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THERMAL AGING ANALYSIS IN POLYURETHANE INTAKE MAINIFOLD USING NEURAL NETWORK

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Abstract. *Polymer thermal decomposition process was investigated in the present work using a neural network methodology. The polymers application in automotive companies represents an expressive mass reduction in internal combustion engines as well as a reduction of pressure drop in some engine components, improvement in the dimensional tolerances and manufacturing quality. However, if temperatures are increased, thermal decomposition can occur, precluding its usage. A polyurethane sample was collected from an automotive intake manifold and submitted to an isothermal decomposition analysis. The experimental data were treated by the neural network to determine the preferable set of models best describe the decomposition. Among fifteen models, Diffusion and Contraction models were selected based on the neural network residual error. This network architecture allows quantifying the model contributions to the entire process. Due to the mathematical correction in the kinetic model functions, the accuracy of the network is greater when compared with the models separately. The present method is of general applicability proposing an alternative efficient way to predict thermal aging decomposition and to evaluate the lifetime of polyurethane in vehicle using solid thermal decomposition data.*

Keywords: *Thermal Decomposition Analysis, Polyurethane, Artificial Neural Network, Automotive Intake Manifold, Solid Kinetic Models.*

1. INTRODUCTION

Polymers application in automotive companies represents an expressive mass reduction in internal combustion engines. Some engine components also present reduction of pressure drop, improvement in the dimensional tolerances and manufacturing quality, as function of the polyurethane intake manifold usage. However, if temperatures are increased, this application could be susceptible to thermal decomposition, which changes the mechanical properties, presenting failures during the preventive maintenance interventions.

The solid thermal decomposition reactions generally occur in the reagent-product interface. This kinetic process, based on formation and growth of nuclei, can be studied by isothermal decomposition experimental analysis, in which the mass reduction is measured in a period of time. The nuclei reactions are preferentially formed in imperfections of the structure and kinetics models, well established in the literature, Avrami (1939), Avrami (1940), Yeremin (2001), Galwey and Brown (1999), are used to explain experimental curves. A chosen model is used to fit experimental data, selected by the best decomposition correlation. Nevertheless, in several situations, the residual error of the models is not acceptable in the whole process description, although for specific decomposition regions, the model can be appropriate, being a first approximation in the kinetic studies.

A multilayer neural network is used in the present work to determine the models that best describe the kinetic thermal decomposition of polyurethane, Sebastião, *et. al*,(2004), applied in automotive intake manifold. This analysis allows the physical process determination in the material of research, providing precious information in the mitigation procedure. The present method is not restricted to polyurethane and suggesting a powerful routine method to study polymer thermal decomposition process. For automotive applications, this model could be used to predict the thermal aging decomposition and to evaluate the lifetime in vehicle.

2. METHODOLOGY

2.1 Kinetic Models Theoretical Background

Kinetic study of thermal decomposition can be performed based on nucleation or growth of active nucleus near to the crystal surfaces, described for Avrami (1939), Avrami (1940), Yeremin (2001), Galwey and Brown (1999). The existence of separated reactive points, related to imperfections in the crystals, causes an increase in the Gibbs energy of the system and consequently, its reactivity. Microscopic is a powerful tool to quantitatively study observables nucleus

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in crystal surfaces. Nevertheless, when these nuclei are not evident, physical models are necessary to describe the process. These models are represented by equations of the material fraction, α, normalized to the total mass lost, reacted in the time according to the diffusion process, velocity and kinetic order of the reaction like as Yi, *et al.*, (2009), Erofeev (1946), Jacobs and Tompkins (1953). The models are presented in Tab. 1.

Table 1. Solid Kinetic Models.

Model	Symbol	Kinetic Equation	
Aceleration			
Potencial Law	P_n	$\alpha^{1/n} = kt + k_0 \quad n = 2,3,4,\ldots$	(1)
Sigmoid			
Avrami-Erofeev	A_m	$\left[-\ln(1-\alpha)\right]^{1/m} = kt + k_0 \qquad m = 2,3,4,\ldots$	(2)
Avrami-Erofeev	A_u	$\ln\frac{\alpha}{1-\alpha} = kt + k_0$	(3)
Prout-Tompkins	A_x	$\ln\frac{\alpha}{1-\alpha} = k\ln t + k_0 \qquad k > 1$	(4)
Desaceleration			
Geometric Model			
Linear Contraction	R_1	$1-(1-\alpha) = kt + k_0$	(5)
Area Contraction	R_2	$1-(1-\alpha)^{1/2} = kt + k_0$	(6)
Volume Contraction	R_3	$1-(1-\alpha)^{1/3} = kt + k_0$	(7)
Diffusion Models			
One Dimension	D_1	$\alpha^2 = kt + k_0$	(8)
Two Dimensions	D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt + k_0$	(9)
Three Dimensions	D_3	$\left[1-(1-\alpha)^{1/3}\right]^2 = kt + k_0$	(10)
Ginstling-Brounshtein	D_4	$1-\frac{2\alpha}{3}-(1-\alpha)^{2/3} = kt + k_0$	(11)

The most simple kinetic model, is the constant model, which consider the nucleation process occurring instantly, disabling the subsequently reactions, Erofeev (1946), Jacobs and Tompkins (1953), Carter (1961). However, in some cases the nucleation rate is constant, but the number of active sites changes during the process, and the adequate model is the linear nucleation model. If the nucleation occur in one step and the product is stabilized, the nucleation rate in equivalent sites is random and of first order. For this case the exponential model is more satisfactory to describe the curves.

The nucleus growth can also happen in several consecutive steps. In these models, it is assumed the product of reaction is formed in a sequence of events, in which the active sites is transformed in nucleus of growth and this reaction velocity is described by the potential nucleation model. In some fast reactions, the two initial steps could not occur and the deceleration curves, more appropriate to describe the process, can be divided in diffusion and geometric models, like as Sharp and Brindley (1966), Hulbert (1969), as presented in Tab. 1.

When the decomposition process is governed according Hancook and Sharp (1972), Serra *et. al*,(1998), by a fast development of nucleus in all the extension of the crystal surfaces, the kinetic is determined by the geometry. In this kind of reaction, the induction period is short and the maximum of the velocity curve happens in the beginning of the process. Furthermore, diffusion process can be responsible for the reaction rate control, since the reaction continuity requires the reactants transport to the product layer. For this case, the rate is reduced as the product thickness is increased.

It is important to note the nucleation models are proposed from the behavior of the solid during the decomposition process. The model determination can also be performed by detailed microscopy analysis or mathematical simulation, and is crucial to study the kinetic of the reactions, according Sebastião, *et. al,* (2004), Ng (1975).

2.2 Multilayer Perceptron Neural Networks Background

Artificial neural network, according to Wilde (1995) and Haykin (1997), consists in computer codes used to solve linear and non linear problems in different areas of the science, using human brain model. The multi-layer perceptron

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network, MLP, is composed by input neurons in its first layer, which receive physical information, x_{kj}. The neuron state, o_k, in the intermediate layer can be established as a mathematical function, Eq. (12), calculated by a sum of all neuron contributions connected to him.

$$o_k = f\left(\sum_{j=0}^{m} w_{kj} x_j\right) \tag{12}$$

The weights of interconnection, w_{kj}, between the neurons *k* and *j*, represents the contributions of these *j*-neurons in the previous layer and the information is propagated to the next layer only if the neuron state has been activated by an activation function, f. Connecting this intermediate layer to the output neurons, the network response can be calculated by the same process, i.e. adding the contributions of all intermediate neurons connected to the output layer. In this work, this neural network architecture was proposed and is represented in Fig. 1, like Sebastião, *et al.*, (2004) and Wilde (1995).

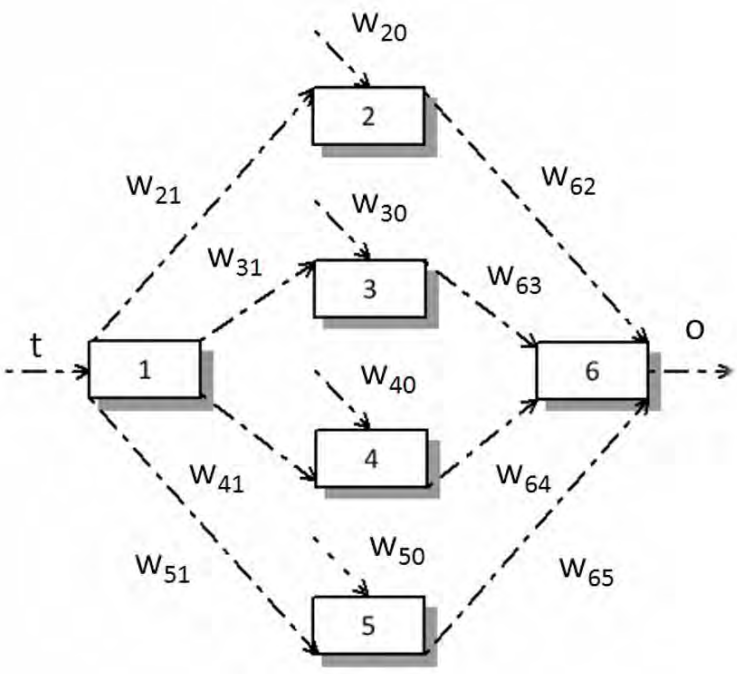

Figure 1. Neural Network architecture.

In the MLP network there is also the bias, assumed as an external parameter influencing the neurons in the network. The bias is constant, generally equal to unity, connected with neurons by an interconnection weight for amplify or reduce the linear correlation of the network. The intermediate neurons can be evaluated by multiplying the weight matrix, w_1, and the input experimental data vector, x. According to Haykin (1997) and Hagan, *et al.*,(1996), to propagate this information to the output layer, it is necessary to apply an activation function in the neuron states, analog the nervous impulse in the brain, and this activation function should have three important characteristics:

(i) Assume fixed values, generally, $f(x) = 0$, before the computation of the neuron state;
(ii) Activate the neurons when assumes values near to the unity and
(iii) Be a crescent function $\frac{df(x)}{dx} \geq 0$, to warranty the energy function minimization.

Since, a linear activation function in the output neurons is assumed, w_2 being the interconnection weights vector in the output layer and considering y as the experimental data, the MLP learning process is performed by an energy function optimization, Eq. (13), from which the output interconnection weights are estimated.

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$$E = \left\| w_2 f\left(w_1 x\right) - y \right\|_2^2 \tag{13}$$

At this point, it is important to emphasize if one assumes the w_1 matrix as the kinetic rates and the activation function of each neuron in the intermediate layer as the kinetic models, as in Tab.1, like as Sebastião, et al. (2004), Cherkassky and Mulier (1998) and Leon (2002), the contribution of each kinetic model to describe the total experimental process can be calculated by Eq. (14).

$$w_2 = \left(B^T B\right)^{-1} B^T y, \;\; which \;\; B = f(w_1 x) \tag{14}$$

2.3 Experimental Section

Thermal decomposition experimental data of a polyurethane sample acquired from an automotive intake manifold (Engine: Fiat Fire 1.0 8V Flexfuel) was obtained in the SHIMADZU TGA50H thermal balance. The TGA curve was obtained in N_2 atmosphere, at 10 ^oC/ min. Due to a significant loss of mass at 400 °C, this experimental curve indicates the temperature of the decomposition process start. Therefore, a kinetic study of this decomposition process at 380, 390, 400 and 410 °C is proposed in the present work. For this, four isothermal experimental kinetic curves were obtained with the same TGA experimental conditions.

3. RESULTS AND DISCUSSION

In the proposed MLP network, shown in Fig. 1, Wilde (1995) and Haykin (1997), there is just one intermediate layer, which is composed by neurons representing the kinetic models. At first, the isothermal experimental data were linear fitted according to the fifteen individual physical model to obtain the rate constant, k, and k_0 in the studied temperatures. From these results, the w_1 matrix of the network is established and the experimental data is treated by the network, giving the w_2 matrix from the optimization process, which corresponds to the individual contribution of each kinetic model in the entire decomposition process. The network residual errors are smaller than the physical model errors when using its original function in all analyzed temperature. This fact can be discussed based on the correction of the model function proposed by the MLP in the description of the experimental data.

Figure 2 shows the experimental data together with the neural network response when all physical models are taken into account for 380, 390, 400 and 410 °C temperatures. The MLP residual errors are 4.81e-04, 8.85e-05, 3.24e-05 and 3.12e-05, respectively for these temperatures.

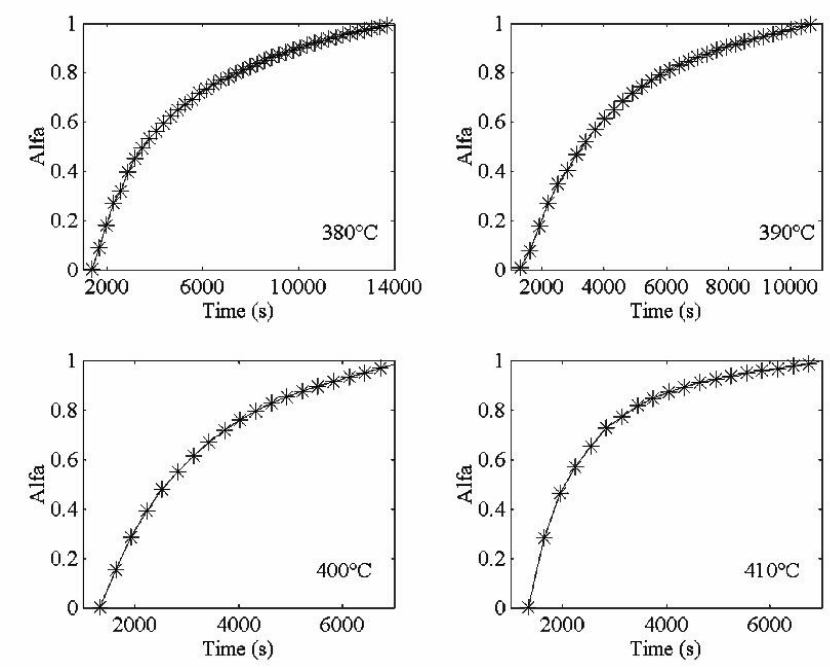

Figure 2. Isothermal experimental data (*) and MLP response (full line).

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Analyzing the experimental curves, one can also observes its similarity with the D_n and R_m model characteristics. Therefore, a detailed study using only these models in the network was performed. The model functions, also presented in Tab. 1, are adequate to be used as neural network activation, since it satisfies all the activation function criteria. For this proposed MLP study, the intermediate neuron states can be represented by Eq. (15).

$$f(w_1 x) = \begin{pmatrix} D_1(w_{21}t + w_{20}) \\ D_2(w_{31}t + w_{30}) \\ D_3(w_{41}t + w_{40}) \\ D_4(w_{51}t + w_{50}) \\ R_1(w_{61}t + w_{60}) \\ R_2(w_{71}t + w_{70}) \\ R_3(w_{81}t + w_{80}) \end{pmatrix} \tag{15}$$

For this neural network, with the D_n and R_m model, the residual errors are 1.61e-03 for 380°C, 2.40e-04 for 390°C; 5.28e-05 for 400°C and 1.76e-04 for 410°C. The model contributions for the experimental data description process in each temperature, respectively, are D_4, D_2, R_3 and D_4 models. With these results another analysis was also made, considering the diffusion, D_n, and contraction, R_m, models in two separated MLP network.

For the diffusion network description, the Ginstling-Brounshtein model, D_4, and the bidimensional diffusion model, D_2, presented great contributions in all analyzed temperatures. The residual errors for this network are 2.03e-03 for 380°C, 1.06e-03 for 390°C, 8.39e-04 for 400°C and 4.85e-4 for 410°C. For the contraction MLP network, the model contributions can be represented as $R_3 > R_2 > R_1$, with residual errors of 2.60e-02, 7.89e-03, 4.14e-03 and 6.02e-03 for 380, 390, 400 and 410 °C, respectively.

The residual error behavior of these three network study can be analyzed in Fig. 3. The network composed by neurons representing only the contraction models showed larger values of error compared with another two networks. On the other hand, the MLP network composed by the diffusion and contraction model and the MLP composed only by the diffusion model presented comparable values of error, indicating the diffusion model as the predominant physical decomposition process.

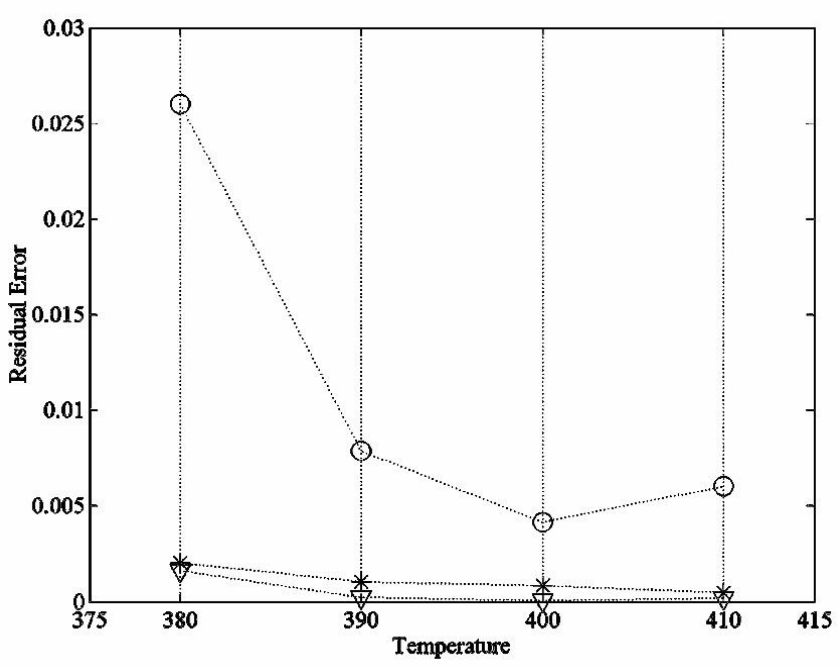

Figure 3. Neural network residual errors: MLP with only D_n models(*), only R_m models (O) and D_n and R_n models(∇) .

The activation energy can be determined from the proposed MLP network, once the first column of the w_1 matrix represents the kinetic rate constants. Considering the Ahrrenius theory, the activation energy values, E_a, were calculated

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and are shown in Tab. 2. For the diffusion models, the E_a average value is 104.5 KJ/mol. This value is in agreement with the E_a values of semi crystalline polymers such polyurethane, polyethylene, polypropylene and polyamide, that typically range from 60 to 130 KJ/mol the according to Braga, *et al.*, (1997), Henstschel and Munstedt (2001) and Lu, *et al*., (2003)

Table 2. Activation Energy according to kinetic models.

Model	E_a/ KJ mol^{-1}
D1	93.70
D3	101.4
D2	116.5
D4	106.2
R1	16.90
R2	98.70
R3	104.0
AM4	99.20
AM2	189.5
AU	106.3
F1	116.1

4. CONCLUSION

Polyurethane thermal decomposition process is studied here using artificial neural network. Due to its characteristics, the kinetic models can be used as nervous impulse and four MLP network, using different set of models in the hidden layer, were constructed. The network architectures were established based on the residual errors of the fifteen models. Among them, the selected ones were the diffusion and contraction models (m=1- 4).

Considering these network architectures and using kinetic models as activation functions, the chemical contents of the problem are not lost in the network. The proposed MLP network, which combines models in the hidden layer, is a powerful approach to treat this kind of problem, once its residual errors are smaller than the results obtained when separated models are used. Also, within this approach the individual contribution of each model can be calculated in the experimental data description.

The combination of kinetic models in the neural network represents a better alternative to describe thermal decomposition process, rather than using individual mechanisms. This has a simple explanation since the neural network proposes two alterations in the kinetic models: *a)* consider the correct asymptotic value of the mass fraction and *b)* changes the time scale of the process. If one compares the average error of the diffusion model (m=1- 4) and neural network error, the network correlation between input and output is increased by a factor of 23 to 380°C, 37 to 390°C, 43 to 400°C and 123 to 410°C. These values confirm the superiority of the neural network.

In the description of polyurethane thermal decomposition, the first neural network proposed has all fifteen models. This network presented a smaller residual error in the experimental data description. However, if it is required to establish a physical model (or a suitable set of models) of the decomposition process, one can restrict the model contributions in the network, controlling the number of neurons in the hidden layer of the network. For this, three networks were proposed: one with the diffusion and contraction model and two with these models separately. Comparing these three networks, it was verified the network with diffusion model and the one with the two models together have comparable residual error, which confirms the diffusion model as the preferable physical description.

The presented method is not restricted to polyurethane, and can be applied to other systems, suggesting a powerful routine method to study polymer thermal decomposition process. For automotive applications, this model could be used to predict the thermal aging decomposition and to evaluate the lifetime in vehicle.

5. ACKNOWLEDGEMENTS

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