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Neural networks for modelling material thermostability

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Abstract

In this paper, a new methodology based on neural networks is proposed to study the thermal degradation process of some cholesteric liquid crystals decorated with ferrocene. First of all, a set of experimental data is obtained applying thermal analysis methods, under dynamic heating conditions. Neural networks were used to predict the thermostability (appreciated by the temperature when the degradation process starts and the temperature corresponding to the maximal degradation rate) as function of some characteristics of the studied compounds (molecular weight, polarizability and some structural parameters determined by molecular modeling).

Keywords: neural networks, thermogravimetrical analysis, prediction material stability, liquid crystals.

1. Introduction

Since the discovery of liquid crystals and especially their important applications in LCD (liquid crystals display)'s, these materials received a great attention in the last years. It is well known that thermotropic liquid crystals are materials in which the ordering in liquid crystalline structures takes place in a certain temperature domain and implies the increasing of the material's temperature [1]. In order to be used for different applications, the first requirements of these

materials are the good thermal stability that is why it is easy to understand the important role that thermal stability plays for liquid crystals. For example, in the case of liquid crystals with the clearing point above the decomposition temperature, a study of thermal degradation process is requested [2]. One of the most important properties of the so-called feed forward neural networks is their ability to work as universal approximator of functions determined by a table (or set) of values of independent and dependent variables [3]. Many approaches are known in literature about efficient modeling and optimization of chemical processes using neural networks: direct modeling, neural networks based soft sensors, inferential modeling, inverse neural network modeling, optimization, process control, molecular design. These problems are reviewed in our previous work [4]. Current advancements, which include application of the neural networks to prediction of properties for both small molecules and macromolecules, show the generality and flexibility of this approach.

2. Problem Statement, background

The use of computational neural network as an artificial intelligence method has rapidly increased over the past years in many different science and technology fields. Some of them are: chemical science, molecular structure design and polymer properties prediction, weld deposits structures and properties prediction as function of very large number of variables etc. [5-7]. Neural networks model the non-linear structure-characteristics correlations more accurately and more easily as compared to other conventional approaches and that is why they are used to solve different difficult problems. The inverse problem concerning molecular design can also be solved by means of neuronal networks optimized with genetic algorithms, based on the fact that, wishing to obtain certain characteristics like, for instance, a good thermal stability, molecular structures are built that could provide such characteristics. The problems raised by molecular design are difficult and complex and therefore require the combined use of various types of artificial intelligence techniques.

3. Paper approach

Our paper is proposed to present a new methodology to study the thermal stability of some ferrocene derivatives with liquid crystals properties and to analyze the influence of some structural factors on the thermal stability. Prediction and optimization of thermal stability of liquid crystals properties is a complex and highly non-linear problem with no easy method to predict cholesteric liquid crystals decorated with ferrocene properties directly and accurately. The neural network modeling is performed to predict the thermal stability based on the structure of the compounds, quantified by a series of molecular descriptors. This procedure may substitute experiments, which are time and material consuming.

In this approach, the prediction of properties is correlated with the chemical structure, type of organic compound, molecular weight and polarizability parameter evaluated using molecular modeling simulation (input parameters of the network). Two outputs are considered for the neural model: T_i – the temperature when the degradation process starts and T_{max} - temperature corresponding to the maximal degradation rate. These parameters were evaluated using thermogravimetric analysis.

3.1. Methodology

Multilayer feed forward neural networks, trained with a backpropagation-learning algorithm, are the most popular neural networks. They are applied to a wide variety of chemically related problems. The basic feed forward network performs a nonlinear transformation of the input data in order to approximate the output data. In general, a neural network consists of processing neurons and information flow channel between the neurons, usually called „interconnections". Each processing neuron calculates the weighted sum of all interconnected signals from the previous layer plus a bias term and then generates an output through its activation transfer function. The adjustment of the neural network function to experimental data (learning process or training) is based on a non-linear regression procedure. Training is done by assigning random weights to each neuron, evaluating the output of the network and calculating the error between the output of the network and the known results by means of an error or objective function [8]. The purpose of developing a neural model is to devise a network (set of formulae) that captures the essential relationships in the data. These formulae are then applied to new sets of inputs to produce corresponding outputs - this is called generalization. Since a neural network is a nonlinear optimization process made up of a learning phase and a testing phase, the initial data set must be split into two subsets: one for training and one for testing. A network is said to generalize well when the input-output relationship, found by the network, is correct for input/output patterns of validation data which were never used in training the network (unseen data).

3.2. Experimental arrangement

New ferrocene derivatives with liquid crystal properties and various molecular designs have been synthesized and their thermal stability analyzed. The synthesis and mesomorphic crystals properties have been reported previously [9,10]. Thermal behavior of the ferrocene derivatives that contain in their molecular structure cholesteryl units and azo, ester or imine type connecting groups was investigated with a MOM-Hungary Derivatograph, which allows simultaneous recording of thermogravimetric, derivative thermogravimetric and differential thermal analysis, in statical air. Aluminum oxide as reference

material, calcined at 1000°C, platinum melter, heating rate of 10 K/min and a sample mass of 26±5 mg have been used. Thermostability was determined by applying as thermal stability criteria T_i – the temperature when the degradation process starts.

3.3. Case study

In finding new properties, thermal stability of the compounds is one of the most important requirements. Because liquid crystals are materials in which mesomorphic properties appear at a certain temperature domain, it is easy to understand the important role played by thermal stability for such compounds. In this paper we used an organic compounds database (47 in all), which includes a wide variety of ferrocene compounds (figure 1). The majority of ferrocene derivatives that contain in their molecular structure ferrocene, cholesteryl units and azo, ester or imine type connecting groups, presented high clearing points, so that the thermal stability study was required. The goal of this paper is to appreciate the thermal stability of certain organic compounds with liquid crystal characteristics using neural networks.

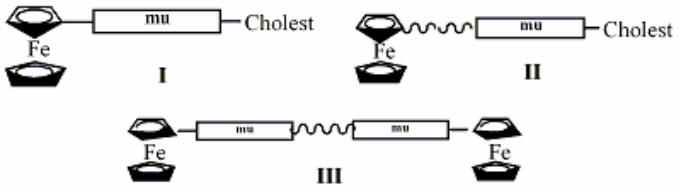

Figure 1. The general structures of the analyzed compounds

3.4. Results & discussions

By applying thermal analysis methods under dynamic heating conditions, the several conclusions regarding thermostability can be drawn. The ferrocene imine derivatives (type I in Fig.1) with three or four aromatic groups presents a reduced thermal stability, the sample starting to loose weight under 300°C. This behavior can be attributed to the increased number of connecting groups that can easily release small molecules such as N_2, CO_2, CO or CH_2O or to the bursting of the azo, imino and ester linkage. In the case of ferrocene derivatives (type II), the thermogravimetric data reveal a reduced thermal stability for ferrocene derivatives with keto group next to the ferrocene unit, as compared with analogues derivatives in which the keto group was reduced to methylene. Disubstituted ferrocene derivatives (type III) have a much lower thermal stability as compared with the monosubstituted ones, loss weight being observed starting with 180 ^{0}C.

Neural networks were used to predict the thermostability as function of some characteristics of the studied compounds. The thermostability is appreciated by the temperature when the degradation process starts (noted T_i) and the temperature corresponding to the maximal degradation rate (T_{max}), these representing the outputs of the network. The parameters considered as inputs of the neural model were: molecular weight (M), polarizability (P) and some structural characteristics: number of the aromatic groups (N_A) number of the ferrocene units (N_F) and number of the cholesteryl units (N_C).

The neural networks employed here are the simple feed-forward networks trained with the backpropagation algorithm. One major problem in the construction of neural networks is determining the network architecture, that is the number of hidden layers and the number of neurons in each hidden layer. An important feature related to the neural network topology is the generalization capability, which means how well does the network answer to unseen (validation) data. An amount of 10 % from training data was selected as validation data within cross-validation procedure used in training phase. The network's prediction performance on the validation data is continuously checked during training, which is stopped at the point where MSE (Mean Squared Error) on the validation data reaches a minimum. Neural network structure was thus determined using cross-validation - a highly recommended method for stopping network training and preventing over-fitting, being considered the point of best generalization. A MLP(5:24:8:2) is obtained with this procedure. Predictions of this neural model on training data proved that the network learned well the behavior of the system because small relative errors (1.32 % for T_i and 0.95 % for T_{max}) and high correlation (0.96) between the two sets of data - experimental and predicted data.

The most important test for the neural model is the validation phase where neural network predictions are compared to unseen data. The MLP(5:24:8:2) has good generalization capability as can be seen in Table 1. The relative errors (Er) under 6 % represented satisfactory predictions of the neural model. Table 1 contains experimental data (T_i and T_{max}) and results of the neural network modeling (T_i net and T_{max} net).

Table 1. Results of MLP(5:24:8:2) on validation data.

M	P	N_A	N_F	N_C	T_i	T_{max}	T_i net	T_{max} net	Er. T_i	Er. T_{max}
898.02	97.91	3	1	1	380	400	371	421	2.37	5.25
410.25	38.73	2	1	0	310	320	323	301	4.19	5.94
674.79	73.26	1	1	1	370	395	389	411	5.14	4.17
647.72	70.63	2	1	0	340	370	338	390	0.73	5.41
1582.9	172.7	4	1	2	240	265	250	253	4.17	4.53
771.05	88.78	2	0	1	240	250	228	237	5.00	5.20

4. Conclusions/Remarks/future work

This paper proposes a neural network based procedure for estimation the thermal behavior of some ferrocene derivative which are important compounds because their liquid crystalline proprieties.
The neural networks possess the ability to learn the behavior of the process without requiring the physical and chemical laws that govern the system. So they are recommended tools for application where the mechanistic description of the interdependence between variables is either unknown or very complex.
Simple architecture neural networks and simple methods of establishing the networks' structure are proposed for process modeling: feed forward networks with two hidden layers. Good prediction for the temperature when the degradation process starts and the temperature corresponding to the maximal degradation rate was obtained. Consequently, this neural network modeling methodology gives a very good representation for the material thermostability analysis.
A future work will deal with a complex analysis of the thermal stability of the compounds in our data base. More input parameters will be taken into account and their importance will be estimated within a genetic algorithm based procedure. A direct neural network modeling that means prediction of proprieties as function of structural parameters will be completed with a inverse modeling procedure in order to appreciate the structures that lead to imposed characteristics.

References

1. C. T. Imrie, C. Loubser, P. Engelbrecht, C.W. McCleland, Y.F. Zheng, J. Organomet. Chem., 48 (2003) 665.
2. D. Apreutesei, G. Lisa, N. Hurduc, D. Scutaru, J. Therm. Anal. and Calorim., 83 (2006) 335.
3. J. Zupan, J. Gasteiger, Neural Networks in Chemistry and Drug Design, 2nd Edition, Wiley-VCH, Weinheim, 1999.
4. S. Curteanu, A.M. Popa, Rev. Roum. Chim., 49 (2004) 3.
5. H. K. D. H. Bhadeshia, ISIJ International, 39 (1999) 966.
6. B. G. Sumpter, G. Getino, D. W. Noid, Annual Reviews, 45 (1994) 439.
7. A. Gakh, B. G. Sumpter, D. W. Noid, R. A. Sachleben, B. A. Moyler, J. of Inclusion Phenomena and Macrocyclic Chemistry, 27 (2004) 201.
8. F.A.N.Fernandes, L.M.F. Lona, Brazilian J. Chem. Eng., 22 (2005) 323.
9. D. Apreutesei, G. Lisa, Hiroki Akutsu, N. Hurduc, S. Nakatsuji and D. Scutaru, AOC (Journal of Applied Organometallic Chemistry) 19 (2005), 1022; b. unpublished results.
10. D. Apreutesei, G. Lisa, D. Scutaru, N. Hurduc, Journal of Optoelectronics and Advanced Materials, 83 (2006), 345.