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Original Article

Artificial neural network approaches for the sorption isotherms, enthalpy and entropy of heat sorption of two types block rubber products

Yutthana Tirawanichakul[1]*, Jutarut Tasara[2] and Supawan Tirawanichakul[3]

[1] *Plasma and Energy Technology Research Laboratory, Department of Physics, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.*

[2] *Department of Industrial Chemistry, Faculty of Science and Technology, Prince of Songkla University, Mueang, Pattani, 94000 Thailand.*

[3] *Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.*

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Abstract

Knowledge of the temperature and relative humidity (or water activity) dependence of moisture sorption phenomena of agro-industrial products provides valuable information about changes related to the thermodynamics of the system. Thus the moisture sorption characteristics in terms of equilibrium moisture contents (EMC), enthalpy and entropy of heat sorption of natural rubber (NR) for producing STR 20 and skim block rubber were investigated. Simulation modeling of water sorption isotherms was performed using the 10 non-linear regression EMC models and the multilayer artificial neural network (ANN) approach. The results showed that the predicted EMC results using the modified Oswin model was the best fitting model for both NR samples. However, the predicted values of ANN model were more accurate than those predicted results using non-linear regression method. Finally, enthalpy and entropy of heat sorption for both NR samples were evaluated by applying the Clausius-Clapeyron equation showing as the negative exponential function of moisture content.

Keywords: block rubber, equilibrium moisture content, heat of sorption, natural rubber, non-linear regression

1. Introduction

Natural rubber (NR) latex, which is extracted from the *Hevea brasiliensis*, is composed of 30-45% weight of dried rubber content (cis-polyisoprene), 4-5% weight of non-rubber constituents such as protein, lipids, carbohydrates, sugar and 50% of water. NR is one of the most important commercial commodities in Southeast Asia countries, Africa and Middle America continent and is widely used in expansive industrial applications such as tires, automobile, shoes, baby bottle teats, elastic thread, gloves, condoms, foam rubber mattresses, adhesives, pillows and aircrafts. Thailand is currently the largest NR producer and exporting country in the world (Rubber Research Institute of Thailand. 2010). There are more than 600 registered rubber-based processing factories in Thailand and these factories are mostly placed in the South part of Thailand. These rubber-based factories produce various types of natural rubber products and over ninety percentage of total rubber exporting quantity results from NR e.g. Standard Thai Rubber (STR) grades, ribbed smoked sheet (RSS), air dried sheet (ADS), crepe rubber, skim rubber and concentrated latex. Since 1999 the Rubber Research Institute of Thailand has identified 6 different block rubber grades of STR, which guaranteed that all the exported block rubbers quality and they are conformed to technically

* Corresponding author.
Email address: yutthana.t@psu.ac.th

standardized block rubber as following by the International Organization for Standardization (ISO). The export market share of STR block rubber is around 60% of total NR products. Due to the huge magnitude of NR production, the STR 20 and skim block rubber processing is given special attention in this paper, especially on their thermo-physical properties. This is because their thermo-physical properties can be used for evaluating how the NR drying process is carried on the optimal drying condition for examples: drying temperature, operating time, packaging, storage and energy consumption etc. One of the most important parameters for determination evolution of moisture transfer during drying process is the equilibrium moisture content. The equilibrium moisture content (EMC) is defined as the moisture content of a material in equilibrium with particular surrounding parameters (temperature and relative humidity). For drying, mixing, packaging and storage, knowledge of the relationship between moisture content sorption and equilibrium relative humidity and temperature is the most essential, as equilibrium isotherm helps establish the suitable final moisture content and compute specific energy consumption of drying and storage. The simulation drying model using EMC value for evaluating moisture transfer and for storage grain kernel longevity were reported (Thompson *et al.,* 1968; Soponronnarit *et al.*, 1996; Soponronnarit, 1997; Tirawanichakul *et al.*, 2004, Tirawanichakul *et al.*, 2008). Moisture sorption isotherm provides valuable information on the thermodynamics of relative humidity, desorption and absorption. Not only determination of the EMC values is presented, but also the isosteric heat and entropy of sorption isotherm can be evaluated by using the Clausius–Clapeyron equation (Chen, 2006; Cortés *et al.*, 2010). Additionally, the determination of the heat of sorption was the aim of several previous studies. Its knowledge is essential for the modeling of various food processes and food storage. In addition, it can be used to estimate the energy requirements of food drying and also provides important information about the state of water in food products (Kaya and Kahyaoglu, 2005). Actually, the adsorption and desorption mechanism of samples are related to surrounding temperatures, relative humidity, water activity, particle size and their own properties (Soponronnarit 1997; Panchariya *et al.*, 2002; Yan *et al.*, 2008; Choudhury *et al.*, 2011). Even though many research works on sorption isotherms, heat of sorption and entropy of food, cereal grain kernel and some agricultural products, and the temperature dependence of isotherms have been reported (Chung and Pfost, 1967; Soponronnarit, 1997; Chen, 2002; Arslan and Togrul, 2006; Chen, 2006; Basu *et al.*, 2006; Janjai *et al.,* 2007; Bahloul *et al.*, 2008; Janjai *et al.*, 2009; Cortés *et al.*, 2010; Choudhury *et al.*, 2011) there are a few works that have focused on thermo-physical property of natural rubber and its composites (Tirawanichakul *et al.*, 2007; Tasara *et al.*, 2012). Among the most conventionally proposed EMC models for grain, cereal, vegetables and fruits, those of the Guggenheim–Anderson–de Boer (GAB) (Bizot, 1983), Oswin (Oswin, 1983), Henderson (Henderson, 1952), Halsey (Halsey, 1948) and Ratti (Ratti *et al.*, 1989) equations etc. have been selected to describe the experimental results. The GAB model (Bizot, 1983) has usually been used to fit the data of food products with satisfactory results by assumpting that food product has one monolayer of structure with a uniform moisture content and its constants are related to temperature (Mullet *et al.*, 2002). The Henderson model provides a good description for various hygroscopic materials such as foodstuffs, agricultural and biomaterials among relative humidity ranging of 10-75% (Henderson, 1952). The Oswin model was a mathematical series expansion for S-shaped curves without considering the temperature effect (Oswin, 1983), while the Halsey model has been developed based on multilayer condensation (Halsey, 1948). In Addition, the Ratti model (Ratti *et al.*, 1989) was developed on the basis of thermodynamic considerations and the effect of temperature including the vapor pressure of pure water. Solving these proposed EMC models is quite complicated and some knowledge of biomaterial mechanism and physical properties needs to be considered. Progress in neurobiology has allowed scientists and engineers to provide mathematical models that simulate neural behavior. The first artificial neural network (ANN) model was presented in 1943 and artificial neural networks (ANN) have been recognized as good tools for dynamic modeling since 1986 (Rumelhar *et al.*,1986). The ANN is one non-linear model based on a simplified model of human brain function and is particularly useful when a phenomenological model of a process is not available or would be far too complex. Additionally, the physical dynamic modeling mostly considers the complex mechanism and usually results in coupled non-linear differential equations with partial derivative, where numerical simulations are very time consuming. However, accuracy of the simulated results depends upon the structure and configuration of the models. Several research studies have reported ANN modeling of drying (Hernández-Pérez *et al.*, 2004), thermal and pressure food processing, (Torrecilla *et al.*, 2004) prediction of food properties such as dough rheological properties (Ruan *et al.*, 1995), inactivation kinetics (Geeraerd *et al.*, 1998), viscosity (Bouchard and Grandjean, 1995) and food quality (Gunasekaran, 1998) etc. The ANN technique has also been applied for modeling of water sorption isotherms of black tea (Panchariya *et al.*, 2002) and longan (Janjai *et al.*, 2009). These previous results showed that the ANN model was better than other mathematical models. However, there are very few reports on moisture sorption isotherms of some natural polymer materials, especially natural rubber. So determination of the sorption isotherms for NR is interesting not only for understanding of natural property among surrounding condition, but also for prediction of drying process during the operating period.

Thus, the objective of this study was to evaluate the equilibrium moisture content, isosteric heat and entropy of two grades natural rubber (STR 20 and skim block rubber samples). Development of mathematical sorption model on experimental data of sorption isotherms using non-linear regression analysis and artificial neural network (ANN) were evaluated among surrounding temperature of 45-60°C and RH of 10-97%. Besides, the net isosteric heat of adsorption of moisture from the experimental data was calculated. Model validation was made with experimental data of both NR samples and, finally, the isosteric heat and entropy of sorption for NR samples using the sorption isotherms curve were presented.

2. Materials and Methods

2.1 Materials

Natural rubber samples in this work used for producing STR 20 and skim block rubber were provided by the Southland Resource Industry Co., Ltd. (Suratthani province) and B-TECH Industry Co., Ltd. (Songkhla province), Thailand, respectively. The NR sample for producing STR20 block rubber normally was made of scrap rubber and low quality of rubber sheet while the NR sample for producing skim block rubber was made of scrap rubber which is taken out of rubber latex wastewater (so-called as skim latex) as shown in Figure 1(a) and 1(b), respectively. The NR samples were prepared in the forms of granular rubber kernel as illustrated in Figure 1(c) and 1(d), respectively. Both fresh natural rubber samples were taken to determine moisture contents under the drying condition of 130°C for 3 h (ASABE, 2007). The average moisture content was determined in triplicate. The initial moisture content was in the range from 40 to 55% dry basis.

2.2 Determination of moisture sorption isotherms

In this study, moisture sorption isotherms were determined in terms of equilibrium moisture content (EMC) by static gravimetric method. Five saturated salt solutions to achieve an EMC stage were used in the experiment: KNO_3, NaCl, $Mg(NO_3)_2$•$6H_2O$, $MgCl_2$•$6H_2O$ and LiCl. These 5 satu-

(a) Unclean scrap rubber and low grade ribbed smoked sheet rubber as raw natural for producing STR20 block rubber

(b) Scrap rubber from wastewater of rubber latex factory as raw natural rubber for producing skim block rubber

(c) Raw scrap natural rubber (after cleaning) provided by the Southland Resource Factory for producing STR20 block rubber

(d) Raw scrap natural rubber provided by B TECH Industry for producing skim block rubber

Figure 1. Natural sample preparation for drying (a) unclean scrap rubber and low grade ribbed smoked sheet rubber, (b) scrap rubber from wastewater of rubber latex factory, (c) Raw scrap natural rubber (after cleaning) provided by the Southland Resource Factory for producing STR20 block rubber and (d) Raw scrap natural rubber provided by B TECH Industry for producing skim block rubber.

rated salt solutions provided the surrounding relative humidity (RH) of 10-97% correlating to the surrounding temperatures of 45-60°C (Tirawanichakul *et al.*, 2007). These surrounding conditions cover all drying conditions because of providing the equilibrium moisture content ranging of 0.5-100% dry-basis (Henderson, 1952; Chung and Pfost, 1967; Iglesias and Chirife, 1976; Pfost *et al.*, 1976; Bala, 1997; Soponronnarit, 1997; Tirawanichakul *et al.*, 2008). The natural rubber samples, which were prepared in small pieces of 3-4 mm diameter, were weighed (20–35 g) and kept in stainless-steel wire nets hanging in glass bottles which contained the saturated salt solutions. The bottles were then placed in an incubator at those constant temperatures listed above. After a few weeks, the rubber samples were in equilibrial state with the saturated salt solutions. This normally takes about 10–15 days, depending on the nature of the samples, sample size and the surrounding temperature inside incubator. Then, the EMC value was acknowledged when three consecutive weight measurements showed significant difference of less than 0.001 g. The moisture contents were determined using ASABE Standards (ASABE, 2007). The average EMC value was determined in triplicate.

2.3 Determination of sorption isotherm model

Ten sorption isotherm models for predicting the EMC value of both natural rubber samples were used to correlate the experimental data with the surrounding temperature and relative humidity of 45-60°C and 10-97%, respectively. These ten EMC models were classified into two model types. Firstly, Model type I described the relationship between moisture content and surrounding relative humidity consisting of Freundlich (Wang and Brennan, 1991), Brunauer *et al.* (1938), Oswin (1946), Smith (Smith *et al.*, 2006), Chung and Pfost (1967) and Iglesias and Chirife model (1976). The Model type II showed equilibrium moisture content as function of surrounding relative humidity and temperature. The EMC models which related to the Model type II were modified Halsey (Rumelhart *et al.*, 1986), modified Oswin, modified Henderson (Soponronnarit, 1997) and modified GAB models (Myhara *et al.*, 1998). All EMC models are listed as Eqs. (1) to (10) in Table 1 and arbitrary constants of these EMC models (A, B and C) were evaluated by non-linear regression analysis. The coefficient of determination (R^2) is the primary criterion for selecting the best fitted equation model to evaluate an equilibrium moisture content of both NR producing STR 20 and skim block rubber products. In addition to R^2, the various statistical parameters such as: root mean square error (RMSE) and mean relative error (MRE) are used to determine the quality of the fit.

2.4 Modeling of sorption isotherm by Artificial Neural Networks (ANN)

Feed-Forward Back Propagation (FFBP) neural networks were utilized for training of experimental data set in some application works related to drying technology (Janjai *et al.*, 2009; Panchariya *et al.*, 2002; Hernández-Pérez *et al.*, 2004). A typical FFBP neural network consists of the following layers: input layer, (single or multi) hidden layer and output layer as illustrated in Figure 1. For studying by FFBP, back propagation (BP) learning algorithm is normally used. In this BP algorithm, the first output layer weights were updated. A desired value (target) exists for each neuron showing as the output layer. During training the FFBP, calculations were conducted from input of network toward output and then error values were propagated to previous layers. Two training algorithms including Bayesian Regulation (BR) back propagation and Levenberg-Marquardt (LM) algorithms were used for updating network weights.

In this work, the selected structure for applying artificial neural network, with its two inputs and single output, is

Table 1. Illustration of equilibrium moisture content models.

Model Type I		
Freundlich	$M_{eq}=A(RH)^{(1/B)}$	(1)
B.E.T.	$M_{eq}=RH/[(1-RH)(A+B(RH))]$	(2)
Oswin	$M_{eq}=A[RH/(1-RH)]^B$	(3)
Smith	$M_{eq}=(A+B)\ln(1-RH)$	(4)
Chung and Pfost	$M_{eq}=[A/\ln RH]+B$	(5)
Iglesias and Chirife	$M_{eq}=(A+B)(RH/(1-RH))$	(6)
Model Type II		
Modified Oswin	$M_{eq}=(A+BT)(RH/(1-RH))^C$	(7)
Modified Henderson	$M_{eq}=[-\ln(1-RH)/A(T+B)^{1/C}$	(8)
Modified Halsey	$M_{eq}=[-\ln(RH)/\exp(A-BT)]^C$	(9)
Modified GAB	$M_{eq}=[AB(C/T)(RH)]/(1-B(RH))[1-B(RH)+(C/T)B(RH)]$	(10)

where M_{eq} is the equilibrium moisture content, decimal (dry-basis), R the universal gas constant (8.314 J/mole K), RH the relative humidity (decimal), T the absolute temperature (K), A, B and C the constant values.

illustrated in Figure 1. The two neurons in the input layer are surrounding relative humidity and surrounding air temperature while one neuron of the output layer is an equilibrium moisture content value. The increasing method was used in order to properly select layers and neuron number for evaluation of various topologies. When the selected topology of neural network is trapped into the local minimum, a new neuron was added to the network. This method has more practical power to detect the optimum size of the neural network. Three threshold activation functions were used and mathematical definition of these transfer functions (purelin, logsig and tansig) which were utilized to reach the optimized status (Janjai *et al.*, 2009; Hernández-Pérez *et al.*, 2004) were expressed in Eqs. (11) to (13) as follows:

Purelin $$Y_j = X_j \qquad (11)$$

Logsig $$Y_j = \frac{1}{1+\exp(-X_j)} \qquad (12)$$

Tansig $$Y_j = \frac{2}{(1+\exp(-2X_j))-1} \qquad (13)$$

where X_j is the sum of weighed inputs for each neuron in the j^{th} layer and is computed by the following equation (14) as shown below:

$$X_j = \sum_{i=1}^{m} W_{ij} \times Y_i + b_j Y_j = \frac{2}{(1+\exp(-2X_j))-1} \qquad (14)$$

In order to determine the dynamic equilibrium moisture content behavior of both type natural rubber samples, the model had a four-layered network, which had a large number of simple processing elements called neurons (Figure 1). The actual values of the input variables were chosen randomly from a fixed set of data in each case. For this set of data, five levels of surrounding air temperature (40, 45, 50, 55 and 60°C); twenty levels of surrounding relative humidity ranging between 10 and 97% were selected for training network with suitable topology and training algorithm. The selection of the number of neurons for each hidden layer was optional. That is a larger number of neurons can interpret the more precisely work corresponding to complications arising to attain proper training. Thus, the number of neurons in hidden layers 1 and 2 of the ANN model are 6 and 2, respectively. Also the data obtained from experiment of 45 and 55°C were used for testing of trained network. The following criterion of mean square error (MSE) to minimize the training error was defined:

$$MSE = \frac{1}{MN} \sum_{p=1}^{M} \sum_{i=1}^{N} (S_{ip} - T_{ip})^2 \qquad (15)$$

where MSE is the mean squared error, S_{ip} is network output in i^{th} neuron and p^{th} pattern, T_{ip} is target output at the i^{th} neuron and the p^{th} pattern, N is number of output neurons and M is number of training patterns.

The suitability of equations and selected prediction method for EMC of natural rubbers were evaluated and compared using coefficient of determination (R^2), root mean square error (RMSE) and mean relative error (MRE), which indicate the fitting ability of a model to a data set for selecting the best equation to describe the experimental data. These three parameters can be defined as below:

$$R^2 = 1 - \frac{SSE}{SSY} \qquad (16)$$

where SEE and SSY values are calculated as the following equation (17) and (18), respectively

$$SSE = \sum_{i=1}^{n} (Y_{exp,i} - Y_{pre,i})^2 \qquad (17)$$

$$SSY = \sum_{i=1}^{n} (Y_{exp,i} - \overline{Y_{exp}})^2 \qquad (18)$$

and the RSME was defined as follows:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i-1}^{n} (Y_{exp,i} - Y_{pre,i})^2} \qquad (19)$$

Finally, the following equation for determination of MRE value was formulated as shown in Eq. (20)

$$MRE = \frac{1}{n} \sum_{i=1}^{m} \frac{|Y_{exp,i} - Y_{pre,i}|}{Y_{exp,i}} \qquad (20)$$

where $Y_{exp,i}$ is the measured in the experiment, $Y_{pre,i}$ is the calculated using the models, $\overline{Y}_{exp}$ is the mean of the measured data and n is the number of data points.

2.5 Thermodynamics properties of sorption

The isosteric heat of sorption means the required energy to remove water content from the mass unit of a solid matrix. Hence, it is an assessment of the binding energy between water molecules and the solid matter of a food product (Mulet *et al.*, 2002). The net isosteric sorption heat represents the difference between the isosteric heat and pure water vaporization energy. In this work, the differential enthalpy or isosteric heat of sorption and differential entropy were evaluated for both dried natural rubber samples. The isosteric heat of sorption was evaluated using Clausius-Clapeyron equations (Chen, 2006; Cortés and Chejne, 2010) correlating with the relative humidity and temperatures at fixed moisture content as defined as

$$\frac{\partial \ln(RH)}{\partial (T)} = \frac{\Delta H}{RT^2} \qquad (21)$$

where RH is the relative humidity (decimal), T is the temperature (K), H is the isosteric heat of sorption (J/mol), R the universal gas constant (8.314 J/mol K).

Integrating Eq. (21) and assuming that the isosteric heat of sorption difference (H) is temperature independent gives the following equation:

$$\ln(RH) = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + C \qquad (22)$$

where C is the arbitrary constant of the equation (22) which is the intercept value of graph plotting relationship between ln(RH) and $(\frac{1}{T})$.

Thus, the slope of graph plot between ln(RH) and $(\frac{1}{T})$ at constant moisture content implies the isosteric heat of sorption value. By the thermodynamics principle, the following equation showing the thermodynamic relationship

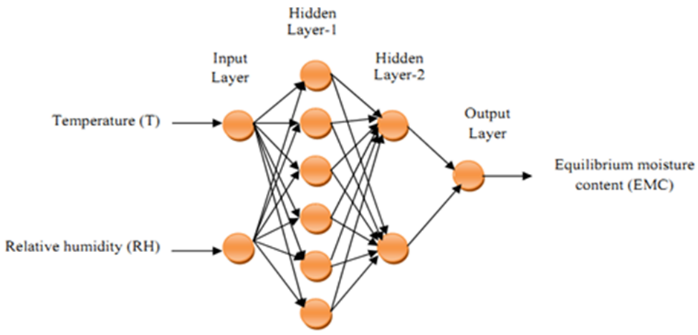
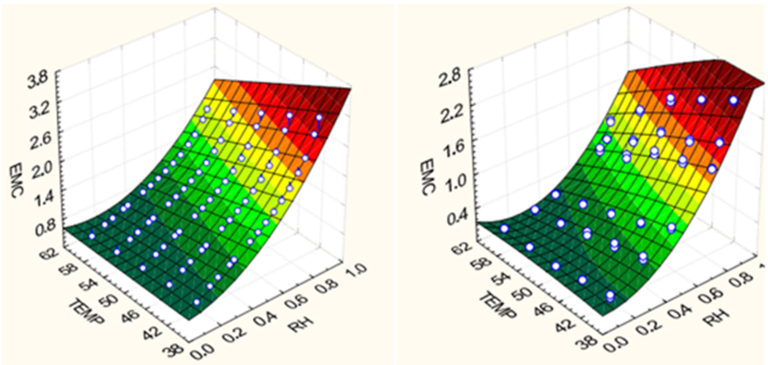
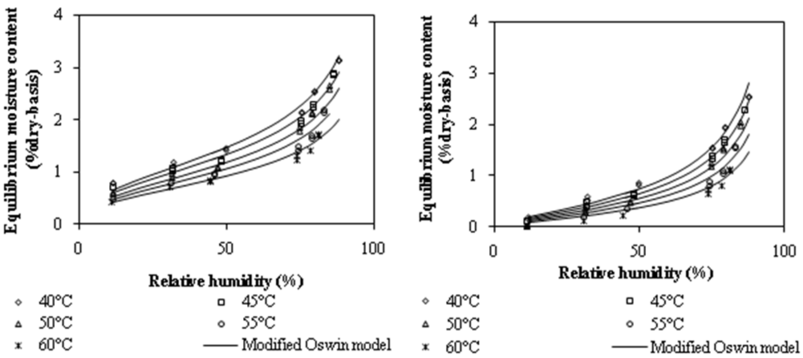


Figure 2. Structure of the articial neural network model of equilibrium moisture content of natural rubber.



(a) STR20 block rubber (b) Skim block rubber

Figure 3. Equilibrium moisture content chart at various surrounding temperature and relative humidity of (a) STR 20 block rubber and (b) Skim block rubber.



(a) STR20 block rubber (b) Skim block rubber

Figure 4. Effect of temperature on equilibrium moisture content of STR 20 block rubber (a) and skim block rubber (b) at temperature of 45-60°C and relative humidity of 10-97% using modified Oswin model and observed data.

between the Gibbs free energy (G) and enthalpy (or isosteric heat of sorption, H) and entropy (S) can be determined by following Eqs. (23) and (24).

$$\Delta G = -\Delta H - T\Delta S \tag{23}$$

where ΔG is the of Gibbs free energy difference (J/mol) and ΔS is the entropy difference (J /mol K).

For moisture sorption isotherm, the temperature in equilibrium state is constant so the change of Gibbs free energy (ΔG) can be written as below:

$$\Delta G = -RT\ln(RH) \tag{24}$$

Substituting ΔG from Eq.(23) into Eq.(24), the following equation is obtained:

$$\ln(RH) = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + \frac{\Delta S}{R} \tag{25}$$

Then plotting curve of ln(RH) value against to $(\frac{1}{T})$ yields a straight line graph with the y-intercept of ΔS/R and the ΔS value can be evaluated. In addition, the value of the slope of this linear relationship between ln (RH) versus ($\frac{1}{T}$) also gives the ΔH value.

3. Results and Discussion

3.1 Experiment moisture sorption isotherms

The EMC value of NR samples for producing STR 20 and skim block rubbers are shown in Figures 4(a) and 4(b), respectively. These EMC curves were done under the conditions of surrounding temperature of 40-60°C correlating to 10-97% of RH. The results showed that the EMC value increased with decreasing of temperature at constant RH. The EMC curves for both types of block rubber showed the same trend form of curving sigmoid forms and the EMC value was relatively dependent on temperature. These results correspond to the previous works (Tirawanichakul *et al.*, 2008; Tasara *et al.*, 2012; Khongchana *et al.*, 2007). Additionally, comparison of EMC value between STR 20 and skim block rubber indicated that the EMC value of NR producing STR 20 block rubber was higher than that of NR producing skim block rubber. This is because the NR producing STR 20 block rubber has higher density and heat capacity than NR producing skim block rubber (Tasara *et al.*, 2012). These EMC values for all NR producing block rubber will be used in evaluation of moisture ratios of empirical and semi-theoretical model simulation.

3.2 Curve fitting of sorption isotherm models by non-linear regression analysis

The ten sorption models which were used to investigate natural rubbers are given in Eqs. (1) to (10). The results of nonlinear regression analysis of fitting the EMC equations to experimental data of STR 20 and skim block rubbers are presented in Tables 2 and 3, which show all 7 empirical EMC models and their arbitrary constants of STR 20 and skim block rubber, respectively. Based on mathematical simulation using non-linear regression analysis based on the highest R^2, the lowest RMSE and MRE values, the simulated data of both NR producing STR 20 and skim block rubber samples fitting with the modified Oswin model yielded a relatively good correlation with the experimental data compared to the other 9 EMC simulation models. For STR 20 block rubber, the R^2, RMSE and MRE values in the modified Oswin model were 0.9815, 0.0010 and 0.0574, respectively, while R^2, RMSE and MRE values for the skim block rubber predicted by modified Oswin model were 0.9773, 0.0011 and 0.0913, respectively, and the relation between the predicted data using the ANN models and experimental data is illustrated on Figure 6(a) while the predicted data using the modified Oswin model and experimental data for skim block rubber is plotted in Figure 6(b). The results show that the predicted EMC data using the ANN model give more accurate prediction than that of the modified Oswin model.

3.3 Validation of proposed EMC model by Artificial Neural Networks (ANN)

The results of ANN model of EMC for both NR samples was developed by training with experimental sorption data with drying temperatures of 40, 50 and 60°C are illustrated in Table 4. The sorption isotherm data at 45 and 55°C were used for testing the model. Comparison between the predicted value and experimented data of EMC of NR at the drying temperatures of 45 and 55°C was evaluated and showed in Figure 4, which shows that the good relation between the predicted and observed EMC value for both NR samples. The MSE, R^2, RMSE and MRE value of the ANN model of STR 20 rubber are 0.00000027377, 0.9952, 0.000523 and 0.0029, respectively while MSE, R^2, RMSE and MRE

Table 2. Equilibrium moisture contents for STR20 block rubber under different models of determination.

Model	Arbitrary constants			R^2	RMSE	MRE
	A	B	C			
Model Type I						
Freundlich	0.0259	1.0470	-	0.7602	0.0036	0.2280
B.E.T.	-10.15	255.54	-	0.8281	0.0030	0.2087
Oswin	0.0117	0.4271	-	0.8555	0.0028	0.1680
Smith	0.0045	-0.0104	-	0.8491	0.0029	0.1708
Chung and Pfost	-0.0033	0.0057	-	0.8786	0.0026	0.1751
Iglesias and Chirife	0.0069	0.0034	-	0.8762	0.0026	0.1794
Model Type II						
Modified Oswin	0.1021	-0.0003	0.3941	0.9815	0.0010	0.0574
Modified Henderson	34.95	-294.44	1.6506	0.9508	0.0016	0.1080
Modified Halsey	-6.05	0.0403	0.5981	0.9576	0.0015	0.1025
Modified GAB	127.17	1.2745	0.0538	0.8191	0.0031	0.2074

Table 3. Equilibrium moisture contents for natural rubber producing skim block rubber under different models of determination.

Model	Arbitrary constants A	B	C	R^2	RMSE	MRE
Model Type I						
Freundlich	0.0283	0.3672	-	0.8238	0.0066	0.4068
B.E.T.	83.83	239.39	-	0.8850	0.0068	1.6551
Oswin	0.0117	0.4271	-	0.8555	0.0028	0.1680
Smith	0.0045	-0.0104	-	0.8491	0.0029	0.1708
Chung and Pfost	-0.0032	-0.00004	-	0.8829	0.0069	2.0220
Iglesias and Chirife	0.0069	0.0034	-	0.8762	0.0026	0.1794
Model Type II						
Modified Oswin	0.0621	-0.0002	0.6768	0.9773	0.0011	0.0913
Modified Henderson	1.4480	-282.09	0.8487	0.9689	0.0013	0.8689
Modified Halsey	-2.5283	0.0195	1.2763	0.9679	0.0013	0.7251
Modified GAB	8.9348	1.3566	0.4985	0.7574	0.0057	3.1660

Table 4. Training algorithm for different neurons and hidden layers for the network and their threshold functions.

Rubber sample	Training algorithm	Threshold function	No. of layers and neuron	MSE	R^2	RMSE	MRE
STR 20	BR	logsig-tansig-purelin	2-6-2-1	0.00000027	0.9952	0.00052	0.0029
Skim	BR	logsig-tansig-purelin	2-6-2-1	0.00000028	0.9949	0.00053	0.0032

Table 5. Training algorithm for different neurons and hidden layers for the network and method.

Rubber sample	Method	R^2	RMSE	MRE
STR 20	*Least square regression*	0.9815	0.00100	0.0574
	Artificial neural network	0.9952	0.00052	0.0029
Skim	*Least square regression*	0.9773	0.00110	0.0913
	Artificial neural network	0.9949	0.00053	0.0032

values for the skim block rubber employing this same model are 0.00000027690, 0.9949, 0.000526 and 0.0032, respectively.

Tables 4 and 5 illustrate the training algorithm for different neurons and hidden layers of ANN model for prediction the EMC values of STR20 and skim block rubber. Then all calculated values using the modified Oswin model and ANN model against with observed values model are plotted shown in Figure 5. The results showed that the indicators for goodness of fit of the proposed neural network model are better than the values obtained by the modified Oswin model of all NR producing STR20 and skim block rubber samples. This was correlated to the residuals values of the predicted EMC values and experimental values of sorption. The residual value plots are illustrated in Figure 7 for EMC of STR 20 (Figures 7(a) and (b)) and skim block rubber (Figure 7(c) and (d)), respectively.

3.4 Determination of isosteric heat of sorption

The isosteric heat of sorption values were evaluated from the equilibrium moisture content data at different temperature by using the Clausius-Clapeyron equation as formulated in Eq.(25). Figures 8 and 9 illustrate the plots of the simulated data provided by Clausius-Clapeyron equation for STR 20 and skim block rubbers at selected moisture contents, respectively.

The slopes of the plots between ln(RH) versus $(\frac{1}{T})$ gave the isosteric heat of sorption. The slopes were calculated by linear regression analysis. The natural rubber (NR) heat of sorption for different moisture content levels of STR 20 and skim block rubbers is presented in Figure 10 and Figure 11, respectively.

All NR heat of sorption was found to be decreased

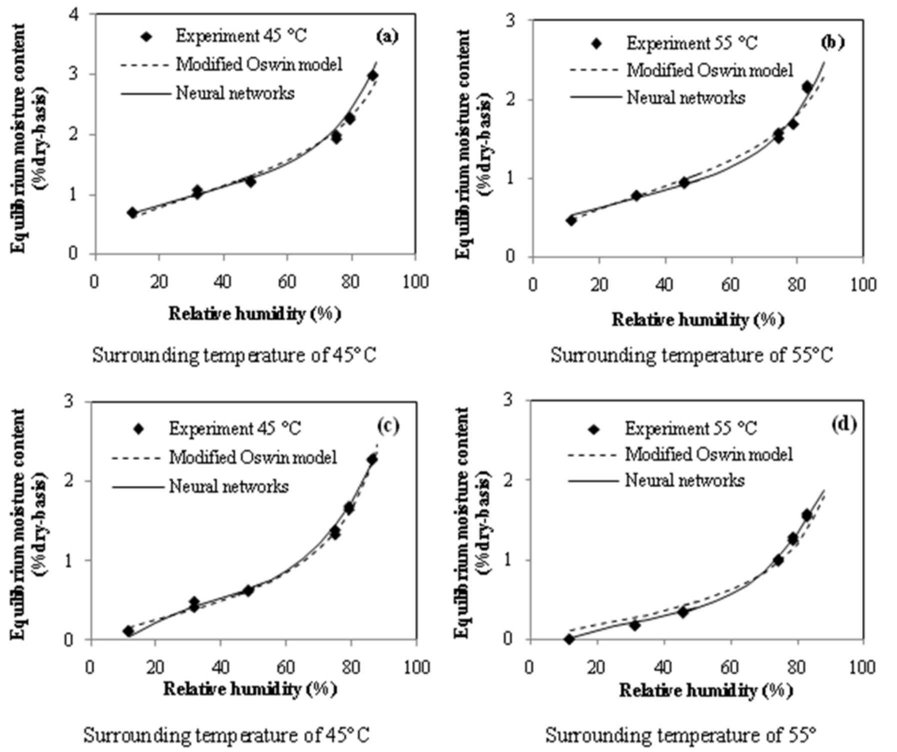


Figure 5. Predicted values of equilibrium moisture content using modified Oswin model and artificial neural networks versus experimental values for testing data set: (a), (b) for STR 20 block rubber, (c) and (d) for skim block rubber.

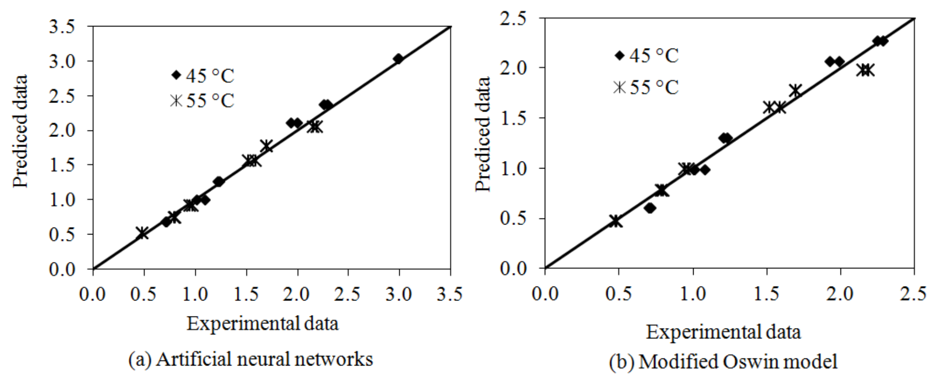


Figure 6. Predicted values of equilibrium moisture content of skim block rubber using artificial neural networks (a), modified Oswin model (b) versus experimental values for testing data set (45 and 55°C).

with increasing EMC at low moisture content. It is observed that for the temperature ranging from 40 to 60°C and moisture content ranging from 0.8% to 3.8%.dry-basis and 0.1% to 5.0% dry-basis for STR 20 block rubber, the net isosteric heat of sorption ranged from 250 to 50 J/mol (Figure 10). For skim block rubber at temperature of 40-60°C and moisture content ranging from 0.8% to 3.8%.dry-basis, the net isosteric heat of sorption ranged from 170 to 20 J/mol (Figure 11). These results indicated that at low moisture contents, the heat of sorption is higher than at high moisture contents. This trend is identical to those reported in studies on agricultural and food products as well as medical and aromatic plants (Kiranoudis *et al.*, 1993: Bahloul *et al.*, 2008: Lahsasni *et al.*, 2004: Phomkong *et al.*, 2006). The experimental results of NR heat of sorption were found to be fitted a power model. The following equation was developed for NR as below:

$$Q_{est,\, STR\, 20} = 129.14M^{-0.999} \qquad (26)\; R^2 = 0.9999$$

$$Q_{est,\, Skim} = 86.977M^{-1.002} \qquad (27)\; R^2 = 0.9999$$

The NR entropy of sorption for STR 20 and skim block rubbers which is illustrated in Figures 10 and 11 on the right

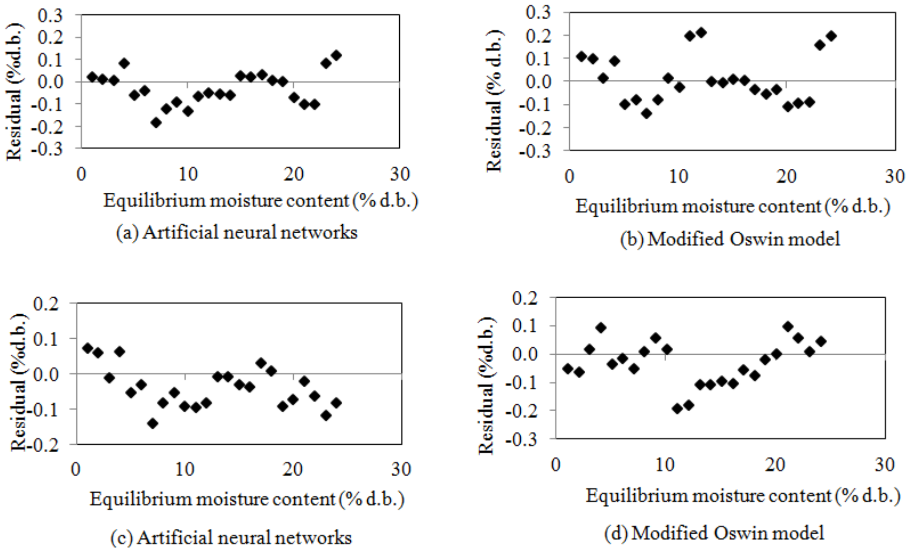


Figure 7. Residual plots for equilibrium moisture content using artificial neural networks and modified Oswin model: (a), (b) for STR 20 block rubber, (c) and (d) for skim block rubber.

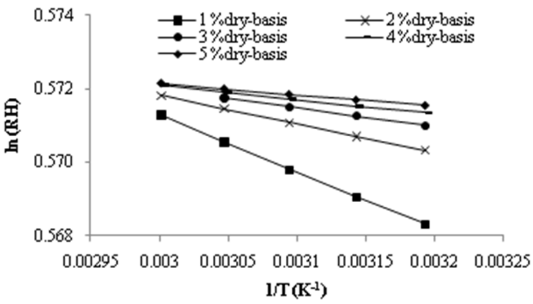


Figure 8. The Clausius-Clapeyron plot for STR 20 block rubber at selected moisture contents.

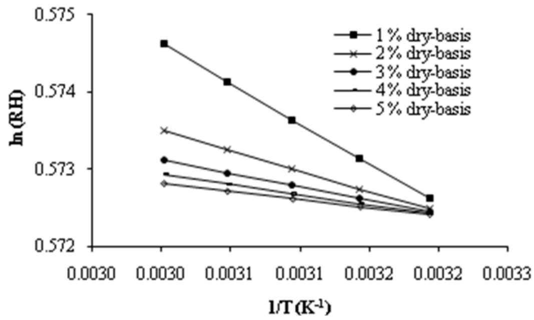


Figure 9. The Clausius-Clapeyron plot for skim block rubber at selected moisture contents.

hand vertical axis, respectively, is presented in dot line curve. By curve fitting with non-linear regression analysis, the results showed that the entropy value of NR producing both block rubbers is a function of moisture content and the following model is fitted to data as shown in Eqs. (28) and (29) for STR and skim block rubber, respectively.

$$\Delta S_{STR\,20} = \frac{4.344\,M^{0.564}}{-0.155+0.539M} \qquad (28)\ R^2 = 0.9989$$

$$\Delta S_{Skim} = \frac{4.489\,M^{1.165}}{-0.037+1.173M} \qquad (29)\ R^2 = 0.9981$$

The fitted curve for prediction of NR entropy has a good relation to the experimental data. These results showed that the NR entropy decreases with increase in moisture content. Similar trends were reported on the entropy of some agricultural products such as potato (Chen, 2002), tea (Arslan *et al.*, 2006) and olive (Bahloul *et al.*, 2008). Heat and entropy of sorption equations are necessary for calculation of relative humidity of sample during drying process and storage of NR samples.

4. Conclusion

Simulation modeling of water sorption isotherms carried out by the traditional non-linear regression equations and artificial neural network approach showed that the artificial neural network without any chemical compositional results and physical results has the supremacy in prediction of equilibrium moisture content of all NR types. All simulated EMC results using ANN model had a relatively high accuracy compared to those results simulated by the traditional EMC models. Moreover, the net isosteric heat of sorption of NR producing STR20 and skim block rubber calculated using the Clausius–Clapeyron equation showed a power law relation with moisture content. Entropy of both NR block rubber samples developed in this study was also described by a polynomial model. The net isosteric heat equation is suggested for use in the computation of heat of sorption for NR while both the isosteric heat and entropy equations are essential to compute the humidity during simulation of stored dried NR producing STR20 and skim block rubber.

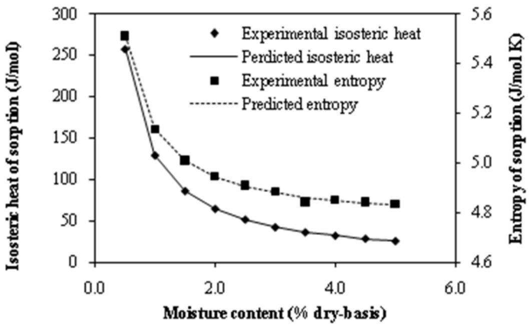


Figure 10. Experimental values and predict of isosteric heat and entropy of sorption at different equilibrium moisture contents of STR 20 block rubber.

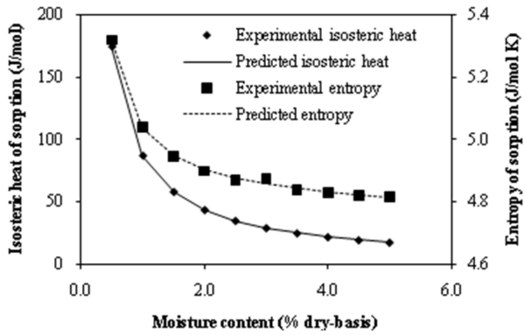


Figure 11. Experimental values and predicts of isosteric heat and entropy of sorption at different equilibrium moisture contents of skim block rubber.

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