Environmental Engineering and Management Journal *April 2018, Vol.17, No. 4, 821-826*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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MULTIPLE LINEAR REGRESSION (MLR) MODELS USED TO PREDICT THE THERMAL STABILITY OF SOME POLYIMIDES

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Abstract

Two multiple linear regression (MLR) models were developed with the aim to estimate the decomposition temperature of a series of polyimides. Two parameters, T_{ni} and T_{ai}, corresponding to the temperature of 10 % weight loss of the sample, determined by dynamic thermogravimetric analysis under conditions of N_2 inert atmosphere and air, respectively, were used as a criterion for thermal stability. The obtained MLR models correlate thermostability with a series of characteristics of the studied polymers, such as Van der Waals volume, density, molecular weight, number of aromatic cycles, number of C=O bonds, number of CH_3 groups and the number of CF_3 groups. The results showed that the MLR models can be successfully used to predict the thermal stability of polyimides, the mean percentage errors being below 3%, regardless of the work environment.

Key words: MLR models, polyimides, prediction, thermal stability

Received: May, 2017; Revised final: February, 2018; Accepted: March, 2018; Published in final edited form: April 2018

1. Introduction

Polyimides are performance materials used in various fields, such as: microelectronics (Cha et al., 1996; Hokazono et al., 2014; Olariu et al., 2017; Park et al., 2012), aerospace (Yu et al., 2004), automotive industry (Yano et al., 1997), environmental protection (Bi et al., 2010; Li et al., 2004; Xiao et al., 2005), in obtaining biofuel (Ong et al., 2012), as well as in medicine, in the treatment of neurological disorders (Chen et al., 2009). Many of the practical applications of polyimides are a consequence of their special properties, namely: high thermal stability, good processability and mechanical properties, fire and wear resistance, high glass transition temperature, low dielectric constants and high chemical resistance. All these properties turn them into good insulators, widely used as dielectric layers manufacturing semiconductor chips and multichip packaging structures (Lisa et al., 2009). However, there are certain limits that restrict their use in actual practice, encouraging further research in the field for the purpose of developing new materials as well as improving existing materials (Lisa et al., 2009). This study follows the same direction of research. As it has already been mentioned, one of the most important properties of polyimides is their high thermal stability. Certain types of polyimides are the only commercially available polymers that can withstand temperatures above 400°C (Lisa et al., 2009). In a previous study, with the help of various types of neural networks, Lisa et al. determined the relationship between structure and thermostability for a series of polyimides and demonstrated that neural networks offer the possibility to replace experiments with estimations (Lisa et al., 2009). An alternative to applying neural models is the statistical processing of experimental data using the multiple linear regression method (MLR).

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The advantage of MLR models stands in their simplicity and ease with which they can be applied by other researchers as well in the possibility to estimate various properties (Lisa et al., 2015). Fayet et al. (Fayet et al., 2009; Fayet et al., 2010) used the quantitative structure-property relationship (QSPR) methodology to predict the thermal stability of a number of 22 nitroaromatic derivatives, while Lu et al., (2011) used it to study the thermal decomposition of 16 organic peroxides. Decomposition enthalpy, or T_{onset} temperature, experimentally determined by differential scanning calorimetry (DSC), were used as indicators of thermal stability for these compounds. The semi-empirical models containing equations with three or more parameters obtained by these authors offer a good correlation between the calculated values and those experimentally determined, correlation coefficients being above 0.9.

Pucci et al. (2016) used both neural and MLR models to predict the melting temperature (T_m) of the wild-type protein. The root-mean-square deviation between the values calculated using the models obtained and the experimental ones for ΔT_m is reduced from 4.2°C to 2.9°C when the authors eliminate 10% of the abnormal values. MRL models have been successfully used by researchers in the field of environmental protection, as well. Mokarram (2016) used such models for the prediction of groundwater quality, while Cemek et al. (2016) used them for the prediction of nutrient concentrations in runoff from feedlots to facilitate management practices.

Recently, He et al. (2018) compared the performance of two different models: MLR and support vector machine (SVM) designed to determine the self-accelerating decomposition temperature (SADT) for a series of organic peroxides. SADT is an important parameter for the description of the thermal hazard of organic peroxides in process industries. The average absolute error obtained with the MLR model is approximately 8.5°C, while with SVM it is 8.1°C.

In this paper, the experimental data referring to various polyimides were statistically processed using the *SigmaPlot 11.2* software. Multilinear regressions between the parameters that characterize thermostability (T_{ni} or T_{ai}) and molecular descriptors (Van der Waals volume, density, molecular weight, number of aromatic cycles, number of C=O bonds, number of CH_3 groups and the number of CF_3 groups) were obtained. The results were comparable with previous ones (Lisa et al., 2009) obtained by modelling with the help of neural networks. However, the advantage of the MLR models is the ease with which they can be applied by other researchers to predict the thermal stability of polyimides.

2. Data and methodology

2.1. Data

The used database contains information regarding the thermal stability of a number of 54 polyimides with a wide structural variety (Lisa et al., 2009). Some of the analysed polyimide structures are selectively in Table 1.

2.2. Methodology

The *Multiple Linear Regression (MLR) module* of the *SigmaPlot 11.2* software allows to develop models of the following type: Property = f (characteristics). The models obtained have the following form: $Y = A_0 + A_1X_1 + A_2X_2 + ... + A_nX_n$ where Y is the modelled property – *dependent variable*, X_i are characteristics of the systems - *independent variables* and A_i are coefficients of the models. Apart from the possibility to obtain MLR models, this software also allows to carry out a rigorous analysis of their performances.

With the help of the *Materials Studio 4.0 – Accelrys* software, various molecular descriptors were calculated and selected to study the relationship between structure and termostability for polyimides. The Open Force Field (OFF) module was used to simulate properties. This uses a polymer consistent force field (PCFF) parameterized for a wide variety of organic compounds, for biopolymers and synthetic polymers. Moreover, the 15.5 Å cut-off parameter was used to estimate remote interactions. The load distribution, due to Coulomb-type interactions, was estimated using the Rappe-Goddard method. The molecular dynamics calculations (MD) were done at 298 K for every simulated structure, using the isothermal and isochoric ensemble (NVT) module. The simulation times used for MD-NVT were of 500 - 1000 ps, depending on the size of the investigated system (frequency of up to 2000 steps).

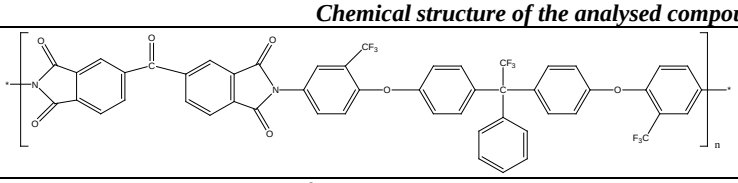
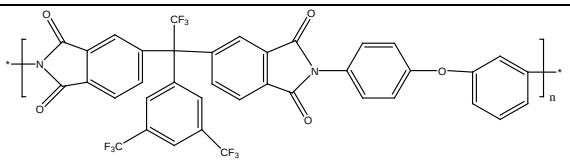
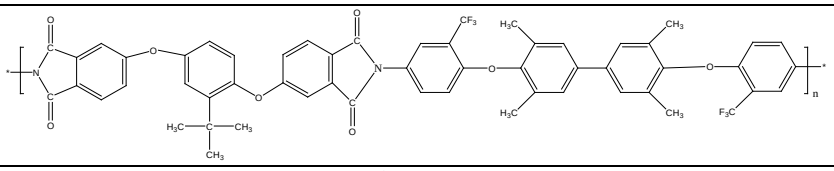
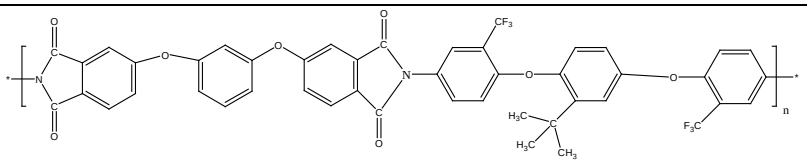
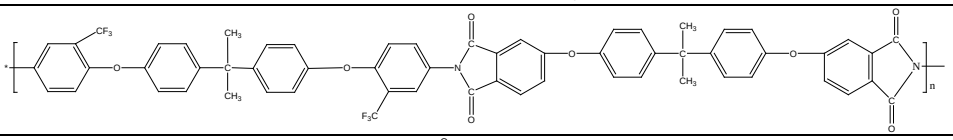
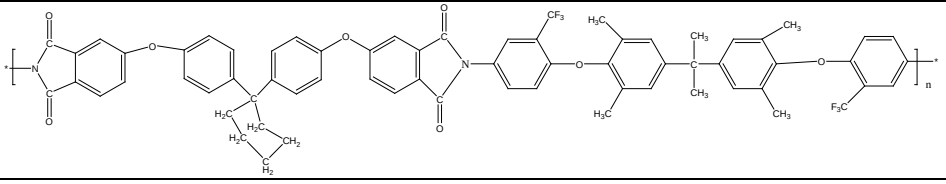
The following molecular descriptors obtained using the *Synthia* model of the *Materials Studio* software: Van der Waals volume - **V**, density - **D**, molecular weight - **M**, and a series of structural parameters, such as: number of aromatic cycles - $\mathbf{N_{ac}}$, number of C=O bonds - $\mathbf{N_{C=O}}$, number of CH_3 - $\mathbf{N_{CH3}}$ groups and the number of CF_3 - $\mathbf{N_{CF3}}$ groups, were selected as *independent variables* in the MLR models.

The temperatures at which 10% of the initial amount of the sample subjected to a thermal degradation process was lost under an inert atmosphere of N_2 (T_{ni}) and air (T_{ai}) were used as a criterion for thermal stability (*dependent variables*) by the built MLR models.

3. Results and discussion

With the help of the *Materials Studio* software, the optimized structures for the 54 analysed polyimides were obtained, and molecular descriptors were determined on this basis. Table 2 presents, for some of the studied polyimides, the optimized structures, the molecular descriptors selected as *independent variables* in MLR models, and the *dependent variables* quantifying thermal stability, respectively, the temperature at which, following degradation, 10% of the initial amount of the sample subjected to analysis under an inert atmosphere of N_2 (T_{ni}) and air (T_{ai}) is lost.

Table 1. The structure of polyimides whose thermal stability was modelled using the MLR module from the *SigmaPlot 11.2* software package

No.	*Chemical structure of the analysed compounds*
5.	
13.	
23	
34.	
45.	
54.	

The values of the Van der Waals volume marked with **V** and those of the molecular weight marked with **M** were normalized. In Figs. 1 and 2, the experimental values for T_{ni} and T_{ai}, as well as the corresponding calculated values using the obtained MLR models are comparatively presented. The mathematical expressions for the MLR models have the form given by Eq. (1):

$$Y\,(T_{ni}\ or\ T_{ai}) = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_5 + A_6X_6 + A_7X_7 \quad (1)$$

where X_1 is $\mathbf{V}x10^{-3}$; X_2 is **D**; X_3 is $10^6/\mathbf{M}$; X_4 is $\mathbf{N_{ac}}$; X_5 is $\mathbf{N_{C=O}}$; X_6 is $\mathbf{N_{CH3}}$, and X_7 is $\mathbf{N_{CF3}}$.

Table 3 shows the values of the constants A_0, A_1,....A_7 and the obtained mean values of the percentage estimation errors (*Ep%*) (Eq. 2).

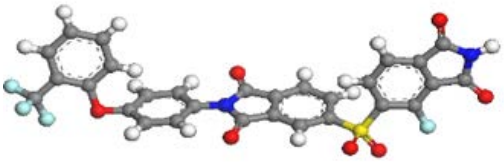
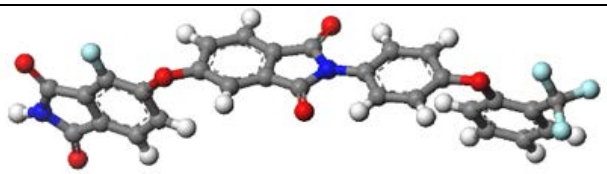
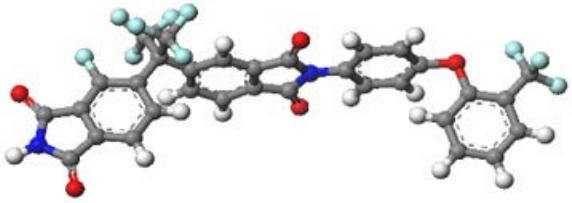
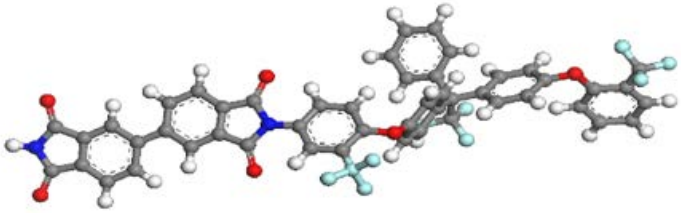
$$Ep\% = \left|\frac{\left(Y_{model} - Y_{experimental}\right)\cdot 100}{Y_{experimental}}\right| \quad (2)$$

The mean percentage errors are comparable with those reported in a previous study (Lisa et al., 2009) having the same database, but using feed forward neural networks and modular neural networks. The advantage of the two MLR models developed in this paper consists in the fact that they can be easily used by other researchers in order to estimate the decomposition temperature of a series of polyimides. It was calculated by means of Eq. (3), where *n* represents the number of experimental data for the two MLR models obtained and the average absolute error. In that way, for T_{ni} we obtained AAM = 12.2°C and for T_{ai} AAM = 10.8°C.

$$AAM = \frac{\sum_{i=1}^{n}\left|Y_{model} - Y_{experimental}\right|}{n} \quad (3)$$

The performances obtained in this work, respectively an average absolute error (AAM) of approximately 11.5°C, for the prediction of the initial decomposition temperature for a series of polyimides by applying MLR models, are comparable to those presented by other researchers in specialized literature. He et al. (2018) obtained, for a larger experimental database, an average absolute error of about 8.5°C for the prediction of the self-accelerating decomposition temperature (SADT) for a series of organic peroxides. They also achieved promising results with the support of a vector machine (SVM) model, i.e. an average absolute error of 8.1°C.

Table 2. Optimized structures of polyimides and values of the *dependent and independent variables* used to obtain the MLR models

Optimized structures	***Dependent and independent variables from the MLR models built***
	**V**x10^{-3}=0.2675; **D**=1.57; 10^6/**M**=1.873 $\mathbf{N_{ac}}$=4; $\mathbf{N_{C=O}}$=4; $\mathbf{N_{CH3}}$=0; $\mathbf{N_{CF3}}$=1 T_{ni}=515°C; T_{ai}=546°C
	**V**x10^{-3}=0.2513; **D**=1.514; 10^6/**M**=2.6596 $\mathbf{N_{ac}}$=4; $\mathbf{N_{C=O}}$=4; $\mathbf{N_{CH3}}$=0; $\mathbf{N_{CF3}}$=1 T_{ni}=591°C; T_{ai}=584°C
	**V**x10^{-3}=0.2964; **D**=1.599; 10^6/**M**=1.3193 $\mathbf{N_{ac}}$=4; $\mathbf{N_{C=O}}$=4; $\mathbf{N_{CH3}}$=0; $\mathbf{N_{CF3}}$=3 T_{ni}=555°C; T_{ai}=545°C
	**V**x10^{-3}=0.4274; **D**=1.467; 10^6/**M**=5.882 $\mathbf{N_{ac}}$=7; $\mathbf{N_{C=O}}$=4; $\mathbf{N_{CH3}}$=0; $\mathbf{N_{CF3}}$=3 T_{ni}=588°C; T_{ai}=568°C

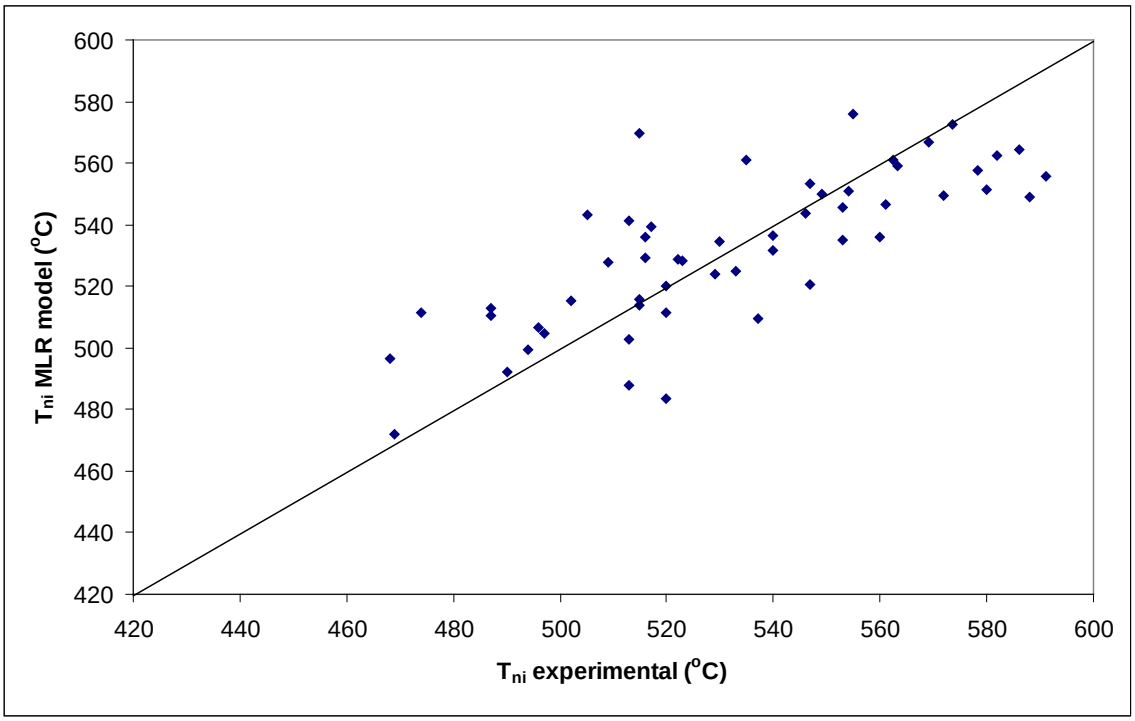


Fig. 1. Comparing the experimental values with those calculated using the MLR model for the temperature at which, following the degradation process, 10% of the initial amount of the sample subjected to analysis under an inert atmosphere of N_2 (T_{ni}) is lost

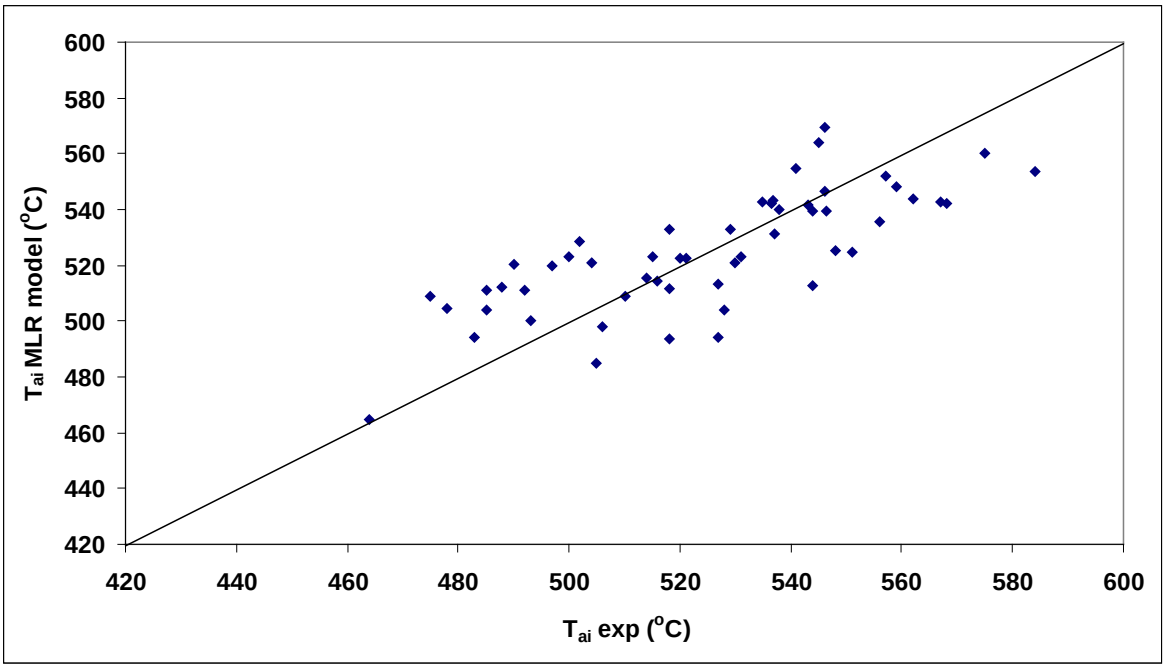


Fig. 2. Comparing the experimental values with those calculated using the MLR model for the temperature at which, following degradation, 10% of the initial amount of the sample subjected to analysis in air (T_{ai}) is lost

Table 3. Parameters of the obtained MLR models

Y	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	*Ep (%) average*
T_{ni}	212.318	30.674	199.519	-3.374	3.688	7.228	-5.709	-1.293	2.97
T_{ai}	151.559	90.556	239.338	-1.183	1.072	5.845	-4.151	-7.738	2.82

4. Conclusions

The research undertaken in this paper is in line with recent concerns to reduce the number of experimental tests by applying modern methods of modelling to correlate the relationship between structure and properties. Thus, two MLR models were developed to predict the thermal stability of polyimides.

The mean percentage errors estimating the temperature at which, following the degradation process, 10% of the initial amount of the sample subjected to thermogravimetric analysis is lost were below 3%, regardless of work environment.

The advantage of the two MLR models presented here consists in the fact that they can be easily used by other researchers in order to estimate the decomposition temperature of a series of polyimides.

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