Revue Roumaine de Chimie, **2009**, *54*(11-12), 1133–1142

Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

NEURAL NETWORKS USED FOR THE PREDICTION OF THE STRUCTURE-THERMAL STABILITY RELATION

Cătălin LISA, Gabriela LISA* and Silvia CURTEANU

"Gheorghe Asachi'' Technical University, Chemical Engineering and Environment Protection Faculty,
B-dul D. Mangeron, no. 71, Iaşi 700050, Roumania

Received May 19, 2009

This paper presents comparatively the findings obtained with the help of various types of neural networks in relation to the prediction of the thermal stability of some polyimides. The conceived models correlate thermal stability with a series of characteristics of the analyzed compounds: volume, density, molecular weight, number of aromatic cycles, number of C=O bonds, number of CH_3 and number of CF_3 groups. The thermal stability is assessed through the temperature at which 10 % of the initial quantity of the sample subject to analysis under circumstances of inert atmosphere of N_2 (T_n) and air (T_a) is lost due to the degradation process. The obtained results have shown that the feedforward neural networks, as well as modular networks, can be successfully used for the prediction of the thermal stability of a polyimide, the average percentage errors obtained with these being under 5 %.

INTRODUCTION

The modern industry needs new materials, with special properties, as requested by various applications where the form and the structure are factors which play a decisive role. The engineering of certain properties, particular for the targeted field, involves a control of the composition, structure and physical properties. Organic polymer materials are of extreme interest in the industry of microelectronics, being used as insulators in electronic devices due to the fact that they have small dielectric constants and a good processing capacity. Moreover, polyimides have a high level of thermal stability, a high mechanical tension, a good processing capacity and high chemical resistance, properties that recommend them as good insulators, used at large scale as dielectric layers for the manufacturing of semiconductive chips and multichip packaging layers.[1,2] For these applications, the dielectric material must have very low or even equal to zero values for dielectric constant and interfacial voltage, which lead to high performance devices, with an increased functional capacity. There are certain limits that restrict their use and justify to the continuation of research in order to develop new materials and to improve the existing ones. Over the last couple of years, studies in this field have been dominated by polyimide and copolymaleimide compounds that lead to various application in optoelectronics, telecommunications or in the aircraft industry.

Certain types of polyimides are the only polymers available on the market that can resist to temperatures higher than 400 ^oC. The polyimide films have low weight, insulating properties and smoother surfaces than metal sheets, but have a much smaller thermal stability and a higher thermal expansion index. Only some of them have an appropriate thermal expansion index and are compatible with vacuum processing. Normally, this index increases at temperatures that exceed the glass transition temperature, which is situated, in most cases, below the decomposition temperature.

* Coresponding autor: gapreot@ch.tuiasi.ro

Therefore, for certain applications, the restrictions are given by the great gap of the thermal expansion index, and not by the thermal instability of the sub-layer.

The alternative methods for determining the structure – thermal stability relation for a series of polyimides may contribute to the discovery of new materials that meet the desired properties, for the purposes of using them in the industry of microelectronics, telecommunications etc. The various types of artificial neural networks, as proven in previous papers[3-6] related to the prediction of other properties, represent a simple and user friendly tool and may offer the possibility of replacing experiments with predictions.

This paper presents the prediction of thermal stability and an analysis of the influence of several structural factors on the thermal degradation of some polyimides. The neural models are employed in order to find out and to generalize the relation between the structure of the compounds, quantified with the help of a series of molecular descriptors, and their thermal stability. The built neural models use as criteria of thermal stability the temperature at which 10 % of the initial quantity of sample subject to analysis under circumstances of inert atmosphere of N_2 (T_n) and air (T_a) is lost, due to the degradation process,.

METHODOLOGY

Artificial neural networks (ANN), sometimes also called neurocomputers, are an attempt towards the partial stimulation of the structure and functions of the brain, of living organisms.

From a functional perspective, a neural network is a system that receives input data (similar to the initial data of a problem) and output data (that can be interpreted as responses to the analyzed problem). An essential feature of neural networks is their capacity of adjusting to the information environment that corresponds to a concrete problem via a learning process.[7-9] This way the network extracts from the examples the relation between inputs and outputs, that means it learn the behavior of the process .

Multilayered perceptron (MLP) is one of the most used types of feedforward neural network for property prediction.[10-12] Feedforward neural networks can be trained from examples without knowing particular details of the problem under consideration and their success consists in their ability of generalization in most cases.

A feedforward network has a layered structure (Figure 1). Each layer is built out of units which receive their input from a layer immediately below, and send their output to units in the next layer above. There are no connections within the layer itself.

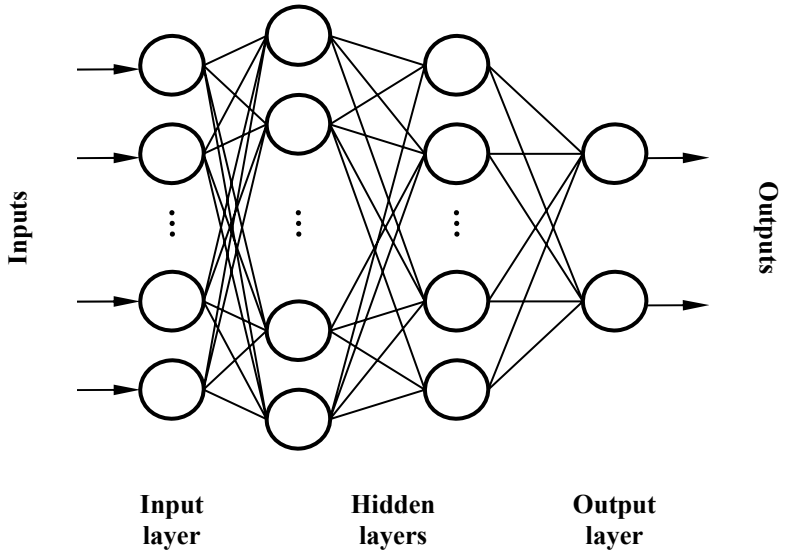


Fig. 1 – A schematic illustration of a multilayered perceptron with two hidden layers.

Numerous researchers have shown that, by combining multiple neural networks, we can obtain more accurate simulations than by using a single network because different aspects of the process can be thus quantified by different networks. Modular neural networks (MNN) are a special class of multilayer perceptrons. These networks process their input using several parallel MLPs, and then recombine the results (Figure 2).

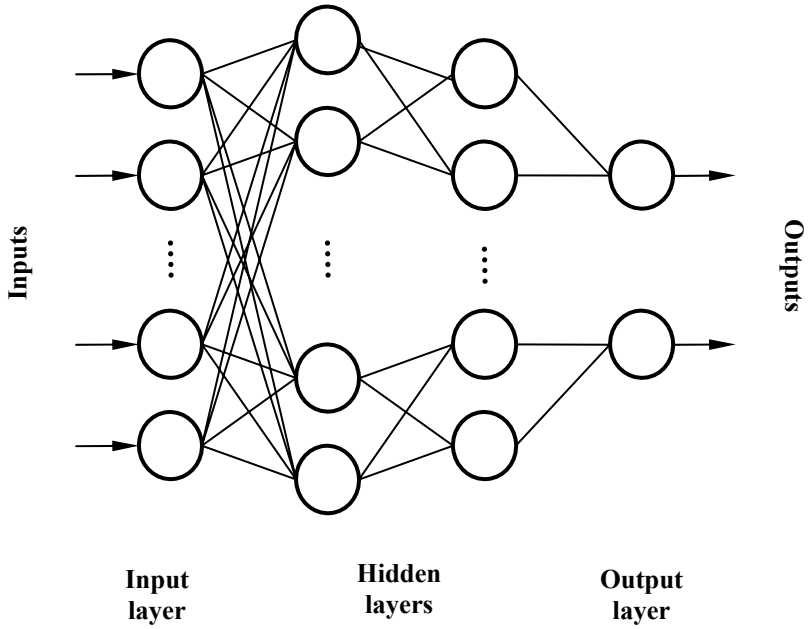


Fig. 2 – Modular neural network architectures with two slabs and the possibility of two activation functions.

Modular neural networks are obtained by using several modules that, taken together, can solve complex problems, especially classification and approximation ones. All the employed modules are neural networks. The architecture of a single module is simple and it definitely has a smaller number of neurons than a traditional, monolithic neural network. The modular structure of an MNN reduces the complexity of a single MLP and enhances its functional approximation capabilities.

EXPERIMENTAL ARRANGEMENT AND CASE STUDY

The built database comprises information related to the thermal stability of a number of 54 polyimides,[13-21] with a large structural variety. Table 1 selectively presents some of the analyzed structures.

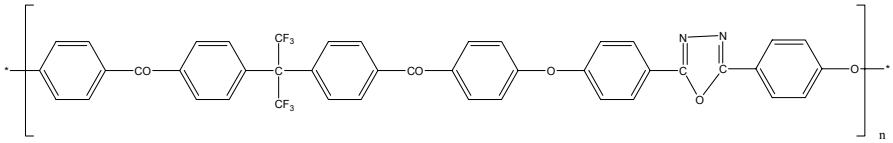
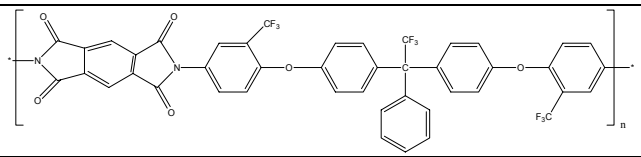
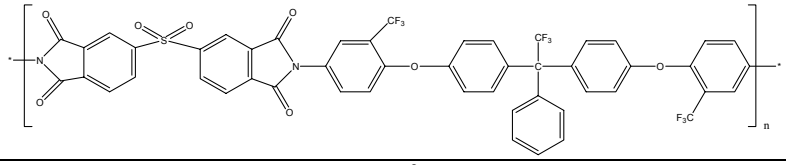
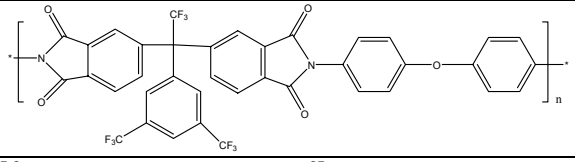
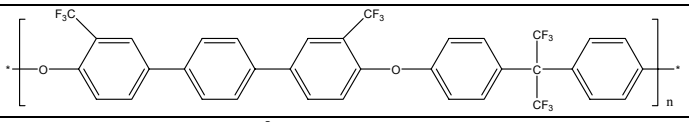
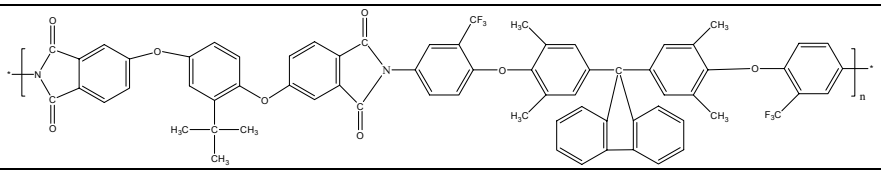
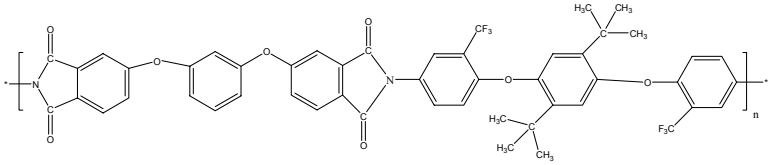
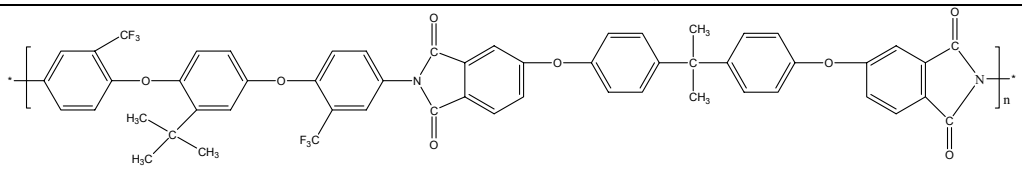
Following the analysis of the previously obtained findings[22] in relation to the prediction of the thermal stability of some small molecular compounds with Materials Studio 4.0 – Accelrys software, different molecular descriptors have been calculated and selected for the study of the structure – thermal stability relation. In a previous paper[22], the thermal stability of some ferrocene derivatives with liquid crystal properties and various molecular designs have been analyzed. The thermostability is appreciated by the temperature when the degradation process starts and the temperature corresponding to the maximal degradation rate. The parameters considered with significant influence on the studied property were: molecular weight, polarizability and some structural characteristics (number of the aromatic groups, number of the ferrocene units and number of the cholesteryl units).

The molecular modeling for the data base which comprises information concerning 54 polyimides with various structures was performed with a special software, Materials Studio 4.0 – Accelrys. The following steps were performed within the molecular modelling procedure: drawing the molecules, their transformation from 2D into 3D, optimization of the molecule geometry built by using the Forcite module and the Compass field of forces, obtaining the molecular descriptors via geometrical or topological measures and determination of other properties with the help of the Synthia module.

The molecular descriptors selected as input data were: volume, V, density, D, molecular weight, M and a series of structural parameters such as: the number of aromatic cycles, N_{ac}, the number of bonds C=O, $N_{C=O,}$ the number of CH_3, N_{CH3} and the number of CF_3, N_{CF3}.

Table 1

Structures of the polyimides whose thermal stability has been modeled with neural networks

Sample code	Chemical structure of the analyzed compounds
1	
5	
9	
11	
16	
28	
35	
41	

RESULTS AND DISCUSSION

The main objectives of this paper are the quantification of the thermal stability of some polyimides with feedforward neural networks (MLP and MNN), as well as the comparison of the performances of the two types of models. The 54 pairs of input – output values in the database have been built as follows: 39 data for the training stage and 15 data for the validation of the results.

Various types of neural networks with an input layer of seven neurons (for the seven input variables), one, two or three hidden layers, and an output layer with two neurons (for the two output parameters) have been tested. The number of neurons in the hidden layers varied between 4 and 20. The performances of the neural models are presented in Table 2.

Table 2

Performances of the neural network models

No.	Network topology	MSE	r^2	E_p(%)
1.	MLP(7:4:2)	0.010	0.972	1.00
2.	MLP(7:8:2)	0.000091	0.99979	0.077
3.	MLP(7:10:2)	0.000007	0.99998	0.015
4.	MLP(7:12:2)	0.000005	0.999996	0.0071
5.	MLP(7:14:2)	0.00001	0.999976	0.010
6.	**MLP(7:16:2)**	**0.000001**	**0.999998**	**0.0022**
7.	MLP(7:20:2)	0.000003	0.999994	0.0041
8.	MLP(7:4:4:2)	0.00489	0.9875	0.630
9.	MLP(7:8:8:2)	0.000002	0.999995	0.0058
10.	MLP(7:10:10:2)	0.000015	0.99997	0.0363
11.	**MLP(7:12:12:2)**	**0.0000001**	**0.999999**	**0.0002**
12.	MLP(7:14:14:2)	0.000002	0.99996	0.0037
13.	MLPS(7:12:12:12:2)	0.0000005	0.999999	0.0020
14.	**MLP(7:14:14:14:2)**	**0.0000002**	**0.999999**	**0.0011**

In order to establish the topology of the modular neural networks several types of networks, similar to those presented in the previous paper,[23] with 7 inputs, a hidden layer with 4...28 neurons and two outputs have been tested. The parameters employed as selection criteria for the best topology were: mean squared error (MSE), the correlation index (r^2) and the percentage error (Ep). Table 3 presents the findings obtained during the training stage with various types of modular neural networks.

The mean squared error was computed using the following formula:[24]

$$MSE = \frac{\sum_{j=1}^{P}\sum_{i=1}^{N}(d_{ij} - y_{ij})^2}{N \cdot P} \quad (1)$$

where P is the number of output processing elements (in this case, P = 2), N is the number of exemplars in the data set, y_{ij} is the network output for exemplar i at processing element j, and d_{ij} is the desired output for exemplar i at processing element j.

In addition, the absolute fraction variance (r^2) and mean absolute percentage error are calculated by using equations (2) and (3), respectively.

$$r^2 = 1 - \left(\frac{\sum_i (d_i - y_i)^2}{\sum_i (y_i)^2} \right) \quad (2)$$

$$E_p = \left| \frac{d_i - y_i}{y_i} \right| \cdot 100 \quad (3)$$

For all built neural models, the number of training epochs was 100000.

In Table 3, different types of modular neural networks are developed: a) two hidden slabs with possibility of two activation functions; b) two hidden slabs with possibility of three activation functions, and a jump connection; c) two hidden slabs with possibility of four activation functions and a jump connection between hidden layer and output layer; d) two hidden slabs with possibility of five activation functions and a jump connection between hidden layer and output layer.

By analyzing the results in Tables 2 and 3, we can notice that the multilayer perceptrons have better performances than modular networks. The best results for each class of neural networks were written in bold. As an example, Table 4 presents the findings obtained during the training stage with two of the best obtained neural models.

The built neural models were tested during the validation stage by using 15 pairs of input-output data that were not employed during the training stage. The obtained results are given in Table 5. The values whose percentage error exceeds 10 % were written in grey, as we also notice in Figure 3. This figure shows the percentage errors for the 15 pairs of data comprising the validation data set, obtained with MLP (7:12:12:2) topology.

By analyzing the results of the validation stage (Table 5) we may observe that the predictions of the MLPs are better than the predictions for MNNs. The results are in contradiction with those obtained for the prediction of the thermal stability of some small molecular compounds.[22] This can be

due to the fact that, for the small molecular compounds, the number of input – output data pairs was smaller. In this case, specialized literature recommends the use of modular networks. In order to compare the performances of the two types of neural models, Figures 4 and 5 present comparatively the experimental values and the predictions obtained during the validation stage for the networks with the best performances of each type. The chosen temperature was that at which 10 % of the initial quantity of the heated sample in inert atmosphere of N_2 (T_n) and air (T_a) is lost, due to the degradation process. We may notice that MLPs have better results with T_n output data; for T_a the results are comparable for both types of neural networks, MLP and MNN.

Table 3

Performances of the modular neural networks

No.	Network type and topology	MSE	r^2	E_p(%)
1.	a)MNN(7:4:2)	0.00319	0.9916	0.531
2.	a)MNN(7:8:2)	0.000274	0.99932	0.141
3.	a)MNN(7:12:2)	0.000205	0.99948	0.128
4.	**a)MNN(7:16:2)**	**0.000251**	**0.99937**	**0.121**
5.	b)MNN(7:4:2)	0.001597	0.99594	0.398
6.	b)MNN(7:8:2)	0.000454	0.99884	0.1835
7.	b)MNN(7:12:2)	0.000366	0.99907	0.1644
8.	b)MNN(7:16:2)	0.000231	0.99948	0.1266
9.	b)MNN(7:20:2)	0.000183	0.99953	0.122
10.	**b)MNN(7:24:2)**	**0.000065**	**0.9998**	**0.067**
11.	b)MNN(7:28:2)	0.00025	0.99939	0.124
12.	c)MNN(7:4:2)	0.0013	0.9967	0.3468
13.	c)MNN(7:8:2)	0.000582	0.99854	0.2292
14.	**c)MNN(7:12:2)**	**0.000305**	**0.9992**	**0.1590**
15.	c)MNN(7:16:2)	0.000192	0.99995	0.1300
16.	d)MNN(7:4:2)	0.001920	0.9951	0.4387
17.	d)MNN(7:8:2)	0.000287	0.9992	0.1586
18.	d)MNN(7:12:2)	0.000253	0.99936	0.1414
19.	d)MNN(7:16:2)	0.000290	0.99927	0.1437
20.	d)MNN(7:20:2)	0.000069	0.999822	0.0677
21.	**d)MNN(7:24:2)**	**0.000015**	**0.99997**	**0.0363**
22.	d)MNN(7:28:2)	0.000324	0.999161	0.1478

The mean percentage errors obtained with MLP (7:12:12:2) were of 4.84 % for T_n and 3.82 % for T_a. For the modular models, the best performances were obtained with the networks with two columns of hidden neurons and the possibility of using five activation functions, a connection of the first layer of hidden neurons with the output layer and a connection of the output layer with the input layer (MNN(7:24:2) type d). The mean percentage errors obtained in this case were of 5.10 % for T_n and 3.28 % for T_a.

This case study illustrates the very good results obtained for the prediction of the thermal stability of some polyimides. We have shown that multilayer perceptrons, as well as modular networks, can be successfully used for the prediction of the thermal stability of some polyimides.

CONCLUSIONS

This paper proposes the application of different types of the neural network models for the prediction of the thermal stability of some polyimides.

Simple architecture neural networks and simple methods of establishing the networks' structure are proposed for process modelling: multilayer perceptrons and modular neural networks with one or two hidden layers. Good prediction for the decomposition temperature at which a 10 % weight loss in air and nitrogen atmosphere was obtained. Consequently, this neural network modelling methodology gives a very good representation for the material thermal stability analysis.

Acknowledgements: This research occurred in the framework of the Project PN II ID_600/ no.64/1.10.2007 and ID_592 no.59/1.10.2007, for which the authors acknowledge financing authority.

Table 4

Predictions during the validation stage, obtained with some of the two types of employed neural networks

Input Data							Output Data		MLP(7:12:12:2)		MNN(7:24:2) type d	
$V/10^3$	D	$10^6/M$	N_{ac}	$N_{C=O}$	N_{CH3}	N_{CF3}	T_n (exp)	T_a (exp)	T_n (net)	T_a (net)	T_n (net)	T_a (net)
0.4317	1.472	5.55556	7	4	0	3	580	562	580	562	580	562
0.50924	1.35	2.95858	7	4	0	2	517	529	517	529	518	528
0.50501	1.32	3.17460	7	4	3	2	502	488	502	488	502	488
0.37843	1.35	2.15517	6	2	0	2	520	510	520	510	520	510
0.5599	1.31	3.15457	8	4	0	2	516	502	516	502	516	503
0.39145	1.451	1.00000	6	4	0	3	578	546	578	546	578	546
0.47682	1.528	3.92157	7	4	0	5	569	559	569	559	569	559
0.41577	1.369	1.69205	6	4	6	2	496	478	496	478	496	478
0.45057	1.363	1.19048	7	4	3	2	516	490	516	490	515	492
0.57839	1.27	3.55872	8	4	2	2	515	518	515	518	515	518

Table 5

Predictions during the validation stage, obtained with some of the two types of employed neural networks

Input Data							Output Data		MLP(7:16:2)		MLP(7:12:12:2)		MLP(7:14:14:14:2)		MNN(7:24:2) type d	
$V/10^3$	D	$10^6/M$	N_{ac}	$N_{C=O}$	N_{CH3}	N_{CF3}	T_n (exp)	T_o (exp)	T_n (net)	T_o (net)	T_n (net)	T_o (net)	T_n (net)	T_o (net)	T_n (net)	T_o (net)
0.51972	1.28	1.34771	7	4	5	2	513	506	549	535	532	533	546	540	582	564
0.32173	1.44	6.80272	7	5	0	4	505	500	598	582	597	577	595	559	598	584
0.4898	1.309	1.30378	7	4	7	2	468	527	550	550	515	518	543	538	516	520
0.25837	1.514	2.29358	4	5	0	1	586	575	596	587	595	585	593	583	594	587
0.44945	1.36	4.7619	7	4	4	2	487	492	489	491	486	495	507	505	497	500
0.44	1.37	1.43266	7	4	2	2	553	551	521	499	515	493	551	512	536	510
0.56884	1.318	2.08768	10	2	0	2	530	515	494	498	480	495	510	474	489	519
0.53928	1.375	2.12766	7	4	3	4	523	516	513	503	530	519	568	547	568	544
0.5645	1.313	1.1655	10	2	0	2	540	520	501	483	514	512	508	474	520	564
0.44007	1.38	5	7	4	2	2	533	531	522	515	524	518	527	520	517	509
0.3425	1.485	0.41667	5	4	0	3	562	536	547	517	566	536	552	527	532	499
0.4059	1.38	5.88235	6	4	3	2	520	527	549	539	536	526	531	529	536	536
0.40596	1.387	5.55556	6	4	3	2	515	514	540	534	538	525	529	528	520	522
0.57356	1.35	1.31752	10	4	2	2	561	556	500	494	539	512	520	494	510	497
0.5485	1.3	2.95858	8	4	4	2	474	475	502	508	498	490	501	500	491	494

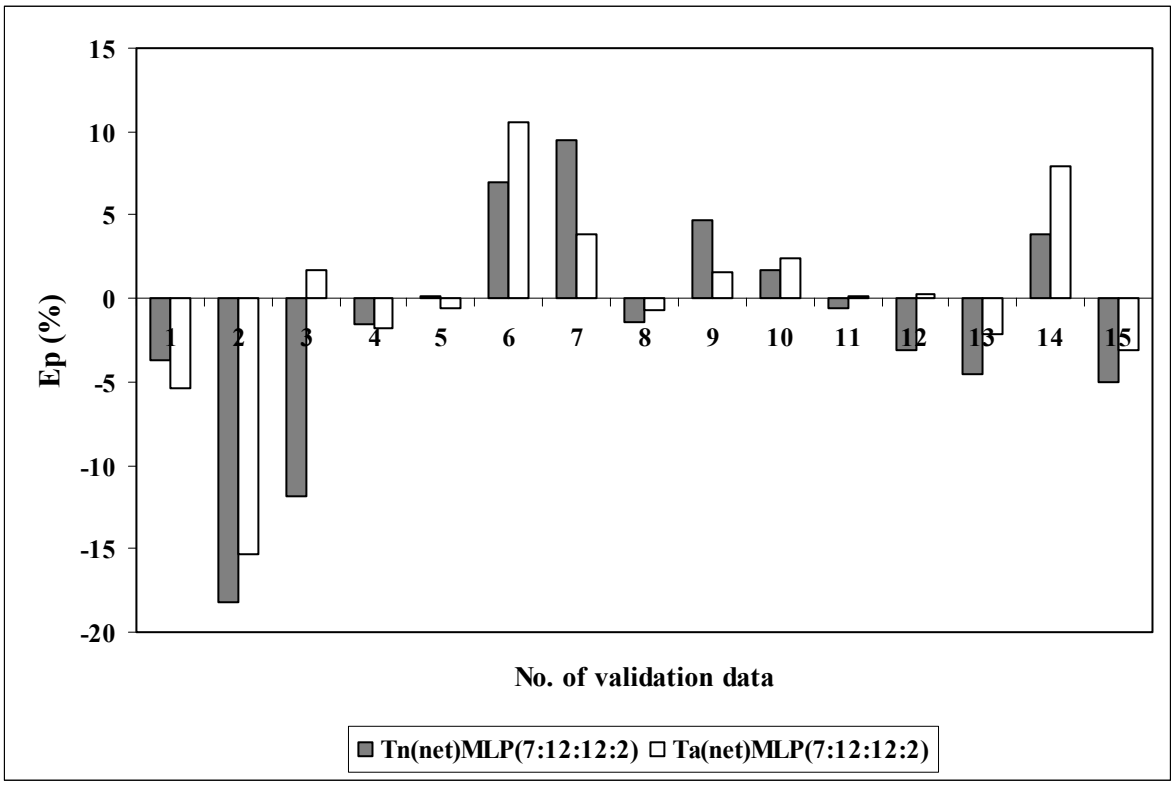


Fig. 3 – Values of the percentage errors obtained with MLP (7:12:12:2).

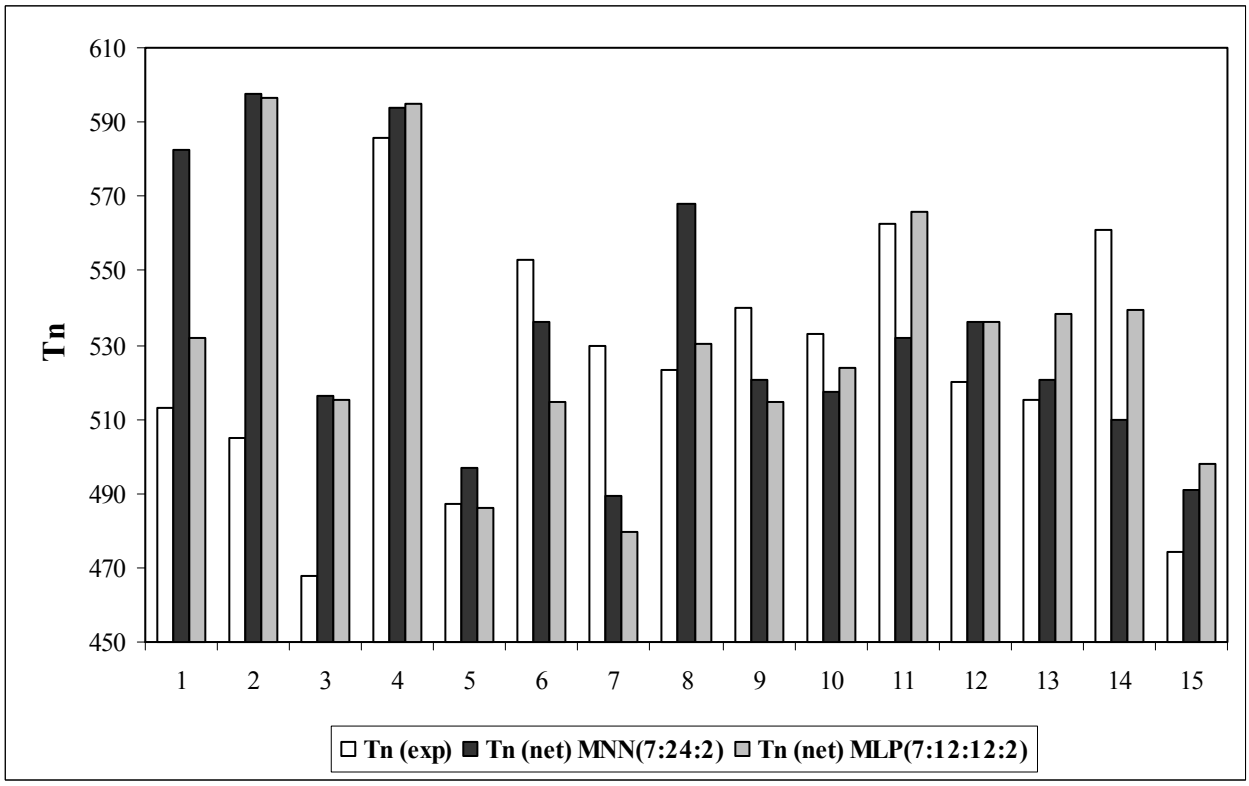


Fig. 4 – Experimental values for T_n, compared with the values obtained with neural models.

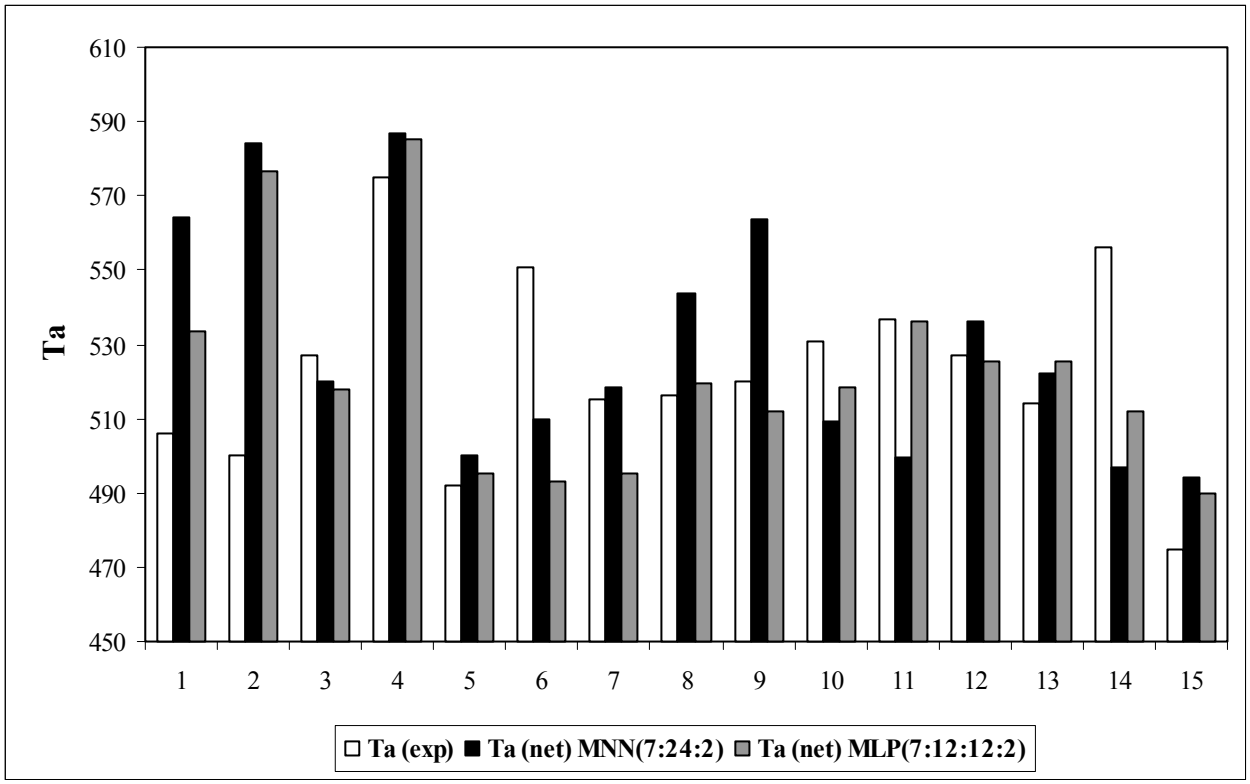


Fig. 5 – Experimental values for $T_{a,}$ compared with the values obtained with neural models.

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