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Modeling the molecular weight and number average molecular masses during the photo-thermal oxidation of polypropylene using neural networks

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Abstract

This work investigates the potential of artificial neural network (ANN) model to predict the molecular weight (M_W) and number average molecular masses (Mn) during the photo-thermal oxidation of polypropylene (PP). A set of 116 data points were used to test the neural network, 80%, 10%, and 10% of the database were used, or the training, the validation, and the test of the model. The optimal topology of ANN model obtained with the architecture of (3 inputs, 23 hidden and 2 output neurons). Statistical analyses of neural network model show good agreement with experimental data (a coefficient of correlation equal to 0.9864 and 0.9688, and a root mean square error equal to 11.1250 kg/mol and 3.5284 kg/mol for the predicted molecular weight and number average molecular masses respectively), considering, a three layer feed-forward backpropagation neural network with BFGS quasi-Newton (trainbfg) training algorithm, a hyperbolic tangent sigmoid and logarithmic sigmoid transfer function at the hidden and the output layer respectively. The comparison between the experimental and calculated results show that the ANN model is able of predicted the molecular weight and number average molecular masses during the photo-thermal oxidation of polypropylene.

Keywords: *molecular weight, number average molecular masses, photo-thermal oxidation, polypropylene, neural networks.*

1.Introduction

Plastics are categorized into four main groups: thermoplastics, elastomers, thermosets, and polymer compounds. This classification depends on molecular structure and physical properties of polymer materials [1]. Most of the polymers used are thermoplastic materials consisting of linear chains which may have longer or shorter branches [2]. Among the product thermoplastics, polypropylene (PP) has been one of the most popular candidates as a matrix material due to its versatility to accept numerous types of fillers and reinforcements [3]. PP based materials are widespread in the automotive industry and food packaging due to their low cost, chemical resistance, good mechanical properties or even recyclability [4]. The main drawback of polypropylene is its degradation under the combined effects of oxygen with temperature (thermal oxidation) or UV-light (photo oxidation). Indeed, most of the alteration of both mechanical and aspect properties (loss of gloss, whitening, chalking…) has been ascribed to the occurrence of macromolecular chain scissions and the subsequent formation of a lattice of micro-cracks [5-7]. The influence of temperature, usually described with an Arrhenius rule, was widely studied in the case of thermochimical oxidation, but rarely in the case of photo-thermochimical oxidation [8, 9]. The effects of the UV light intensity on the photo-degradation were investigated for various types of polymers including coatings, polycarbonates, poly (vinyl chloride) and also polyolefins [10]. The term oxidation degradation of macromolecules denotes all processes which lead to a lower of polypropylene properties. It may eventually imply physical processes, such as polymer crystallization, or denaturation of protein structures. Chemical processes related to degradation may lead to a reduction of average molar mass due to macromolecular chain bond split or to a raise of molar mass due to crosslinking rendering the polymer insoluble [11].

The very particular field of the photo-thermal oxidation of PP does not escape the attempts of modeling and the industrial demand is strong for an approach that would allow, After short analysis periods, or even very short, to predict the long-term behavior of PP materials under conditions of actual use. Many researchers have adopted artificial intelligence approaches to predict material behaviors, characteristics and attributes under changing circumstances (e.g. aging over time, heat treatment due to temperature changes, etc) [12], these approaches, such as Artificial Neural Networks (ANN), indeed, the networks of formal or ANN always arouse a keen interest in most areas of engineering. They find their applications, not only in static modeling but also in dynamic modeling of evolutionary processes over time: form recognition, non-destructive testing, textual information filtering, bioengineering, formulation of new materials, industrial process modeling, and control of the environment…etc. ANN which can be viewed as a universal approximation tool with an inherent ability to extract from experimental data the highly non linear and complex relationships between the variables of the problem handled [13]. The ANN approach was newly introduced into the field of wear of polymers and it was shown that ANN is a helpful mathematical tool in the structure-property analysis of polymers based on a limited number of measurement results [14-17]. To the best of our knowledge, no studies have been reported in the literature that has used ANN for modeling the process of photo-thermal oxidation of polypropylene. In this work, we developed a neural networks NN model, in order to predict the molecular weight and number average molecular masses during the photo-thermal oxidation of PP.

2. Materials and Methods

The methodology of modeling the molecular weight and the number average molecular masses during the photo-thermal oxidation of PP is based on four essential steps as depicted in Figure 1.

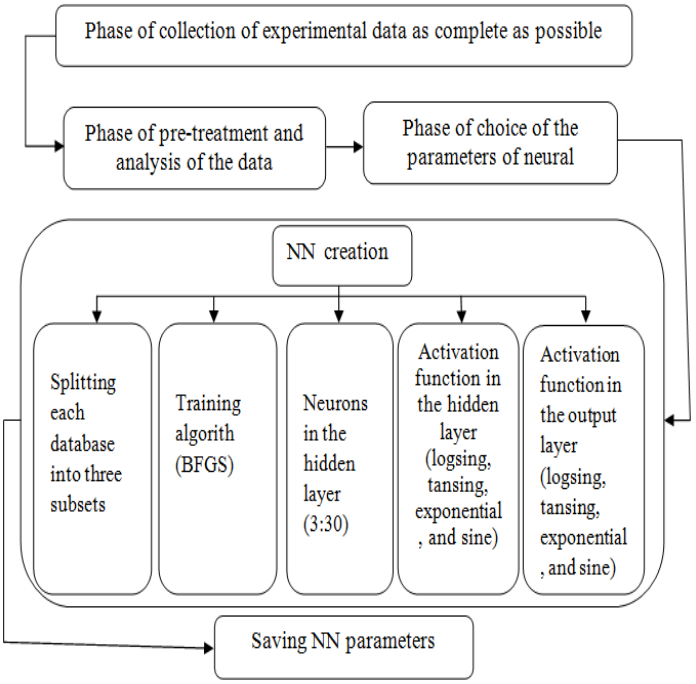


Figure 1: Procedure for photo-thermal oxidation of polypropylene neural network modeling.

2.1. Data collection and analysis

Data for this study were collected using data available in the literature [4, 10]. In order to model molecular weight (M_W) and number average molecular masses (Mn) by one ANN model, three variables have been selected as inputs: time (h), irradiance (W/m^2), and temperature (°C). The choice of the input and output variables was based on the effect of aging conditions (irradiance and temperature), on the molecular weight and number average molecular masses of the PP films as a function of oxidation time. The polypropylene properties are shown in Table 1.

***Table 1**: Properties of polypropylene used in this work.

Molecular weight (kg/mol)	250
Number average molecular masses (kg/mol)	67
Thickens film (µm)	80-135

The values of the standard deviations (STD), mean (Mean), minimum (Min), and maximum (Max) of the used database are shown in Table 2.

Table 2: Parameters statistics of inputs and outputs.

Variable category	Parameters	Symbol	Unit	STD	Mean	Min	Max
Inputs	Time	t	h	26.3481	30.0085	1	102.8040
	Irradiance	I	W/m^2	86.0061	118.8621	38	265
	Temperature	T	°C	12.0061	64.1121	45	80
Outputs	Number average molecular masses	M_W	kg/mol	67.8679	93.1194	15.4401	259.8
	Molecular weight	Mn	kg/mol	14.2288	25.1256	6.6265	67.1721

2.2. ANN Development Procedure

Artificial Neural Networks (ANNs) are information-processing systems that have certain performance characteristics in common with biological neural networks [18]. The proposed ANN model is based on experimental results [17]. The great advantages of these models is their ability to learn (store experimental knowledge), generalize (make the knowledge available) or extract automatically rules from complex data [19]. One of the most popular neural network paradigms applied to the modeling of a wide range of nonlinear systems, especially chemical and biological engineering processes, is the feed-forward back propagation neural network (FFNN) [20], which has been used throughout this paper with forecasting horizon and supervised learning. The fundamental unit or building block of the ANN is called an artificial neuron [21], these neurons are arranged in layers and are interconnected by weights and biases between the layers. The input layer receives inputs (x_i) from the real world and each succeeding layer receives weighted outputs ($w_{ji}\ x_i$) from the preceding layer as its input resulting therefore a feed-forward ANN, in which each input is fed forward to its succeeding layer where it is treated. The outputs of the last layer constitute the outputs (y_j) to the real world. A schematic representation of a feed-forward neural network is shown in Figure 2.

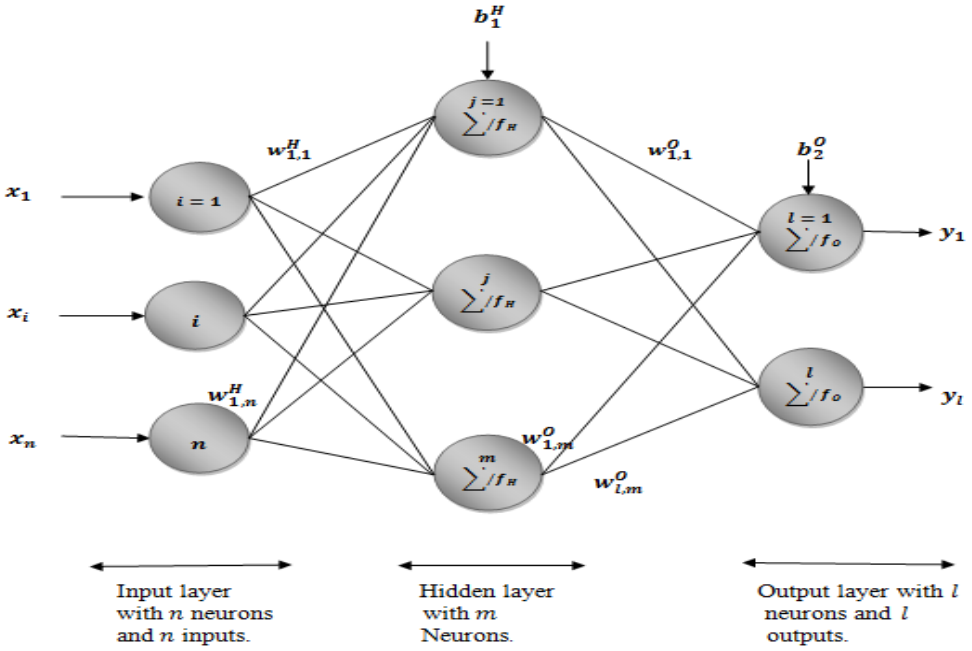


Figure 2: Three-layer feed-forward neural network.

The experimental data points were randomly divided into three subsets: (94 data points) 80% for the training, (11 data points) 10 % for the validation and (11 data points) 10 % for the test set; the validation is used in parallel with the training set. Figure 3 shows the molecular weight and number average molecular masses data as a function of time.

The BFGS quasi-Newton (trainbfg) training algorithm was applied in this work. The adopt NN model contains three layers of neurons: one input layer with three neurons, one hidden layer with a number of neurons optimized during training, and one output layer with tow unit that generated the estimated value of molecular weight (M_W) and number average molecular masses (Mn). The number of neurons in the hidden layer was changed from 3-35; in the hidden layer, the selection of neurons must generally be performed by trial and error. The tangent sigmoid (tansig): $f(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$, the log sigmoid (logsig): $f(x) = \frac{1}{1+e^{-x}}$, the exponential: $f(x) = e^{-x}$, the pure linear (purelin): $f(x) = x$, and sin (sine): $f(x) = \sin(x)$ transfer functions were used at the hidden layer and output layer. The ANN modeling of the molecular weight and number average molecular masses during the photo-thermal oxidation of

polypropylene was performed using STATISTICA software. The architecture of the neural network used in this work is shown in Figure 4.

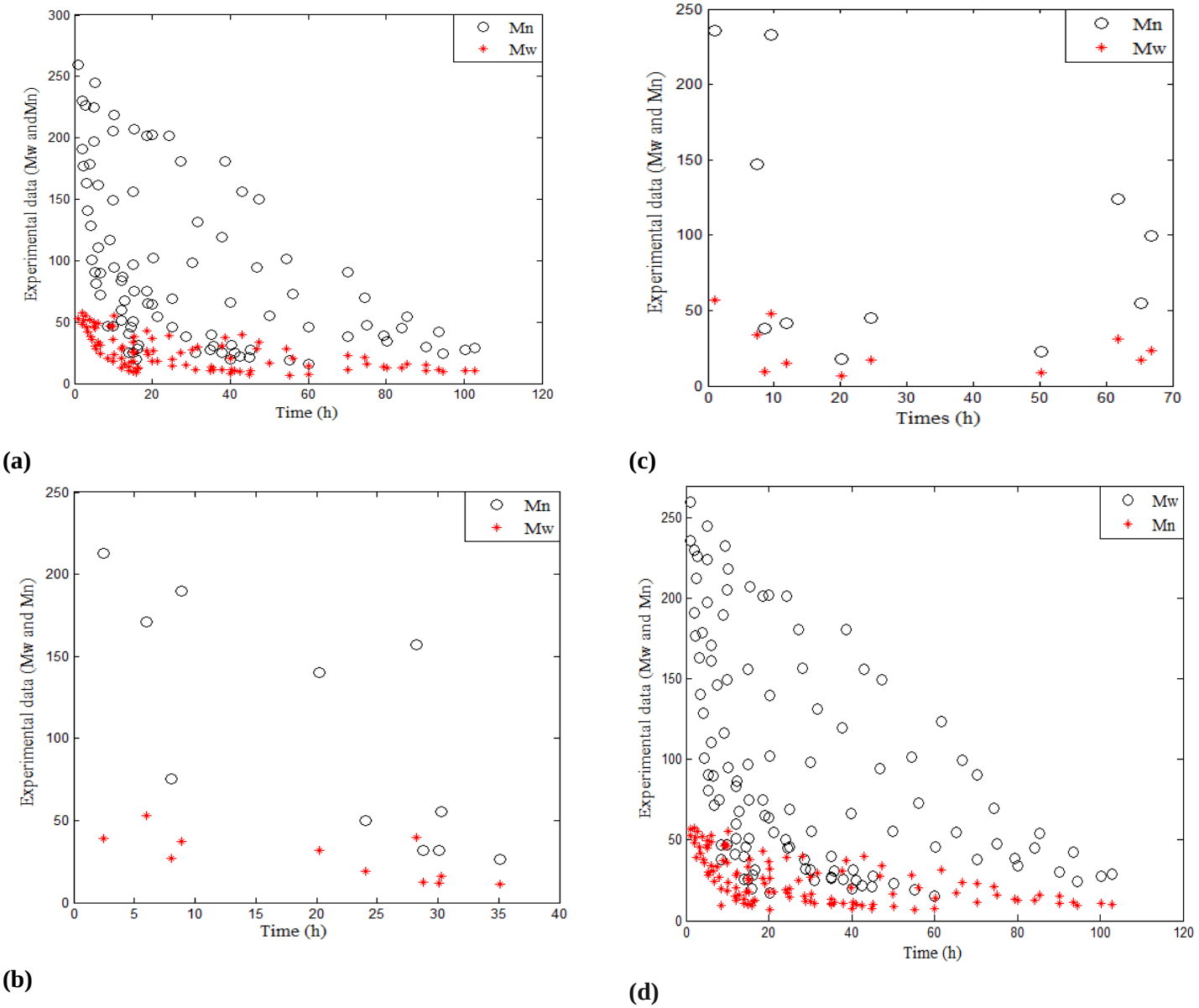


Figure: 3 molecular weight and number average molecular masses data as a function of time: (a) training, (b) validation, (c) test, and (d) total dataset.

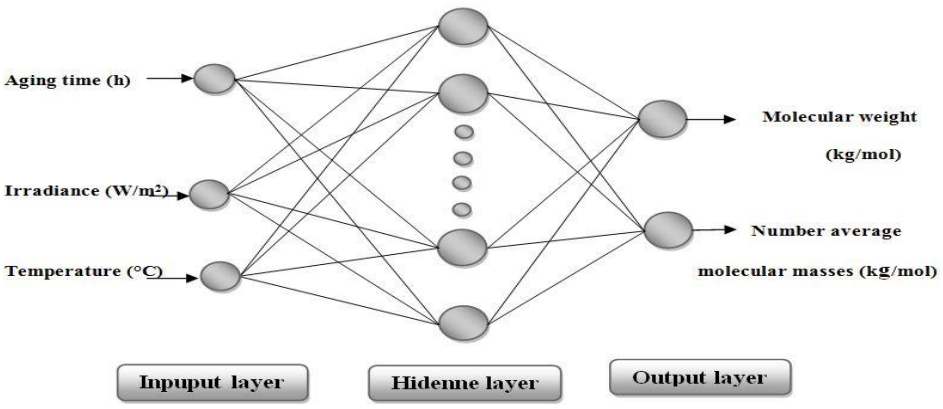


Figure 4: ANN architecture used for estimation in this work.

3. Results and discussions

3.1. Model Performance

The artificial neural network (ANN) model was developed with the aim of predicting molecular weight and number average molecular masses. The best ANN algorithm obtained in this study was a multilayer feed-forward back propagation network that consisted of a 3-23-2 topology. The parameters and results of the optimized NN models are depicted in Table 3.

Table 3: Architecture of the optimized NN model.

Type of network	Training algorithm	Input layer	Hidden layer		Output layer	
		Neurons number	Neurons number	Activation function	Neurons number	Activation function
FFNN	BFGS quasi-Newton	3	23	Tangent Sigmoid (Tansig)	2	Logarithmic sigmoid (Logsig)

Table 4: Weights and bias of the optimized NN model.

Input and hidden layer connections				Hidden layer and output connections		
W^I				W^H		
Time	Temperature	Irradiance	b_1^H	M_W	Mn	b_2^O
-5.5112	0.6179	-0.4026	1.0269	2.0759	1.4945	
-1.0504	3.0068	0.2039	1.3613	0.7969	0.0267	
-0.7416	-0.3928	0.8104	-0.1371	-0.4782	5.4625	
2.6046	0.3201	2.3095	2.2433	1.6319	1.0158	
0.7756	-1.8113	-0.6004	-2.0049	0.0059	4.3386	
-3.2889	-0.3499	0.7985	-0.9087	1.6343	-0.3949	
0.3268	7.3411	-1.0126	1.3579	-2.7346	-0.7201	
1.2068	0.6597	-0.0288	1.1708	-0.2522	-0.1758	
-0.1095	1.7289	-1.4762	0.4525	2.2709	-1.0502	
3.0592	-0.2892	2.5271	-2.5832	2.4144	-0.1654	
-1.4234	0.0881	0.6343	-0.1215	0.5508	3.0880	
0.1915	-0.5518	0.1244	-0.8818	-0.1221	1.5330	-1.6022
0.2826	1.7115	-0.8296	-1.7558	2.7590	1.2542	2.0201
-0.5582	0.7321	-0.7178	-2.4488	-0.7486	-0.7011	
-0.5193	8.5218	0.0557	-0.9225	4.8837	0.1061	
-10.8696	-0.0739	1.1974	-2.3305	1.7362	-2.1150	
-0.1516	-1.4260	0.2667	-0.0863	3.1831	1.1049	
0.8609	0.6407	-0.5354	-0.4362	0.8222	-2.2032	
2.0526	-0.1711	1.0151	1.6126	0.6275	-0.2804	
-0.5103	-0.2241	-4.5831	-1 .1075	0.3299	1.3456	
-1.7512	-0.1707	-0.1530	-1.1978	-1.5208	1.5554	
0.2877	0.1203	-1.1638	0.6641	-0.4543	0.7822	
-2.1086	-2.5140	-0.2384	-1.2331	2.8076	-0.7624	

The weight matrices and bias vectors of the NN model are listed in Table 4, where W^I (23, 3) is the input and hidden layer connection weight matrix (23 rows x 3 columns); W^H (23, 2) is the hidden and output layer connection weight matrix (23 rows x 2 column). The plot and the parameters of the linear regression are, straight forwardly, obtained using. "***Postreg***" MATLAB function. Figure 5 shows the validation agreement plot for the molecular weight with an agreement vector approaching the ideal [α, β, R] = [0.9939, -0.4256, 0.9864]. Figure 6 shows the same plot for number average molecular masses with an agreement vector equal to [α, β, R] = [0.9880, -0.0103, 0.9688] Table 5 listed the validation agreement vector calculated for the training, validation, test, and total data sets. The performance of NN model was statistically evaluated by the terms of correlation coefficient (R) and root mean squared error (RMSE). RMSE is defined below [22-24]:

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

where n is the total number of data points, Y_{exp} is the experimental value, and Y_{cal} represents the calculated value from the neural network model.

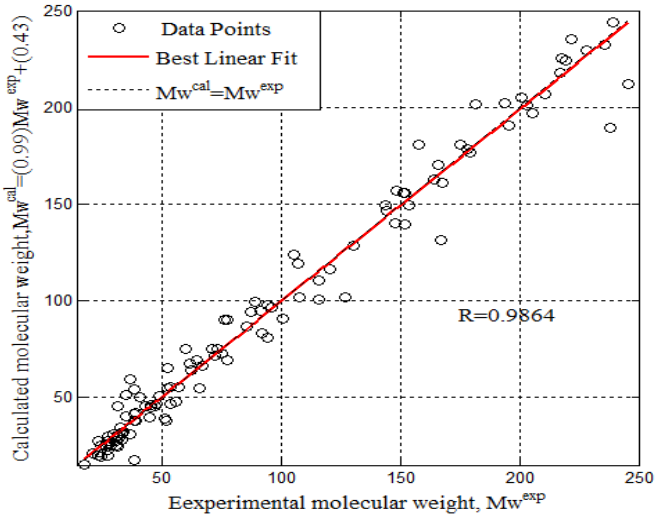


Figure 5: Regression analysis plot for the model between experimental and calculated molecular weight (M_W).

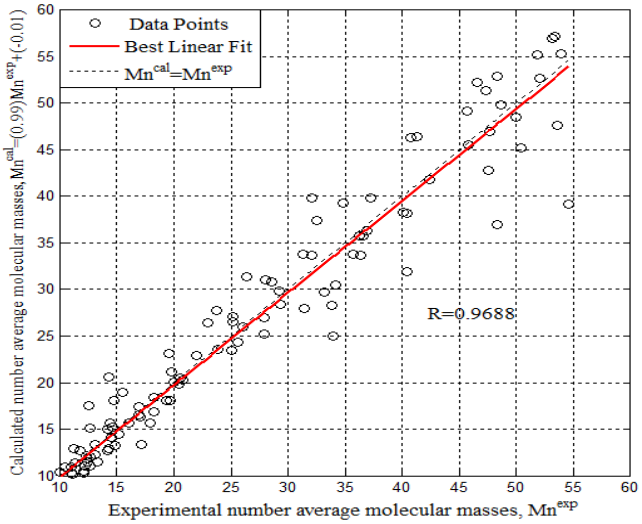


Figure 6: Regression analysis plot for the model between experimental and calculated number average molecular masses (M_n).

Table 5: Linear regression vectors [linear equation: $Y_{cal} = \alpha Y_{exp} + \beta$, with α=slope, β =y intercept. R=correlation coefficient] and RMSE (Roots Mean Squared Error).

		α	β	R	RMSE
Mw	Training phase	1.0132	-0.5325	0.9890	9.8665
	Validation phase	0.8416	10.8252	0.9844	18.5106
	Test phase	1.0716	-7.4954	0.9909	11.4291
	Total	0.9939	0.4256	0.9864	11.1250
Mn	Training phase	1.0224	-0.4829	0.9806	2.7719
	Validation phase	0.7799	4.1707	0.9238	6.6389
	Test phase	1.0330	-2.5383	0.9617	4.6427
	Total	0.9880	-0.0103	0.9688	3.5284

The Figure 7 shows a comparison between the experimental data (indicated by empty circles) and the prediction results (indicated by red stars) of the molecular weight as function of temperature and irradiance, It shows an acceptable agreement between experimental data from the literature and the results of predictions of the neuronal model for the two parameters tested, which shows the reliability and robustness of our developed model.

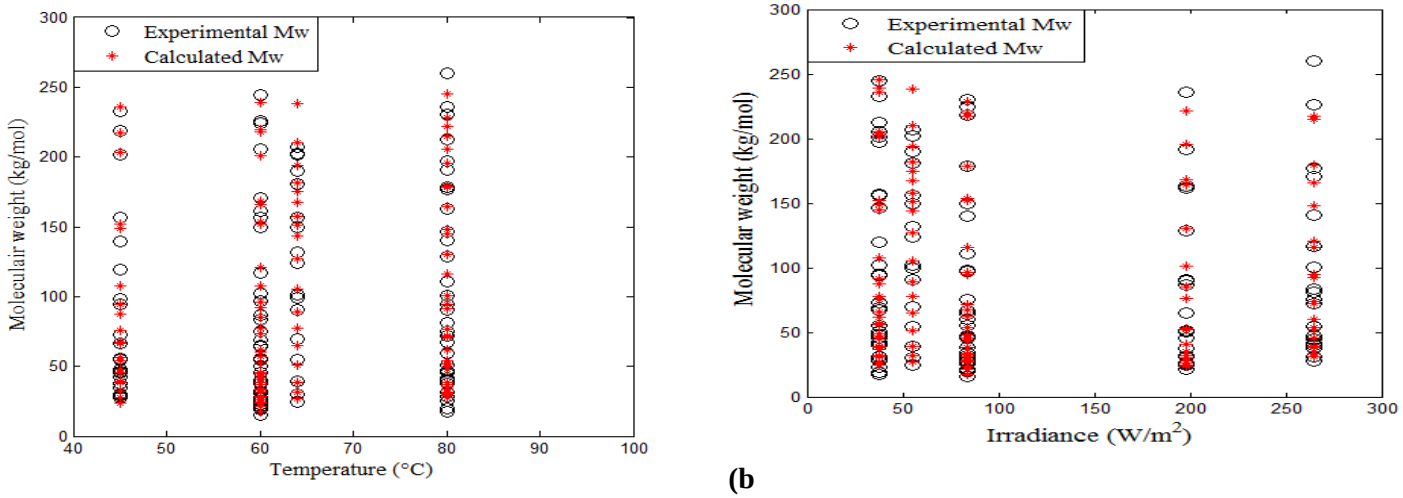
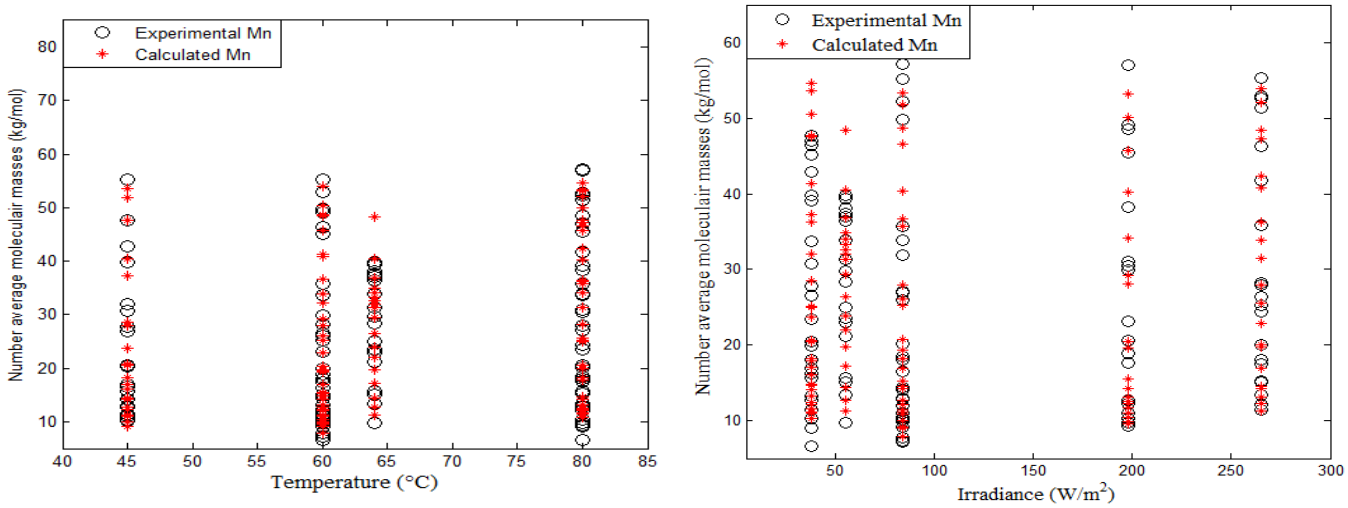


Figure 7: The comparison of experimental and calculated molecular weight (M_W) as function of **(a)** temperature, **(b)** irradiance.

The experimental and calculated number average molecular masses as function of temperature and irradiance are shown in Figure 8. In general, a good relationship can be seen between the calculated and experimental number average molecular masses during photo-thermal oxidation for the two parameters tested.



(a) **(b)**

Figure 8: The comparison of experimental and calculated number average molecular masses (M_n) as function of **(a)** temperature, **(b)** irradiance.

The mathematical formula of the predicted molecular weight (M_W) and number average molecular masses (M_n) is given by the equation (4):

For M_W the instance outputs (h_j) of the hidden layer is calculated as:

$$h_j = f_H\left[\sum_{i=1}^{3} w_{(j,i)}^{H} x_i + b_1^H\right] = \frac{exp\left(\sum_{i=1}^{3} w_{(j,i)}^{H} x_i + b_1^H\right) - exp\left(-\sum_{i=1}^{3} w_{(j,i)}^{H} x_i + b_1^H\right)}{exp\left(\sum_{i=1}^{3} w_{(j,i)}^{H} x_i + b_1^H\right) + exp\left(-\sum_{i=1}^{3} w_{(j,i)}^{H} x_i + b_1^H\right)} \quad (2)$$

while the output (M_W) of the network is given by:

$$M_W = f_O\left[\sum_{j=1}^{23} w_{(l,j)}^{O} h_j + b_2^O\right] = \frac{1}{1+exp\left(-\sum_{j=1}^{23} w_{(l,j)}^{O} h_j + b_2^O\right)} \quad (3)$$

$$M_W, M_n = \frac{1}{1+exp\left(-\sum_{j=1}^{23} W_{(l,j)}^{O}\left[\frac{exp\left(\sum_{i=1}^{3} W_{(j,i)}^{H} x_i + b_1^j\right) - exp\left(-\sum_{i=1}^{3} W_{(j,i)}^{H} x_i + b_1^j\right)}{exp\left(\sum_{i=1}^{3} W_{(j,i)}^{H} x_i + b_1^j\right) + exp\left(-\sum_{i=1}^{3} W_{(j,i)}^{H} x_i + b_1^j\right)}\right] + b_2^O\right)} \quad (4)$$

Where j is the number of neurons in the hidden layer (j = 23), i is the number of neurons in the input layer (i = 3), W^I ($W_{(j,i)}^H$) and b_1^H are weights and bias between input and hidden layer, W^H ($W_{(l,j)}^O$) and b_2^O are weights and bias between hidden and output layer, l is the number of neurons in output layer (l = 2). This mathematical equation for predicting the molecular weight and number average molecular masses contain just the required degree of complexity, comprise the important relevant features that are the oxidation conditions and oxidation of time on the properties of the polypropylene, and thus can be easily applied in industry for criticize and enhance the representativeness of accelerated aging testing and to predict the lifetime of polypropylene parts in the use conditions.

3.2. Sensitivity analysis

To see the contribution as well as the variation profile of each input variable (t (h), T (°C), and I (W/m^2)) on the two outputs (M_W and Mn), a sensitivity analysis was carried out using the "Weight" method. This method, proposed by Garson [25], gives a quantification of the relative importance (RI) of the different inputs on the outputs of the neural network. The process of calculating the relative importance by the "Weight" method is based on following four steps [26]:

Step 1: $P_{ij} = |W^I W^H|$

Step 2: $Q_{ij} = \frac{p_{ij}}{\sum_{i=1}^{n_i} p_{ij}}$

Step 3: $S_i = \sum_{j=1}^{k_j} Q_{ij}$

Step 4: $RI_i(\%) = 100 \frac{S_i}{\sum_{i=1}^{n_i} S_i}$

The results of contributions are shown in Figure 9. From this figure, all the input variables were influenced on the two outputs.

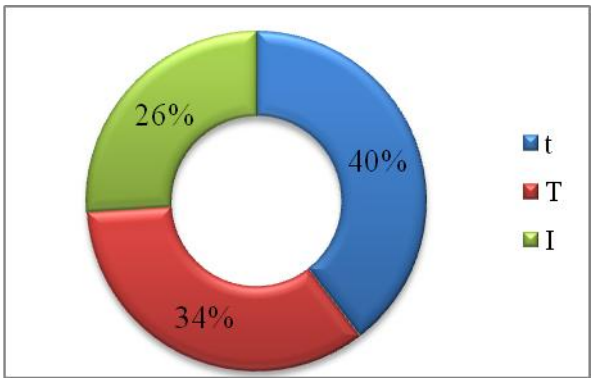


Figure 9: Relative importance (RI) of inputs variables (t (h), T (°C), and I (W/m^2)) on the outputs (M_W and Mn) of the neural network model.

4. Conclusions

The purpose of the current study was the development of an ANN model able to predict the molecular weight (M_W) and number average molecular masses (Mn) during photo-thermal oxidation of polypropylene. This model can predict the molecular weight and number average molecular masses using some commonly available parameters time, irradiance, and temperature as inputs parameters. ANN based on back-propagation method was measured using the criteria root mean square error and the correlation coefficient. The network model presented good results (a coefficient of correlation equal to 0.9864 and 0.9688, and a root mean square error equal to 11.1250 kg/mol and 3.5284 kg/mol for the predicted molecular weight and number average molecular masses respectively). The comparison between the experimental and calculated results show that the ANN model is capable of predicted the molecular weight and number average molecular masses during the photo-thermal aging of polypropylene.

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References

[1] H. A. Maddah, Am. J. Poly. Sci, 2 (2016) 61-11.
[2] O. Zaki, Thèse de doctorat. l'Université de Paris-Est. (2008). France.
[3] Z. A. M. Ishak, B. N. Yow, B. L. Ng, H. P. S. A. Khalil, H. D. Rozman, J. Appl. Polym. Sci. 81 (2001) 742-753.
[4] A. François-Heude, E. Richaud, E. Desnoux, X. Colin, J. Photochem. Photobiol., A: Chem. 296 (2015) 48-65.
[5] B. Fayolle, L. Audouin, J. Verdu, Polymer. 45 (2004) 4323-4330.
[6] B. Fayolle, X. Colin, L. Audouin, J. Verdu, Polym. Degrad. Stab. 92 (2007) 231-238.
[7] D. Vaillant, Université Blaise-Pascal. Clermont-Ferrand. (1993).
[8] L. Audouin, S. Girois, L. Achimsky, J. Verdu, Polym. Degrad. Stab. 60 (1998) 137-43.
[9] O. Karpukhin, E. Slobodetskaya, J. Polym. Sci A Polym. Chem. 17 (1979) 3687-94.
[10] A. François-Heude, E. Richaud, E. Desnoux, X. Colin. Polym. Degrad. Stab. 100 (2014) 10-20.

[11] E. Yousif, R. Haddad, Springer Plus. 2 (2013) 398.
[12] B. F. Yousef, A. I. Mourad, A. Hilal-Alnaq, Procedia. Eng. 10 (2011) 2713-2718.
[13] C. Si-Moussa, S. Hanini, R. Derriche, M. Bouhedda, A. Bouzidi, Braz. J. Chem. Eng. 25 (2008) 183-199.
[14] Z. Zhang, K. Friedrich, Compos. Sci. Technol. 63 (2003) 2029-2044.
[15] Z. Jiang, Z. Zhang, K. Friedrich, Compos. Sci. Technol. 67 (2007) 168-176.
[16] Z. Jiang, L. A. Gyurova, A. K. Schlarb, K. Friedrich, Z. Zhang, Compos. Sci. Technol. 68 (2008) 734-742.
[17] E. Burgaza, M. Yazici, M. Kapusuz, S. H. Alisir, H. Ozcan, Thermochim. Acta. 575 (2014) 159-166.
[18] M. B. Karakoç, R. Demirboğa, İ. Türkmen, İ. Can, Sci. iran A. 29 (2012) 41-50.
[19] S. Haykin, Neural networks: a comprehensive foundation. Prentice Hall, New Jersey. (1998).
[20] R. G. Silva, A. J. G. Cruz, C. O. Hokka, R. L. C. Giordano, R. C. Giordano, Braz. J. Chem. Eng. 17 (2000) 587-598.
[21] H. El Kadi, Compos. Struct. 73 (2006)1-23.
[22] M. Hamadache, O. Benkortbi, S. Hanini, A. Amrane, L. Khaouane, C. Si Moussa, J. Hazard. Mater. 303 (2016) 28-40.
[23] Y. Ammi, L. Khaouane, S. Hanini, Korean. J. Chem. Eng. 32 (2015) 2300-2310.
[24] M. Sediri, S. Hanini, M. Laidi, S. Abbas Turki, H. Cherifi, M. Hamadache, Mor. J. Chem. 2 (2017) 236-243.
[25] G. D. Garson, AI Expert. 6 (1991) 46.
[26] M. Gevrey, I. Dimopoulos, S. Lek, Ecol. Modell. 160 (2003) 249-264.