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Estimation of Average Comonomer Content of Ethylene/1-Olefin Copolymers Using Crystallization Analysis Fractionation (Crystaf) and Artificial Neural Network (ANN)

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Summary: An artificial neural network (ANN) with a 4-3-3-1 architecture was developed to estimate average comonomer content of ethylene/1-olefin copolymers from crystallization analysis fractionation (Crystaf) results. The ANN was trained with a back propagation algorithm. It was found that average comonomer contents predicted from ANN agree well with experimental results for both training and testing data sets. The developed ANN was also used to systematically investigate the effects of chain microstructures and Crystaf operating conditions on Crystaf calibration curves.

Keywords: artificial neural network (ANN); crystallization analysis fractionation (Crystaf); modeling; polyethylene

Introduction

Crystallization analysis fractionation (Crystaf) is a characterization technique that fractionates polymer chains according to their chain crystallizabilities in a dilute solution, providing information on the weight fraction of polymer chains crystallized at each temperature (*i.e.*, Crystaf profiles).[1–4] For ethylene/1-olefin copolymers, comonomer content is the key structural parameter that affects chain crystallizabilities. Therefore, chemical composition distribution (CCD) and average comonomer content of ethylene/1-olefin copolymers can be estimated from Crystaf profiles using Crystaf calibration curves (*i.e.*, a relationship between average comonomer content and peak crystallization temperature).

Crystaf calibration curves can be constructed experimentally by performing the Crystaf analysis of a series of narrow-CCD copolymer samples with known average comonomer contents covering a broad range of crystallization temperatures.[1,5–10] This approach is quite tedious and has a limited usage as Crystaf calibration curves depend on operating conditions and polymer chain microstructures. Recently, a new approach for constructing Crystaf calibration curves using a kinetics Crystaf model was proposed.[11–13] Although this computational approach can fasten the process of constructing a custom-made Crystaf calibration curve, the implementation of this phenomenological model is still rather complicated and several model parameters have to be estimated appropriately.

Artificial neural network (ANN) is a ''black-box'' modeling technique designed to mimic the way biological nervous systems process information.[14] It is capable of solving highly non-linear, complex problems without prior knowledge on detailed mathematical model of the system by capturing relationships between input and output variables from a given patterns. Recently, ANN has been widely used to predict polymer properties and interpreting

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polymer characterization results, especially when the phenomenological models are extremely complex, if at all possible, to develop.[15–18] By using ANN, average comonomer content can be estimated from Crystaf results without the need of Crystaf calibration curves. Moreover, ANN can potentially be used to simulate Crystaf calibration curve for converting a Crystaf profile to CCD as well.

In this work, ANN was developed to estimate average comonomer content when polymer chain microstructures (*i.e.*, number average molecular weight and comonomer type), cooling rate during Crystaf analysis, and peak crystallization temperature are known. The ANN was trained and tested using a collective set of experimental data reported in the literature. The ANN was also used to systematically investigate the effects of molecular weight, comonomer type, and cooling rate on Crystaf calibration curves.

Artificial Neural Network

Artificial neural network (ANN) is a branch of artificial intelligence (AI) that mimic the way biological nervous systems (*e.g.*, brain) process information. It is composed of a large number of highly interconnected processing elements (*i.e.*, neurons) working in union to solve specific problem.[14] ANN can learn from examples (*i.e.*, an archive of data sets) and will develop an internal model representing the real process model while learning.

A four layer, feed forward ANN with a 4-3-3-1 architecture (*i.e.*, four input neurons, two hidden layers each with three neurons, and one output neuron) was used in this study (see Figure 1). Four input neurons are for number average molecular weight (M_N), a number of carbons in comonomer, cooling rate during Crystaf analysis, and peak crystallization temperature measured from Crystaf. The result from the output neuron is estimated average comonomer content.

In this investigation, experimental Crystaf results reported in the literature during the year 1994–2008 were used as an archive of data sets for training and testing ANN. 13 randomly selected data sets from this database were used for the testing and the other 97 data sets were used for the training. Table 1 and 2 summarize the information of training and testing data sets.

To minimize the effect of differences in parameter magnitude, the reduced variables were used for training and testing ANN. All variables were reduced to the dimensionless variables within a range between -1 and 1 using the following relationship:

$$X_{reduced} = \frac{2(X - X_{\min})}{(X_{\max} - X_{\min})} - 1 \qquad (1)$$

where $X_{reduced}$ is a reduced variable, X is an original variable, X_{min} is the minimum value of variable X, and X_{max} is the maximum value of variable X.

Except neurons in the first layer, each neuron in the network receives inputs from

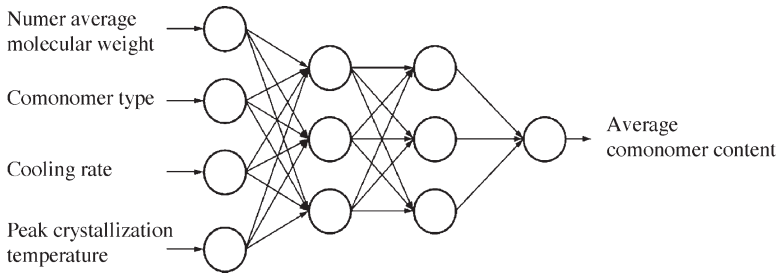

Figure 1.
ANN with a 4-3-3-1 architecture used in this study.

Table 1.
Training data set.

Comonomer type	Cooling rate (°C/min)	Comonomer content (mol %)	Number average molecular weight	Crystallization temperature (°C)	Reference
1-butene, 1-octene	0.2	0.3–8.9	8,190–54,300	32–83	da Silva Filho et al.[7]
1-propene, 1-hexene, 1-octene, 1-dodecene	0.1	0.73–462	34,300–45,300	49–83	Anantawaraskul et al.[19]
1-decene, 1-tetradecene, 1-octadecene	0.1	0.5–6	31,000–77,000	57–85	Graef et al.[20]
1-octene	0.2	3.8–5.6	40,700–84,000	46–61	Soares et al.[5]
1-pentene	0.1	0–6.9	142,600–630,300	80–88	Luruli et al.[21]
1-hexene	0.0033–0.5	0.68–3.14	34,300–37,200	53–81	Anantawaraskul et al.[22]
1-hexene	0.1	0–4.2	34200–38700	52–86	Sarzotti et al.[9]
1-octene	0.2	0.8–4.7	15600–62100	40–80	Monrabal et al.[1]

all neurons in the previous layer. The combination of weighted inputs (x) can be calculated as follows:

$$x = \sum_{i=1}^{n} w_i x_i \tag{2}$$

where w_i and x_i are the weight and the input from the ith neuron in the previous layer to the neuron of interests. n is the number of neurons in the previous layer. Prior to the training, all weights in the network were assigned a random value between -1 and 1. During the training, these weights are adjusted to minimize the difference between the experimental outputs from the archival data and ANN predicted outputs of the training data sets.

The combination of weighted inputs is used as single input variable into a neuron. A tan-sigmoid transfer function given in Equation (3) is used as an activation function to compute the output from a neuron for neurons in the input and hidden layers.

$$\sigma(x) = \frac{2}{1 + \exp(-x)} - 1 \tag{3}$$

An output is sent as an input to the other neurons in the successive layer. The information in ANN is processed in the forward direction from the input layer to the hidden layers and finally to the output layer through all the neurons. The linear transfer function ($\sigma(x) = x$) is used for a neuron in the output layer. The output from this neuron is an estimated average comonomer content.

The back propagation technique with Levenberg-Marquardt method was used to train ANN. The objective of training is to

Table 2.
Testing data set.

Comonomer type	Cooling rate (°C/min)	Comonomer content (mol %)	Number average molecular weight	Crystallization temperature (°C)	Reference
1-octene	0.2	2.9	32,400	62	da Silva Filho et al.[7]
1-propene	0.1	2.67	40,900	64.5	Anantawaraskul et al.[19]
1-hexene	0.1	2.31	34,900	67.3	Anantawaraskul et al.[19]
1-dodecene	0.1	0.97	36,000	77.9	Anantawaraskul et al.[19]
1-decene	0.1	1.79	31,000	78.8	Graef et al.[20]
1-tetradecene	0.1	2.83	54,000	73.2	Graef et al.[20]
1-octadecene	0.1	1.77	87,000	78.9	Graef et al.[20]
1-octene	0.2	4.16	22,000	61	Soares et al.[5]
1-pentene	0.1	3.7	5,000	82.7	Luruli et al.[21]
1-hexene	0.1	0.68	37,165	79.1	Anantawaraskul et al.[22]
1-hexene	0.1	1.51	36,291	71.8	Anantawaraskul et al.[22]
1-hexene	0.1	0.6752	37,165	80.4	Sarzotti et al.[9]
1-octene	0.2	2.66	38,500	61.8	Monrabal et al.[1]

minimize an error function (E) by finding the optimal weights within the network. The error function used in this study is the mean square difference between experimental and ANN predicted outputs of the training data sets. This error was used to adjust the network weights to be used for the next training epoch. The mean square difference between the experimental and ANN predicted outputs of both training and testing data sets at each training epoch was monitored. The training is stopped and network weights are considered optimum when this parameter reaches minimum, indicating that further training (and adjusting the network weights) will overtrain the network.

Simulated Crystaf Calibration Curve

To simulate Crystaf calibration curves with the trained ANN, the following procedure was used. First, consider a series of model copolymers having various peak crystallization temperatures (40-80°C), all with the same M_N and comonomer type. Second, estimate average comonomer content of these model samples at specified cooling rate using the trained ANN. Finally, obtain the Crystaf calibration curve by linear regression analysis of the relationship between estimated average comonomer content and peak crystallization temperature. The effects of molecular weight, comonomer type, and cooling rate on Crystaf calibration curves were systematically examined by varying each parameter while other parameters were kept constant.

Results and Discussion

To validate the trained ANN model, the relationships between average comonomer content obtained from ANN and those obtained from experiments for both training and testing data sets were plotted in Figure 2. Note that testing data sets had not been used in the training so the ability of ANN to predict simply comes from learning through the training data sets. The fact that scattering of data is close to the diagonal line for both training and testing data sets simply indicates good estimations of average comonomer contents from ANN (*i.e.*, ANN predicted results are close to the experimental data).

Figure 3 compares ANN predicted calibration curve for ethylene/1-octene copolymers having M_N of 35,000 with previously reported Crystaf calibration curves for ethylene/1-olefin copolymers at a cooling rate of 0.2 °C/min. The Crystaf calibration curve simulated from ANN

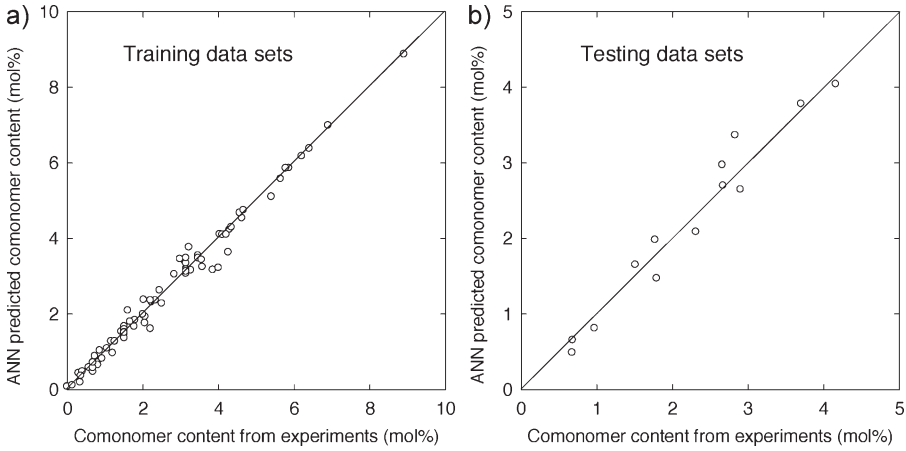

Figure 2.
Comparison between average comonomer contents predicted from ANN and those obtained from experiments. (a) Training data sets and (b) Testing data sets.

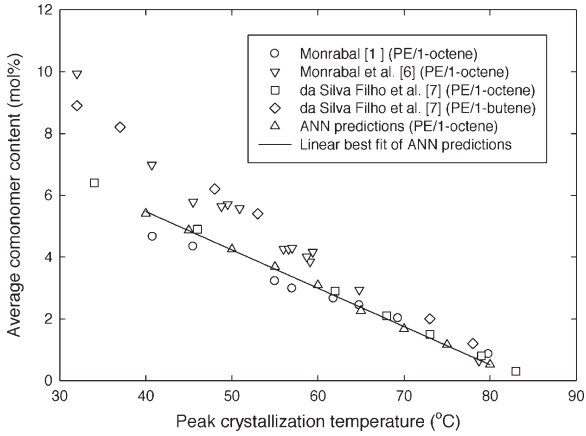

Figure 3.
Comparison between ANN predicted calibration curve for ethylene/1-octene copolymers with $M_N = 35{,}000$ and several experimental calibration curves at a cooling rate of 0.2 °C/min.

agrees reasonably well with the previously reported calibration curves, considering the observed experimental scatter in the data.

Figure 4 shows the effect of molecular weight on simulated Crystaf calibration curves for ethylene/1-octene copolymers at a cooling rate of 0.2 °C/min. As the molecular weight decreases, the calibration curve is shifted slightly to the lower crystallization temperature. This behavior is consistent with previous experimental observations that as the molecular weight decreases, the Crystaf profiles are shifted to lower crystallization temperatures and become broader.[23,24]

Figure 5 shows the simulated Crystaf calibration curves for ethylene/1-olefin copolymers with several comonomer types. The number average molecular weight of all samples was kept constant at 35,000 and the cooling rate for all cases was fixed at 0.2 °C/min. Effect of comonomer type on simulated Crystaf calibration curves is almost unnoticeable. This is because most of the data available is from ethylene/1-octene copolymers with only a few data

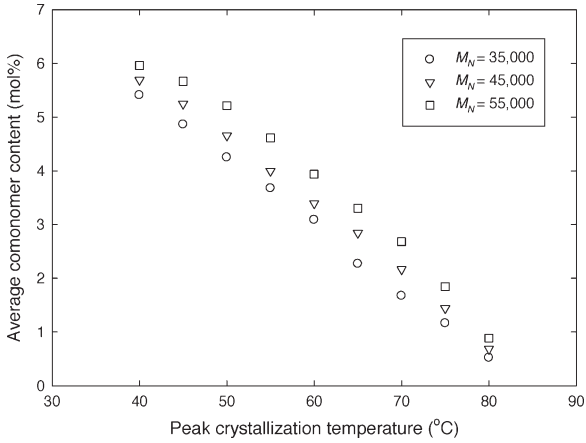

Figure 4.
Effect of molecular weight on Crystaf calibration curves for ethylene/1-octene copolymers simulated at a cooling rate of 0.2 °C/min.

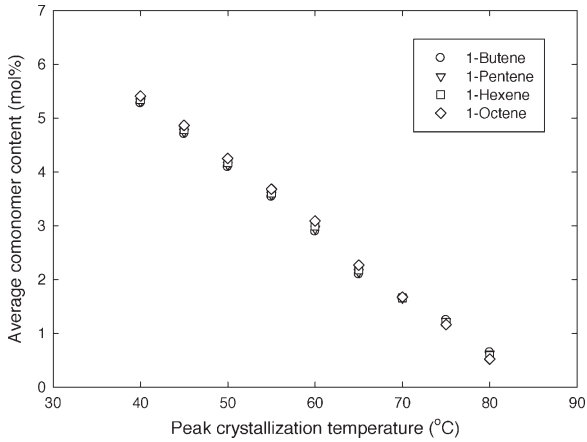

Figure 5.
Effect of comonomer type on Crystaf calibration curves for ethylene/1-olefin copolymers with $M_N = 35{,}000$ simulated at a cooling rate of 0.2 °C/min.

from other comonomer types. Therefore, ANN might not be able to adequately capture the relationship between comonomer type and average comonomer content from the existing database. However, additional training data sets of ethylene/1-olefin copolymers for various comonomer types could improve ANN predictability on the effect of comonomer type.

Figure 6 shows the effect of the cooling rate on Crystaf calibration curves for ethylene/1-octene copolymers with $M_N = 35{,}000$. The results indicate that the cooling rate significantly affects the calibration curves. The calibration curves shift to lower temperatures as the cooling rate increases. This overall trend agrees well with previous experimental observations that the Crystaf profiles are shifted to lower crystallization temperatures and become broader as the cooling rate increases, even when the effect of temperature lag is excluded.[22] The results shown in Figure 6 represent the simulated experimental Crystaf results, which include the effect of temperature lag, however.

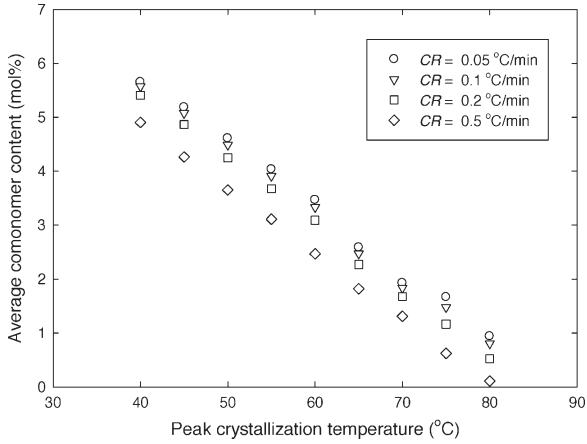

Figure 6.
Effect of the cooling rate on Crystaf calibration curves for ethylene/1-octene copolymers with $M_N = 35{,}000$.

Conclusion

An ANN with a 4-3-3-1 architecture was successfully applied to estimate average comonomer content of ethylene/1-olefin copolymers when number average molecular weight, comonomer type, cooling rate during Crystaf analysis, and peak crystallization temperature obtained from Crystaf are known. It was found that average comonomer contents predicted from ANN are in a good agreement with those obtained from experiments for both training and testing data sets. The ANN was also used to simulate a Crystaf calibration curve and the result was satisfactory when compared with previously reported experimental results. Therefore, the ANN can be a useful tool in interpreting Crystaf results, especially when a sufficient amount of experimental data is available.

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