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ORIGINAL PAPER

Multi-objective simultaneous prediction of waterborne coating properties

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Abstract Multi-objective simultaneous prediction of waterborne coating properties was studied by the neural network combined with programming. The conditions of network with one input layer, three hidden layers and one output layer were confirmed. The monomers mass of *BA*, *MMA*, *St* and pigments mass of TiO_2 and $CaCO_3$ were used as input data. Four properties, which were hardness, adhesion, impact resistance and reflectivity, were used as network output. After discussing the hidden layer neurons, learn rate and the number of hidden layers, the best net parameters were confirmed. The results of experiment show that multi-hidden layers was advantageous to improve the accuracy of multi-objective simultaneous prediction. 36 kinds of coating formulations were used as the training subset and 9 acrylate waterborne coatings were used as testing subset in order to predict the performance. The forecast error of hardness was 8.02% and reflectivity was 0.16%. Both forecast accuracy of adhesion and impact resistance were 100%.

Keywords Neural network · Polyacrylate emulsion · Waterborne coating

1 Introduction

Waterborne coating was composed of film former (namely emulsion), pigments, water and various addition agents. The content of any component might have effect on the whole coating performance. Therefor the coating system should be carefully designed,

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and the optimal scheme is chosen out from all possible design systems. All these processes need a lot of experiments.

Artificial neural network (ANN) is an information processing system. It can achieve the transmission, study and storage of the data by simulating the way of information processing of human brain nervous system and it shows an advantage in handling the non-linear problem. Back-Propagation algorithm was one of the most wide used and influential method in ANN algorithms. Because of the excellent characterizes of self-learning, self-adaptation, knowledge distribution storage and highly nonlinear description ability, ANN technology has been widely applied in many fields, such as chemistry [1,2] , biology [3] and medicine [4–6] . Zupan [7] and Sumpter [8] have given detailed reviews of the application of neural network to chemical science. Philip Plumb [9] investigated the effect of experimental design strategy on the modeling of a film coating formulation by ANNs. Ludmila Dolmatova describes a neural network method for the quantitative analysis of paper coatings. Ming-Der Jean [10] develop an efficient method of depositing alloys with a favorable surface morphology by artificial neural network. Amit [11] reported the use of neural networks to predict the brightness of a double-coated paper product. Above all, the neural network technology was a reliable and effective analysis tool in the chemistry study.

This paper presents the application of ANN in the multi-objective simultaneous prediction of waterborne coating properties based on the Matlab neural network toolbox (nntool) and programming. The results showed it is a convenient and accurate method.

2 Experiment

2.1 Main reagents and instruments

Butyl acrylate (BA, 99 + %, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Octyl-phenyl polyoxy ethylene (*OP-10*), Sodium dodecyl benzene sulfonate (*ABS*), ammonium persulfate (*APS*), and sodium bicarbonate ($NaHCO_3$) were all analytically pure. Titanium pigment (TiO_2) and light calcium carbonate ($CaCO_3$), were industrial grade.

Hardness was measured by QBY-II swing-bar hardness tester (China) according to GB/T 1730-93 "Determination of hardness of the paint films -Pendulum damping test". Adhesion was measured by QFZ-II adhesion tester according to GB/T 1720-1979(1989) "Determination of adhension of the paint films". Impact resistance was measured by QCJ paint film impacter according to GB/T 1732-93 "Determination of impact resistance of the paint films". Reflectivity was measured by reflectivity determinator (UK).

2.2 Coating preparation

The polyacrylate latex was prepared through the emulsion polymerization of BA, MMA and styrene in the presence of composite surfactants OP-10 and ABS [12].

Table 1 Components content ranges of the latices

	Monomers	Content (g)	Pigments	Content (g)	Water (g)
	BA	15–21	TiO_2	15–30	37
	MMA	6–16	$CaCO_3$	0–15	
	St	1–13			
Total:		33		30	37

36 different coatings were prepared by a series of different components content which the total amount of monomers, pigments and water were controlled at the certain ratio of 33:30:37

36 kinds of coatings were prepared by various latices of different monomer content. The general content can be seen in Table 1.

3 Using neural network in waterborne coating system

Neural network algorithm was different from the general Chemometrics methods, because it only emphasized the inputs and outputs, rather than physical and chemical processes. Therefor the neural network was suitable for accomplish the multi-objective simultaneous prediction of waterborne coating properties.

3.1 Design of neural network structure

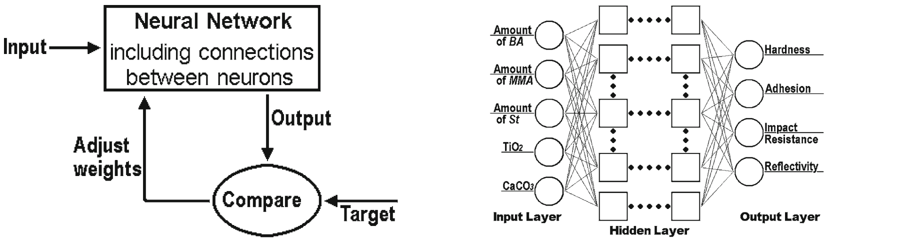
Neural network was made up of one input layer, one output layer and three hidden layers for our sutdy. The contents of *BA*, *MMA*, *St* and TiO_2, $CaCO_3$ in the acrylate coatings system were used as the input nodes ($N_I = 5$) and four coating's primary properties, hardness, adhesion, impact resistance and reflectivity, were used as the output node ($N_O = 4$), which can be seen in Table 2. There were 12, 13 and 12 nodes in the three hidden layers respectively.

Figure 1 presented the calculating process of neural network. Figure 1 presented the architecture of neural network applied. A three-layers neural network was taken example for describing the training process detailedly as follows:

(1): All the initial values of weight (w_{ji}, w_{kj}) and threshold (θ_j, θ_k) were set randomly ranging from 0 to 1. (i stands for input layer, j stands for the hidden layer and k stands for the output layer.)

Table 2 Input & output data of network

Net input nodes	Net output nodes
I_1: Amount of *BA* (g)	O_1: Hardness (ratio)
I_2: Amount of *MMA* (g)	O_2: Adhesion (grade)
I_3: Amount of *St* (g)	O_3: Impact Resistance (cm)
I_4: Amount of TiO_2 (g)	O_4: Reflectivity (%)
I_5: Amount of $CaCO_3$ (g)	



(a) *Calculating process of neural network* **(b)** *Architecture of the neural network applied*

Fig. 1 Calculating process and architecture of the neural network

(2): The training subset which was made up of 36 samples was provided. The coatings raw material of 36 samples were assigned to X_i as input data and their experimental results were assigned to T_k as target values.

(3): The output of hidden layer and output layer were calculated:

$$x_j = F_{ji}\left(\sum_i w_{ji} X_i + \theta_j\right) \quad \text{(hidden layer)}$$

$$y_k = F_{kj}\left(\sum_j w_{kj} x_j + \theta_k\right) \quad \text{(output layer)}$$

(4): Network error E was calculated:

$$E = \sqrt{\frac{1}{2}\sum_p ||T_k - y_k||^2}$$

If the network error E was smaller than 10^{-3}, the training was completed. If E bigger than 10^{-3}, the training was continued.

(5): Training error δ_k and δ_j were calculated:

$$\delta_k = y_k(1 - y_k)(T_k - y_k) \quad \text{(output layer)}$$
$$\delta_j = x_j(1 - x_j)\sum \delta_k w_{kj} \quad \text{(hidden layer)}$$

(6): Weight values and threshold values were revised. η was the learn rate and α was momentum term in the formulas.

$$w_{kj} = w_{kj} + \eta \cdot \delta_k \cdot y_k + \alpha \cdot \Delta w_{kj}, \quad \theta_k = \theta_k + \eta\delta_k + \alpha\Delta\theta_k$$
$$w_{ji} = w_{ji} + \eta \cdot \delta_j \cdot x_j + \alpha \cdot \Delta w_{ji}, \quad \theta_j = \theta_j + \eta\delta_j + \alpha\Delta\theta_j$$

The calculation was recurred to step(3) for the recalculating of y_k by using the revised w_{ji}, w_{kj}, θ_j and θ_k the until the network error satisfying condition. The whole calculation was accomplished by programming and by means of MATLAB Neural Network Toolbox (NN Toolbox). There were large numbers of neural network function in the toolbox written in modular. Tansig function was used as F_{ji} in hidden layers and Purelin function was used as F_{kj} in output layer. The learn rate η was 0.20 and the epoch was 100, 000 times. The training subset was consisted by 36 measured samples. The testing subset was made up of 9 random samples. Based on the above conditions, neural networks were built to predict the four properties of coatings.

3.2 Evaluation of the prediction accuracy of multi-objective network

Coatings were complicated system, and there were many properties of which needed to be characterized. Some of them were continuous functions, others were discrete functions. In this study, the hardness and reflectivity were continuous functions, and adhesion and impact resistance were discrete functions. The errors description of continuous functions and discrete functions were different. The errors of continuous functions were calculated by using the mean squared error, which was showed in Eq. 1a. The errors of discrete functions were calculated by using the proportion of wrong prediction, which could be seen in Eq. 1b.

$$E_i = \mathrm{MSE}(y'_{n,i} - y_{n,i}) \times 100\% \quad (i = 1, 4; \quad n = 1, 2, \ldots, 36) \tag{1a}$$

$$E_i = \frac{1}{36} \times N_{(y'_{n,i} \neq y_{n,i})} \times 100\% \quad (i = 2, 3; \quad n = 1, 2, \ldots, 36) \tag{1b}$$

The prediction accuracies of four properties were calculated by Eqs.1a and b. However it was difficult to judge which network condition was the best one using the four errors because their repugnant character. In order to solve this problem, a total evaluation standard standing for the prediction error was more needed rather than four properties errors'. Therefor in this work, we refer to the statistical method of chemometrics to put forward a prediction accuracy formula which contain the four errors, see Eq. 2.

$$\text{Prediction Accuracy }(\%) = 1 - \sqrt{\mathrm{MSE}(E_i)} = \left(1 - \sqrt{\frac{1}{4} \times \sum_{i=1}^{4} E_i^2}\right) \times 100\% \tag{2}$$

Function MSE was the mean squared error of the four properties errors. The judgment of network performance was given by Matlab NNtool using the errors between measured and simulated results. It was unreasonable for used in the discrete functions. Prediction accuracy has the same ability for describe the network performance of the ANN however it was more suitable for the discrete functions. Therefor the network was evaluated by prediction accuracy instead of network performance.

4 Results and discussion

4.1 Transformation of input & output data

The data of training samples, including input value and output value, should be normalization processed before used. In this study, five input nodes in coatings system were divided into monomers groups, including *BA*, *MMA*, *St* contents, and pigments group, containing TiO_2 and $CaCO_3$ amount. The monomers and pigments group were converted by Eqs. 3a and b.

$$I_i' = \frac{I_i}{I_1 + I_2 + I_3} \quad (i = 1, 2, 3;) \tag{3a}$$

$$I_i' = 0.25 + 0.5 \times \frac{I_i}{I_4 + I_5} \quad (i = 4, 5;) \tag{3b}$$

In coatings system, the units of the four outputs were inconsistent. The hardness and reflectivity were ratio value, the range of which were from 0 to 1. The adhesion was classified by grade. The measured adhesion of all samples were from Grade I to Grade III. The impact resistance were 40 cm, 45 cm and 50 cm. The different units would led to the low accuracy because of the unbalanced error distribution. Therefore it was necessary to transform the data before they were input the ANN for training. The transformation formula can be seen in Eq. 4.

$$O_i' = \frac{O_i - O_i^{\min}}{O_i^{\max} - O_i^{\min}} \times 0.25 + 0.5 \quad (i = 1, 2, 3, 4;) \tag{4}$$

The prediction accuracies of transfer function Logsig and Tansig were calculated at different hidden neuron numbers which was showed in Fig. 2. The graph showed that the prediction accuracies of converted data were much higher than original data.

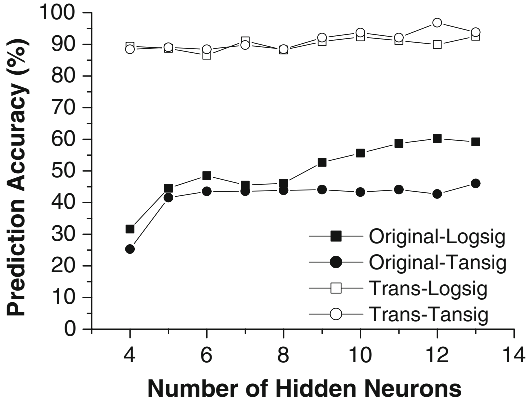


Fig. 2 Comparison of input data transform

4.2 Neurons number of the first hidden layer

The selection of hidden neurons was so important that it would influence the network calculation time and discriminating ability. The optimum neurons number can be found by placing a different number of neurons in the first hidden layer for the same data subset by comparing the network errors [13] . Kolmogorov theorem put forward an empirical formula to determine the hidden neurons number which can be seen in Eq. 5.

$$N_H = \sqrt{N_I + N_O + 1} + a \quad a = 1 \sim 10 \tag{5}$$

where N_I was the number of input layer neurons and N_O was the number of output layer neurons. In the coating system of our researched, $N_I = 5$, $N_O = 4$. According to Eq. 5, the range of hidden neurons number N_H was from 4 to 13. The optimum neurons number was found between this range by comparing the prediction accuracy.

Figure 3 was the network model's prediction accuracy which was calculated at the different hidden neurons numbers by Eq. 2, (Learning epochs = 100,000; Learn

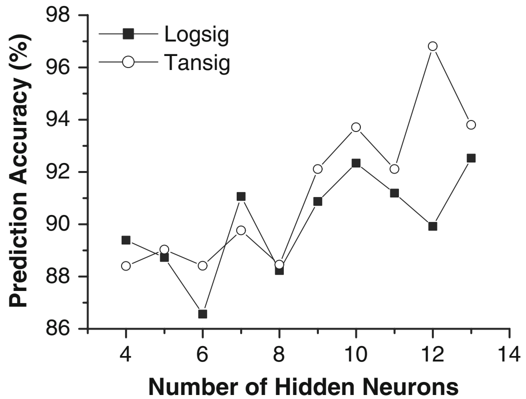


Fig. 3 Selection of hidden neurons

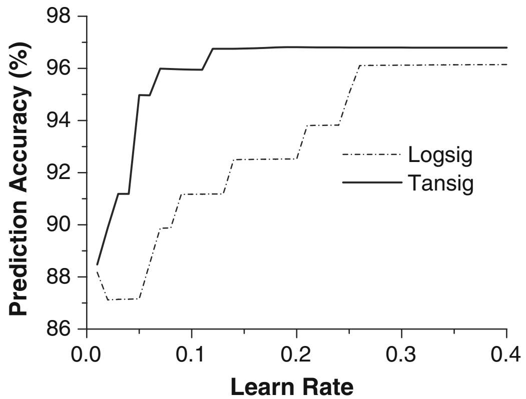
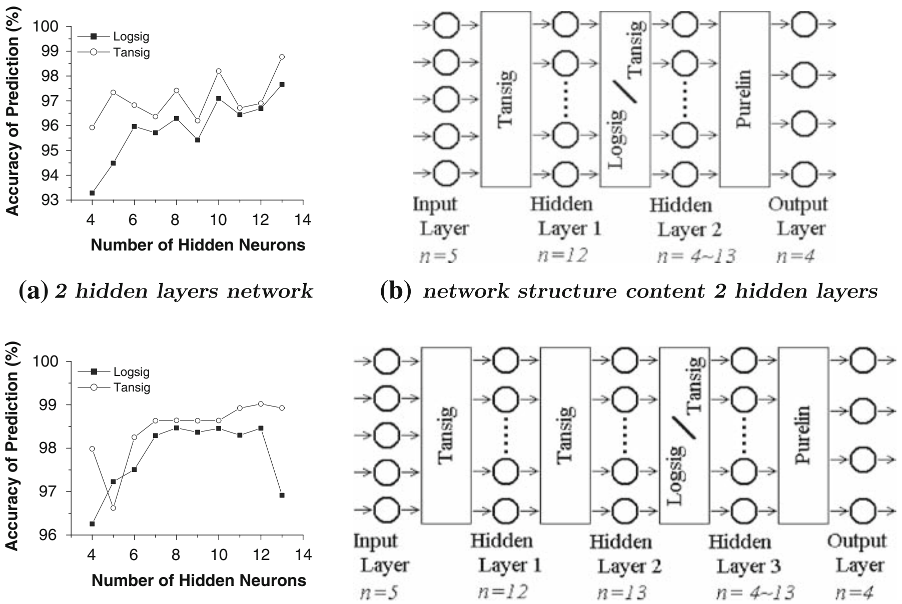


Fig. 4 Selection of learn rate



(a) ***2 hidden layers network*** **(b)** ***network structure content 2 hidden layers***

(c) ***3 hidden layers network*** **(d)** ***network structure content 3 hidden layers***

Fig. 5 Comparison of multi-hidden layers network

rate=0.20). Tansig trans-function has a better prediction accuracy than Logsig and the optimum number of hidden neurons was 12.

4.3 Selection of learn rate

Learn rate was an important parameter of zero error approach method. The lower learn rate would delay the training time and the higher learn rate would led to an unsteady performance. In order to choose out the proper learn rate, the network prediction accuracies were computed in the range of learn the rate from 0.01 to 0.30, (transfer function: Logsig / Tansig, Learning epochs = 100,000). The result was showed in Fig. 4.

From the Fig. 4 it was obvious that the prediction accuracy of Logsig and Tansig trans-function were increased with the rise of learn rates. When the learn rate was 0.20, Tansig trans-function could get a good accuracy.

4.4 Selection of the number of hidden layers

A common single-layer BP neural model includes one input layer, one hidden layer and one output layer. Multilayer BP network has more hidden layers. In the multi-objective simultaneous prediction of waterborne coating properties, more hidden layers were considered for choosing the best results. One and two hidden layers were added to the network established in Sects.4.2 and 4.3. The structures of the network with two and three hidden layers were showed in Fig. 5b and d. The prediction accuracy of

Table 3 Formulation of coating and measured/predicted properties and error calculation

No.	Formulation of coating					Measured properties				Predicted properties				Absolute error			
	BA	MMA	St	TiO_2	$CaCO_3$	H	A	IR	R	H	A	IR	R	E_H	E_A	E_{IR}	E_R
1	16.0	12.0	5.0	30.0	0.0	0.668	I	45	89.0	0.709	I	45	88.9	0.041	T	T	−0.003
2	15.6	15.0	2.4	22.5	7.5	0.588	I	45	90.1	0.638	I	45	90.0	0.050	T	T	−0.003
3	15.0	10.4	7.6	30.0	0.0	0.707	I	40	89.4	0.734	I	40	89.2	0.027	T	T	−0.009
4	16.8	15.2	1.0	30.0	0.0	0.611	I	45	90.8	0.660	I	45	90.8	0.049	T	T	0.000
5	14.8	12.2	6.0	15.0	15.0	0.604	II	45	87.6	0.646	II	45	87.3	0.042	T	T	−0.015
6	14.4	5.6	13.0	22.5	7.5	0.716	I	40	88.7	0.749	I	40	88.7	0.033	T	T	−0.001
7	16.0	9.0	8.0	30.0	0.0	0.653	I	45	90.7	0.699	I	45	90.6	0.046	T	T	−0.003
8	15.0	10.0	8.0	30.0	0.0	0.687	II	40	90.6	0.733	II	40	90.8	0.046	T	T	0.010
9	15.0	12.0	6.0	30.0	0.0	0.675	III	40	91.3	0.715	III	40	91.3	0.040	T	T	0.001
										Average relative error (%):				8.02	0.00	0.00	0.16
										Prediction accuracy (%):				91.98	100	100	99.84
										Total prediction accuracy (%):				97.96			

H, Hardness (ratio); A, Adhesion (Grade); IR, Impact Resistance (cm); R, Reflectivity (%); (T, true, F, false) two hidden layers network could be seen in Fig. 5a, and the best performance of two hidden layers network was under the condition of 13 hidden neurons nodes and Tansig transfer function. The prediction accuracy of three hidden layers network could be seen Fig. 5c, the best performance of three hidden layers networks was under the condition of 12 hidden neurons and Tansig transfer function.

In the studied coating system, the best prediction accuracy of one, two and three hidden layers networks were 96.81, 98.77 and 99.02% respectively. Three hidden layers was helpful for the accuracy increasing. Therefore, three hidden layers network and the network condition were chosen for the prediction of testing sample subset.

4.5 Prediction of testing sample subset

The properties of 9 coating formulas were measured and simulated using the chosen network condition. Table 3 showed the measured and predicted results and the absolute errors between them. Average relative errors of the four properties were calculated by the average of absolute errors.

Table 3 showed the prediction accuracy of hardness and reflectivity were 91.98% and 99.84%. The adhesion and impact resistance were both 100%.

5 Conclusion

By neural network technology combining with chemometrics programming and data transformation, the multi-objective simultaneous prediction of waterborne coatings properties such as hardness, adhesion, impact resistance and reflectivity, were accomplished. Good prediction results were received. The average relative errors of all testing samples were about 2%. The method of neural network provided a simple and forthright way for prediction of the waterborne coatings properties, and it was helpful for the preparation of coatings.

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