.5/150/0/0–40/0}$, are also in good agreement [Fig. 5(b)]. A mathematical model relating the % gel content with radiation dose was developed by Vijayabaskar et al.[30] The lifetime of spurs, an important criterion for overlapping of spurs, can be determined for any system using this model.

$$G = a(1 - e^{-bD}) \tag{5}$$

Here, G is the gel content, and the lifetime of spurs is determined by the critical shift factor b. The volume fraction of rubber, which is highly dependent on % gel content, shows a similar variation with radiation dose (Fig. 6). The % gel content in the mathematical model could be replaced with V_r, and lifetime of spurs b could be determined. The critical shift factor b was determined for the system $M_{1.5/0.5/0–300/0/0/0}$ from the experimental values in Table VII. This b value was then deduced, also using an ANN, from the predicted volume fraction for the same system $M_{1.5/0.5/0–300/0/0/0}$. This shows the effectiveness of the network in predicting the results that are validated with this mathematical model.

CONCLUSIONS

1. An ANN was implemented for predicting the mechanical properties of nitrile rubber, influenced by six significant factors (radiation dose, sensitizer, filler, antioxidant, accelerator, and sulfur).
2. It was found that the efficiency of prediction increased with the number of training data, and the quality of prediction could be determined by the B value or correlation coefficient.

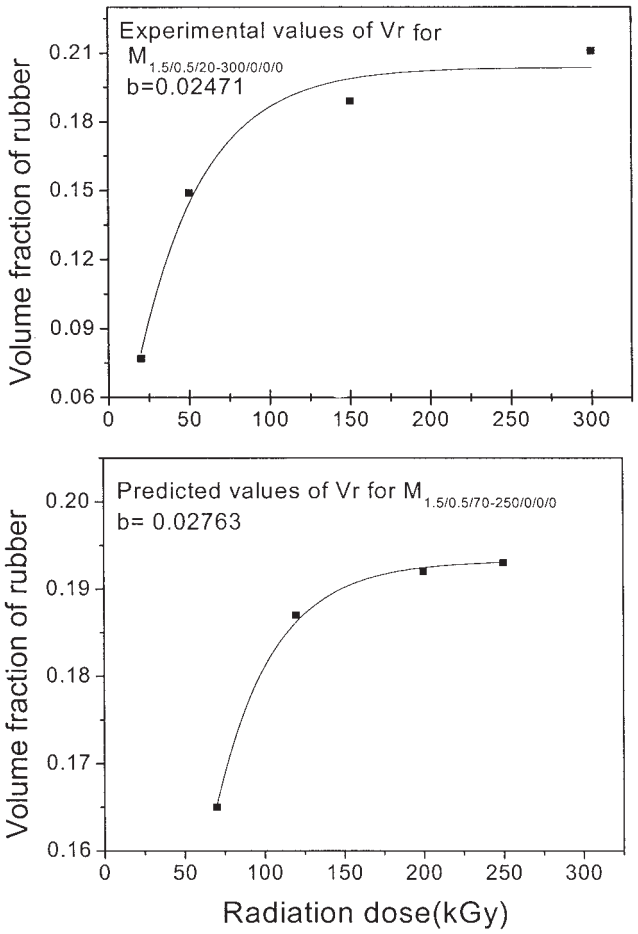

Figure 6 Variation of volume fractions from experimental dataset and predicted values for $M_{1.5/0.5/0–300/0/0/0}$ with different doses.

3. ANN predicted tensile strength, 100% modulus, elongation at break, and volume fraction of rubber accurately for nitrile rubber vulcanizates.
4. Prediction of the above properties was also verified with a different system comprised of styrene butadiene rubber.
5. The critical shift factor b determined from the predicted volume fractions by the ANN was in agreement with that determined from experimental results.

References

1. Bhowmick, A. K.; Hall, M. M.; Benarey, H., Eds. Rubber Products Manufacturing Technology; Marcel Dekker: New York, 1994.
2. Bhowmick, A. K.; Stephens, H. L., Eds. Handbook of Elastomers; Marcel Dekker: New York, 1988.
3. Brown, H. P. Rubber Chem Technol 1963, 36, 931.
4. Zingaro, R. A.; Cooper, W. C. Selenium; Von Nostrand Reinhold: New York, 1974; p 728.
5. Abdullaev, G. B.; Ismailov, T. K.; Abasov, S. A.; Akhmedev, G. G.; Makhtieva, S. I.; Akhmedov, K. R.; Pashaev, T. A. Chem Abstr 1977, 86, 19101u.
6. Kvardashov, V. P.; Kornev, A. E. KhimKhimTechnol 1971, 14, 1757.
7. Chow, Y. W.; Knight, G. T. Plast Rubber Process 1977, 2, 116.
8. Minora, Y.; Yamashita, S.; Okarnato, H.; Matsuo, N.; Irawa, M.; Kottmoto, S. I. Rubber Chem Technol 1979, 52, 926.
9. Trifonov, V. P.; Potim, H. Stroit Mater 1977, 45, 57.
10. Vijayabaskar, V.; Costa, F. R.; Bhowmick, A. K. Rubber Chem Technol 2004, 77, 624.
11. Charlesby, A. Nature 1953, 24, 1348.
12. Bohm, G. G. A.; Tveekrem, J. O. Rubber Chem Technol 1982, 55, 575.
13. Banik, I.; Bhowmick, A. K.; Raghavan, S.V.; Majali, A. B.; Tikku, V. K. Polym Degrad Stab 1999, 63, 413.
14. Banik, I.; Chaki, T. K.; Tikku, V. K.; Bhowmick, A. K. Angew Makromol Chem 1999, 263, 5.
15. Thorn, A. D.; Robinson, R. A. In Rubber Products Manufacturing Technology; Bhowmick, A. K.; Hall, M. M.; Benarey, H., Eds.; Marcel Dekker: New York, 1994; p 97.
16. Jones, S. P.; Jansen, R.; Fusar, R. L. Tribology Transactions 1997, 40, 312.
17. Ebube, N. K.; Ababio, G. O.; Adayaye, C. M. Int J Pharm 2000, 27, 196.
18. Talaie, A.; Romagnoli, J. A. Synth Met 1996, 82, 27.
19. Hertz, G.; Krogh, A.; Palmer, R. G. Introduction to the Theory of Neural Computation; Addison Wesley: Redwood City, CA, 1990.
20. Ni, H.; Hunkeler, D. Polymer 1997, 38,667.
21. Chichocki, A.; Unbehauen, R. Neural Networks for Optimization and Signal Processing; Wiley: New York, 1996.
22. Rumelhart, D. E.; Minton, G. E.; Williams, R. J. In Rumelhart, D. E.; Mcclelland, J. L., Eds.; Parallel Distributed Processing: Explanation in the Microstructure of Cognition; MIT: Cambridge, MA, 1986; Vol. 1, p 318.
23. Zhang, Z.; Friedrich, K. Compos Sci Technol 2003, 63, 2029.
24. Ulmer II, C. W.; Smith, D. A.; Sumpter, B. G.; Noid, D. I. Computational and Theoretical Polym Sci 1998, 8, 311.
25. Talaie, A.; Romagnoli, J. A.; Boger, Z.; Adeloju, S. B.; Yuan, Y. J. Synth Met 1996, 83, 21.
26. Shanmugharaj, A. M.; Bhowmick, A. K. Rubber Chem Technol 2003, 76, 299.
27. Shanmugharaj, A.M.; Bhowmick, A. K. J Appl Polym Sci 2003, 88, 2992.
28. Bhowmick, A. K.; Mangaraj, D. In Rubber Products Manufacturing Technology; Bhowmick, A. K.; Hall, M. M.; Benarey, H., Eds.; Marcel Dekker: New York, 1994; p 363.
29. Ross, P. J. Taguchi Techniques for Quality Engineering; McGraw–Hill: New York, 1996.
30. Vijayabaskar, V.; Bhowmick, A. K.; Bhattacharya, S.; Tikku, V. K. Radiat Phys Chem 2004, 71, 1045.