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The Synthesis of Polyacrylamide-Based Multi-component Hydrogels. A Neural Network Modeling

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The present paper deals with the synthesis and swelling behavior of the semi- and interpenetrated multi-component networks based on polyacrylamide. The networks were prepared by a “single step” process of polymerization/crosslinking and are constituted by a polyacrylamide matrix and a biodegradable interpenetrated polymer. The synthesis was carried out in aqueous medium, for pre-established conditions of temperature, duration and concentrations of the polymerization system components (monomer, initiator, crosslinking agent, inclusion polymer). The yield in crosslinked polymer, the swelling degree and the swelling rate constant were the parameters of interest in this experimental study.

In order to evaluate the quantitative influence of the reaction conditions upon yield and swelling degree, different classes of neural networks are tested. Due to their performance, Jordan Elman networks – a special type of networks – were chosen.

A trial and error method leads to a neural network topology with two hidden layers and different activation functions in context, intermediate and output layers. The predictions provided by this model are in good agreement with the experimental data. A general modeling strategy, useful for different polymerization processes, is also developed.

Keywords: Crosslinked polymer, swelling degree, multi-component hydrogels, Jordan Elman neural networks, modeling strategy

1 Introduction

Semi- or interpenetrating multi-component network-type hydrogels are materials with three-dimensional structure, characterized by a high swelling capacity.

Due to the high water retention ability (more than 90%), such networks possess a flexibility similar to that of the natural tissue. Special properties (mechanical, diffusion and absorption) of the three-dimensional network-type hydrogels make possible their use in various domains – food, cosmetics, pharmaceutical industry, medicine, tissue engineering, agriculture, electrotechnics and electronics etc. (1–6).

For many applications, e.g. controlled-release systems, agrochemical products, these materials are required to present a high capacity of biodegradation under the action of the biologic fluids or of the microorganisms present in the soil.

To achieve this goal, different preparation strategies were considered (7):

- (a) The use of biodegradable natural or synthetic polymers;
- (b) The chemical or biological modification of natural polymers;
- (b) The association of non-biodegradable polymers with polymeric materials with pronounced biodegradability.

The multi-component networks based on polyacrylamide (PAAm) are particularly appropriate for biomedical, pharmaceutical or agricultural applications. Thus, due to the analgesic effects and to their ability to speed up the healing process, polyacrylamide hydrogels (PAAm – 5% and oxygenated water – 95%) are used in aesthetic surgery (5, 8).

Polyacrylamide hydrogels present selective biodegradability under the action of the gastro-intestinal juices, so that they can be used as covering agent for tablets to protect the active principle, to conceal the non-agreeable taste and smell, as well as to control the release of the active principle. Three-dimensional networks based on polyacrylamide are used in ophthalmology as mechanical protectors for iris, retina and corneal endothelia (5).

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Polyacrylamide gels are very useful for soil improvement, i.e. for the stabilization of sandy soils, in promoting the selective sorption of nutrients by plants, in increasing the permeability and agricultural efficiency of non-structured soils or stopping of erosion (6, 9, 10). Multi-component networks based on polyacrylamide are used as controlled release systems for fertilizers and present a high efficiency in the cultivation of saplings and plants on reduced surfaces (green houses, gardens).

The present paper deals with the synthesis and swelling behavior of semi- and interpenetrated multi-component networks based on polyacrylamide. The networks were prepared by a “single step” process of polymerization/crosslinking and consist of a polyacrylamide matrix and a biodegradable interpenetrated polymer (11, 12).

Artificial neural networks (ANN) became alternative models to traditional explicit constitutive ones, especially for complex and non-linear processes. Their critical advantage is the flexibility of the model that can adapt to complex interrelations and is capable to detect even small signals at a large noise level. Hence, ANN are applied where no simple mathematical model can be assumed, many potential parameters interact and the experimental errors are high (13).

Prediction and optimization of polymer properties (especially in the case of high molecular weight polymers), is a complex and highly non-linear problem, with no easy method to solve directly and accurately. The effects of modifying the reaction conditions upon the polymerization and the properties of the resulting polymer are not easy to investigate experimentally, given the large number of possible changes. This severely curtails the design of new polymers with specific end-use properties (14).

Neural networks are frequently used in polymer reaction engineering in different types of applications. The open literature presents many attempts concerning neural network applications for polymerization processes: direct modeling with different types of neural networks (15, 16), neural networks based soft sensors (17), inferential modeling (18, 19), inverse neural network modeling (20–22), optimization (23–26), process control (27–29). These types of applications were reviewed in our precedent work (30).

Fernandes and Lona provide a brief tutorial on simple and practical procedures that can help in selecting and training neural networks and address complex cases where the application of neural networks have been successful in the field of polymerization (31). A significant paper for polymer reaction engineering was published by Roy *et al.* and concerns polymer property prediction and optimization using neural networks (14).

The “single step” preparation process of multi-component hydrogels based on polyacrylamide is a very complex one, so that the neural network modeling was applied to control the synthesis. Different classes of neural networks are tested and, as function of their performance, a special type of networks was chosen – Jordan Elman networks. A trial and error method leads to a neural network

topology with two hidden layers and different activation functions in context, intermediate and output layers. The predictions provided by this model are in good agreement with the experimental data.

The paper develops a general methodology for neural network modeling with high chances to be applied successfully to other complex polymerization processes.

2 Experimental

Mono- and multi-component networks based on polyacrylamide were synthesized by a “single step” procedure (simultaneous polymerization/crosslinking reactions).

Acrylamide (Am) (Merck), formaldehyde (FA), 37% solution (S.C. Chemical Company), potassium persulfate were used as received. The inclusion polymers, i.e., starch (Merck), poly(vinyl alcohol) (Merck) and gelatin (Merck) were commercial products. These polymers were introduced to increase the biodegradation capacity of the polyacrylamidic networks.

The synthesis was carried out in aqueous medium, for pre-established conditions of temperature, duration and concentrations of the polymerization system components (monomer, initiator, crosslinking agent, inclusion polymer). The obtained hydrogels were repeatedly washed to remove the unreacted monomer and crosslinking agent as well as the macromolecular compounds (linear polyacrylamide, inclusion polymer) not immobilized within the network. The reaction products were dried at 40°C up to constant weight.

The yield in crosslinked polymer was determined gravimetrically. The swelling behavior was studied using a homemade device, functioning on the principle of Dogatkin instrument. The measurements were carried out at ambient temperature. The maximum swelling degree was determined using the relation (1):

$$\alpha = W_w W_w / W_p \times 100 \quad (1)$$

where W_w is the mass of absorbed water and W_p the mass of dried polymer.

The swelling rate constant was determined using the Equation 2:

$$\ln \frac{\alpha_{\max} - \alpha_t}{\alpha_{\max}} = k \cdot t \quad (2)$$

where α_{\max} and α_t are the maximum swelling degree and the swelling degree at time t , respectively, and t is process duration.

The experimental results are presented in Tables 1–4, where C_M represents the monomer (acrylamide) concentration, C_I is initiator ($K_2S_2O_8$) concentration, C_A is crosslinking agent (formaldehyde) concentration, PI represents the amount of inclusion polymer (starch, poly(vinyl alcohol) (PVA), gelatin), T is the temperature, t is the reaction time,

Table 1. Experimental data for monocomponent networks of hydrogels based on PAAm

No. crt.	C_M [mol/l]	C_I [% weight]	C_A [mol/l]	T [°C]	t [h]	η [%]	α [%]	k [min ⁻¹]
1	0.28	0.5	12.33	50	5	4.71	2 642	9.18 10 ⁻⁵
2	0.56					9.40	3 876	8.29 10 ⁻⁵
3	0.84					16.04	4 443	7.25 10 ⁻⁵
4	1.12					17.61	4 673	7.58 10 ⁻⁵
5	1.40					21.63	4 870	7.18 10 ⁻⁵
6	1.68					23.50	6 950	5.85 10 ⁻⁵
7	1.96					28.59	9 014	4.92 10 ⁻⁵
8	2.24					38.70	9 035	5.57 10 ⁻⁵
9	3	0.094	12.33	50	5	38.95	1 020	1.20 10 ⁻⁴
10		0.18				40.11	1 100	1.20 10 ⁻⁴
11		0.28				40.17	1 134	0.98 10 ⁻⁴
12		0.37				40.51	1 177	0.97 10 ⁻⁴
13		0.47				41.08	1 211	0.97 10 ⁻⁴
14		0.56				41.59	1 215	0.94 10 ⁻⁴
15		0.66				43.94	1 281	0.93 10 ⁻⁴
16		0.75				44.85	1 486	0.89 10 ⁻⁴
17		0.85				44.85	1 540	0.84 10 ⁻⁴
18		0.94				45.19	1 027	1.10 10 ⁻⁴
19	3	0.5	0.5	50	5	98.15	1 215	9.11 10 ⁻⁵
20			1			92.55	1 250	9.04 10 ⁻⁵
21			1.5			87.43	1 300	8.98 10 ⁻⁵
22			2			86.28	3 262	8.88 10 ⁻⁵
23			4			69.88	4 256	6.23 10 ⁻⁵
24			6			59.74	6 478	5.91 10 ⁻⁵
25			8			51.06	6 811	5.88 10 ⁻⁵
26			10			43.88	7 040	5.82 10 ⁻⁵
27			12			38.92	7 476	5.52 10 ⁻⁵
28			12.33			38.00	7 588	5.46 10 ⁻⁵
29	3	0.5	12.33	30	5	5.92	2 175	8.81 10 ⁻⁵
30				33		19.12	2 686	7.03 10 ⁻⁵
31				35		31.81	5 102	6.14 10 ⁻⁵
32				40		34.26	8 225	5.61 10 ⁻⁵
33				45		35.59	8 377	5.59 10 ⁻⁵
34				47		38.15	8 432	5.59 10 ⁻⁵
35				50		38.70	9 035	5.57 10 ⁻⁵
36				54		42.02	9 986	5.49 10 ⁻⁵
37				57		43.79	10 998	5.44 10 ⁻⁵
38				61		47.39	12 434	4.71 10 ⁻⁵
39	3	0.5	12.33	50	1	29.27	4 663	9.02 10 ⁻⁵
40					2	36.45	4 745	5.20 10 ⁻⁵
41					3	39.26	5 238	5.09 10 ⁻⁵
42					4	40.11	5 575	5.05 10 ⁻⁵
43					5	43.55	5 750	4.72 10 ⁻⁵
44					6	44.21	6 263	4.69 10 ⁻⁵
45					7	46.31	7 444	4.68 10 ⁻⁵

η is the yield in crosslinked polymer, α is the swelling degree and k is the swelling rate constant.

2.1 Neural Network Modeling

High molecular weight polymer system represents complex classes of materials and is very difficult to model. Besides being highly non-linear, there are a large number of pa-

rameters that need to be accurately defined if such systems are to be properly characterized (14). The relationships between the parameters being modeled and the actual behavior of these variables in the real world must be correlated as precisely as possible. However, in most cases, this is not possible and several approximations and simplifications are often made at various stages. When dealing with sparse, noisy or incomplete data, conventional methods frequently

Table 2. Experimental data of bicomponent hydrogels based on PAAm and starch

No. crt.	C_M [mol/l]	C_I [% weight]	C_A [mol/l]	T [°C]	t [h]	PI [g]	η [%]	α [%]	k [min ⁻⁵]
1	0.35	0.5	12.33	50	5	1	13.73	6 194	5.16 10 ⁻⁵
2	0.70						15.24	4 504	6.05 10 ⁻⁵
3	1.05						17.00	2 750	7.75 10 ⁻⁵
4	1.40						19.32	2 575	7.81 10 ⁻⁵
5	1.75						20.30	2 477	7.93 10 ⁻⁵
6	2.10						25.70	2 055	8.06 10 ⁻⁵
7	2.45						30.26	2 023	8.14 10 ⁻⁵
8	3	0.07	12.33	50	5	1	27.13	1 592	9.00 10 ⁻⁵
9		0.14					27.96	1 727	8.76 10 ⁻⁵
10		0.21					29.01	1 791	8.76 10 ⁻⁵
11		0.28					29.12	1 873	8.57 10 ⁻⁵
12		0.36					30.23	1 885	8.41 10 ⁻⁵
13		0.43					32.42	1 887	8.35 10 ⁻⁵
14		0.5					30.26	2 023	8.14 10 ⁻⁵
15	3	0.5	0.5	50	5	1	9.98	1 750	8.56 10 ⁻⁵
16			1				13.22	1 859	8.37 10 ⁻⁵
17			1.5				16.70	2 679	8.26 10 ⁻⁵
18			2				23.61	3 838	8.08 10 ⁻⁵
19			4				24.08	3 882	8.06 10 ⁻⁵
20			6				28.17	4 144	7.89 10 ⁻⁵
21			8				39.16	4 149	7.80 10 ⁻⁵
22			10				42.66	4 217	7.77 10 ⁻⁵
23			12				48.48	5 759	7.75 10 ⁻⁵
24			12.33				30.26	2 023	8.14 10 ⁻⁵
25	3	0.5	12.33	29	5	1	25.62	3 558	6.76 10 ⁻⁵
26				36			26.47	3 051	6.79 10 ⁻⁵
27				43			27.56	2 119	7.59 10 ⁻⁵
28				50			30.26	2 023	8.14 10 ⁻⁵
29				57			34.02	1 565	8.22 10 ⁻⁵
30				64			37.77	1 560	8.49 10 ⁻⁵
31	3	0.5	12.33	50	1	1	27.05	1 536	8.84 10 ⁻⁵
32					2		29.25	1 969	8.71 10 ⁻⁵
33					3		30.06	1 982	8.55 10 ⁻⁵
34					4		30.07	2 002	8.38 10 ⁻⁵
35					5		30.26	2 023	8.14 10 ⁻⁵
36					6		29.06	2 167	7.67 10 ⁻⁵
37	3	0.5	12.33	50	5	0.25	33.97	4 802	6.91 10 ⁻⁵
38						0.50	32.50	3 292	7.47 10 ⁻⁵
39						0.75	32.25	2 112	8.05 10 ⁻⁵
40						1.00	30.26	2 023	8.14 10 ⁻⁵
41						1.25	30.76	1 582	8.57 10 ⁻⁵
42						1.50	30.06	1 548	8.96 10 ⁻⁵

fail. In addition, conventional methods lack generalization, fail to incorporate statistical and systematic fluctuations, and in most cases are limited to finite state spaces. Thus, the important correlations between model developed and the real properties may be lost or not captured correctly (14). Consequently, the modeling with neural networks can overcome these difficulties due to a series of advantages: the possibility to apply this method to complex non-linear processes, the ease in obtaining and using neural models, the possibility to substitute experiments with predictions. Neural models need only input-output data (experimental

or simulation data) and thus their advantages are evident against the complexity of the computation.

The neural network modeling implies the following stages: collecting the training data by experiments, making up the training and testing data sets, developing the neural network topology, training and, finally, establishing the performance of the neural network model by comparing the network prediction to unseen (validation) data.

The available set of data is presented in Tables 1–4 and they are divided into training (a number of 157 data) and

Table 3. Experimental data of bicomponent hydrogels based on PAAm and gelatin

No. crt.	C_M [mol/l]	C_I [% weight]	A [mol/l]	T [°C]	t [h]	PI [g]	η [%]	α [%]	k [min ⁻¹]
1	0.35	0.5	12.33	50	5	1	2.47	1 312	8.15 10 ⁻⁵
2	0.70						3.69	3 132	6.93 10 ⁻⁵
3	1.05						12.86	3 245	6.77 10 ⁻⁵
4	1.40						21.43	3 451	6.55 10 ⁻⁵
5	1.75						24.53	5 214	6.47 10 ⁻⁵
6	2.10						26.28	6 175	6.11 10 ⁻⁵
7	2.45						29.19	6 658	5.73 10 ⁻⁵
8	2.80						34.45	6 796	5.08 10 ⁻⁵
9	3.15						36.91	7 323	4.87 10 ⁻⁵
10	3	0.06	12.33	50	5	1	10.70	6 128	6.30 10 ⁻⁵
11		0.12					28.03	6 183	6.25 10 ⁻⁵
12		0.18					28.59	6 203	6.14 10 ⁻⁵
13		0.25					28.91	6 240	5.90 10 ⁻⁵
14		0.31					29.08	6 343	5.87 10 ⁻⁵
15		0.37					29.26	6 440	5.79 10 ⁻⁵
16		0.5					29.19	6 658	5.73 10 ⁻⁵
17	3	0.5	0.5	50	5	1	18.00	0	0
18			1				18.58	0	0
19			1.5				18.85	0	0
20			2				49.93	1 475	8.48 10 ⁻⁵
21			4				43.00	1 767	8.03 10 ⁻⁵
22			6				34.17	2 682	7.77 10 ⁻⁵
23			8				26.25	3 400	6.76 10 ⁻⁵
24			10				23.16	3 944	6.49 10 ⁻⁵
25			12				20.10	5 053	6.22 10 ⁻⁵
26			12.33				29.19	6 658	5.73 10 ⁻⁵
27	3	0.5	12.33	29	5	1	0	0	0
28				36			10.66	8 520	4.75 10 ⁻⁵
29				43			26.02	6 820	5.17 10 ⁻⁵
30				50			29.19	6 658	5.73 10 ⁻⁵
31				57			30.70	5 155	6.19 10 ⁻⁵
32				64			31.15	3 491	7.39 10 ⁻⁵
33	3	0.5	12.33	50	1	1	12.24	7 520	4.32 10 ⁻⁵
34					2		16.71	7 217	4.45 10 ⁻⁵
35					3		19.10	6 888	4.86 10 ⁻⁵
36					4		20.70	6 710	5.04 10 ⁻⁵
37					5		29.19	6 658	5.73 10 ⁻⁵
38					6		25.83	5 271	6.80 10 ⁻⁵
39	3	0.5	12.33	50	5	0.25	23.79	7 300	4.48 10 ⁻⁵
40						0.5	27.13	6 820	4.72 10 ⁻⁵
41						0.75	28.03	6 728	5.18 10 ⁻⁵
42						1	29.19	6 658	5.73 10 ⁻⁵
43						1.25	30.85	5 622	6.10 10 ⁻⁵
44						1.5	32.22	4 051	6.45 10 ⁻⁵

validation (20 data, approximately 10%) data sets. Seven input variables were considered: C_M (monomer concentration), C_I (initiator concentration), C_A (crosslinking agent concentration), PI (amount of inclusion polymer), T (temperature), t (reaction time) and type of included polymer codified as 1 – no polymer added, 2 – starch, 3 – PVA and 4 – gelatin. The outputs of the neural model are η (yield in crosslinked polymer) and α (swelling degree). Thus, the neural network modeling established the influence

of reaction conditions on reaction yield and swelling degree.

The next task in the modeling technique is to develop the neural network topology. To determine the optimum network configuration, different elements were tested: neural network types, number of hidden layers and neurons, learning rules and activation functions.

In the present paper, four types of neural networks that have as common characteristic the supervised learning

Table 4. Experimental data of bicomponent hydrogels based on PAAm and PVA

No. crt.	C_M [mol/l]	C_I [% weight]	C_A [mol/l]	T [°C]	t [h]	PI [g]	η [%]	α [%]	k [min^{-1}]
1	0.23	0.5	12.33	50	5	1	6.53	750	$9.92 \cdot 10^{-5}$
2	0.46						10.27	1 410	$9.83 \cdot 10^{-5}$
3	0.69						12.24	1 980	$6.63 \cdot 10^{-5}$
4	0.92						12.84	2 030	$5.61 \cdot 10^{-5}$
5	1.15						15.63	2 232	$5.59 \cdot 10^{-5}$
6	1.38						15.75	2 273	$5.54 \cdot 10^{-5}$
7	1.61						16.78	2 276	$5.51 \cdot 10^{-5}$
8	1.84						19.34	2 275	$5.48 \cdot 10^{-5}$
9	3	0.06	12.33	50	5	1	18.51	7 309	$5.08 \cdot 10^{-5}$
10		0.12					18.54	7 504	$5.02 \cdot 10^{-5}$
11		0.18					18.61	7 578	$5.01 \cdot 10^{-5}$
12		0.25					18.76	7 610	$4.94 \cdot 10^{-5}$
13		0.31					19.24	7 640	$4.93 \cdot 10^{-5}$
14		0.37					19.96	7 670	$4.89 \cdot 10^{-5}$
15		0.44					21.06	7 817	$4.80 \cdot 10^{-5}$
16		0.5					19.34	2 275	$5.48 \cdot 10^{-5}$
17	3	0.5	0.5	50	5	1	46.00	3.832	$4.58 \cdot 10^{-5}$
18			1				43.10	3 800	$4.60 \cdot 10^{-5}$
19			1.5				42.23	3 766	$4.63 \cdot 10^{-5}$
20			2				38.77	3 700	$4.63 \cdot 10^{-5}$
21			4				27.61	3 541	$4.82 \cdot 10^{-5}$
22			6				21.90	3 195	$5.00 \cdot 10^{-5}$
23			8				15.85	3 027	$5.19 \cdot 10^{-5}$
24			10				13.26	2 800	$5.26 \cdot 10^{-5}$
25			12				10.42	2 318	$5.48 \cdot 10^{-5}$
26			12.33				19.34	2 275	$5.48 \cdot 10^{-5}$
27	3	0.5	12.33	29	5	1	2.83	4 410	$4.99 \cdot 10^{-5}$
28				36			11.57	4 235	$5.07 \cdot 10^{-5}$
29				43			15.57	3 700	$5.19 \cdot 10^{-5}$
30				50			19.34	2 275	$5.48 \cdot 10^{-5}$
31				57			18.81	2 096	$5.95 \cdot 10^{-5}$
32				64			18.15	1 896	$6.43 \cdot 10^{-5}$
33	3	0.5	12.33	50	1	1	16.36	1 996	$7.63 \cdot 10^{-5}$
34					2		16.56	2 015	$7.07 \cdot 10^{-5}$
35					3		18.29	2 120	$6.85 \cdot 10^{-5}$
36					4		18.53	2 200	$6.25 \cdot 10^{-5}$
37					5		19.34	2 275	$5.48 \cdot 10^{-5}$
38					6		18.70	2 330	$5.29 \cdot 10^{-5}$
39	3	0.5	12.33	50	5	0.25	22.45	5 280	$5.23 \cdot 10^{-5}$
40						0.50	22.32	4 314	$5.32 \cdot 10^{-5}$
41						0.75	21.02	3 380	$5.36 \cdot 10^{-5}$
42						1.00	19.34	2 275	$5.48 \cdot 10^{-5}$
43						1.25	19.17	2 116	$5.98 \cdot 10^{-5}$
44						1.50	18.50	1 792	$6.99 \cdot 10^{-5}$

control (Multi-layer Perceptrons (MLP), Generalized Feed-forward Networks (GFN), Modular Neural Networks (MNN) and Jordan Elman Networks (JEN)) have been tested.

Multi-layer perceptron can approximate any input/output map, but it trains slowly and requires lots of training data. Generalized feed-forward networks are a generalization of MLP, the difference being into the connections that can jump over one or more layers. In practice,

generalized feed-forward networks often solve the problem much more efficiently. Modular feed-forward networks are a special class of MLP, using several parallel MLPs, and then recombining the results. This capability tends to create some structure within topology, which will foster specialization of function in each sub-module. Jordan and Elman networks supply the multi-layer perceptron with context units, which are processing elements that remember past activity. Context units provide the neural network

with the ability to extract temporal information from the data (32).

The determination of neural network topology includes the number of hidden layers, the number of neurons in each layer and the connections between them. The number of neurons in the input and output layers is given by the dimensionality of the problem. In our case, there are seven input quantities and two outputs, corresponding to the chosen input and output variables. Regarding the number of hidden layers, it has been proved that a neural network requires at most two hidden layers to approximate any function to an arbitrary order of accuracy (33).

The procedure for determination of neural network architecture applied in this work is the trial and error method and the number of hidden layers and units was established by training a different range of networks and selecting the one that best balanced generalization performance against network size.

The objective of the training procedure is to find a set of possible weights that will enable the network to produce a prediction (b_i) as similar as possible to the known output (o_i). This is achieved by minimizing the cost function, E , which is the mean square error (33).

$$E = \frac{1}{2q} \sum_1^q (o_i - b_i)^2 \tag{3}$$

where q is the number of the training patterns ($q = 157$ for this case study).

When the error becomes too large, the weights have to be adjusted and the process repeats to evaluate the output of the neural network. This cycle is repeated till the error becomes low or the stop criterion is satisfied (34).

The best results were obtained with MLP and JEN models (Figures 1 and 2).

For JEN networks there are four basic topologies, differing by the layers that feed the context units. The default configuration feeds the context units with the input sam-

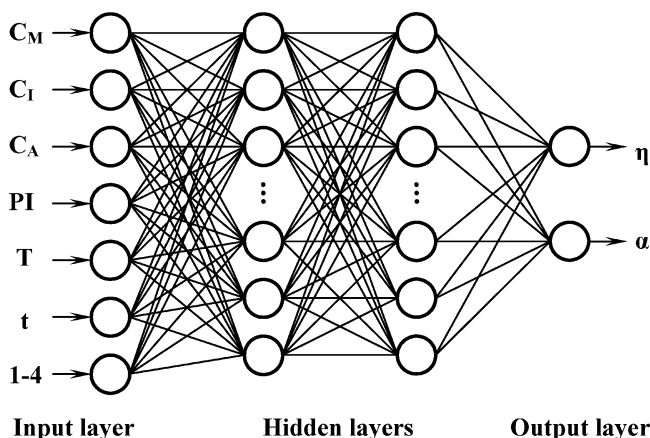


Fig. 1. Topology of MLP model.

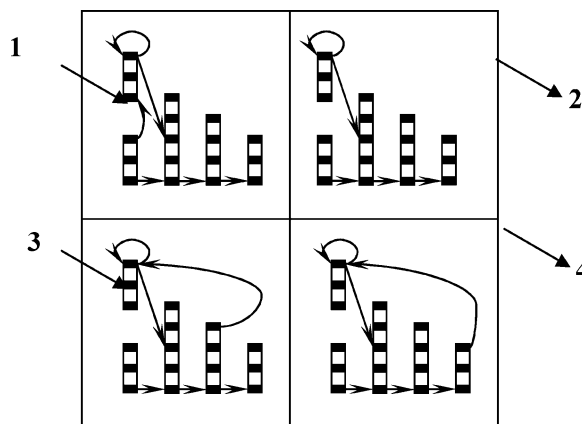


Fig. 2. Topologies of JEN model.

ples, providing an integrated past of the input (memory traces) (configuration 1 in Figure 2). A second configuration creates memory traces from the first hidden layer, as proposed by Elman (32) (configuration 2 in Figure 2). A third possibility is to use the past of the last hidden layer activations as input to the context units (configuration 3 in Figure 2). The final choice is to use the past of the output layer to create the memory traces, as proposed by Jordan (configuration 4 in Figure 2).

Table 5 presents the best topologies for the four types of neural networks tested in the approached case study, with their performances, i.e., mean square error (MSE), correlation between experimental and simulation data (r) and percent error (E_p). The well known back-propagation algorithm was used for network training.

The best neural model in Table 5 is the Jordan–Elman network with two hidden layers having 42 and 14 neurons, respectively, noted JEN(7:42:14:2), in configuration 4 (Figure 2). The advantage of more hidden layers is that different activation functions can be selected. While the most commonly used activation is logistic, in many cases other functions or combinations of functions are known to perform better (14). For the JEN model in Table 5, hyperbolic tangent was used as activation function for hidden and output layers and also for context units. The performance of this neural model can be improved by choosing an adequate combination of activation functions. Many trialed series

Table 5. Different neural networks trained for the synthesis of hydrogels based on PAAm

No. crt.	Network topology	MSE	r	E _p
1	MLP(7:42:14:2)	0.000449	0.9984	1.9583
2	GFF(7:40:20:2)	0.001113	0.9778	8.7477
3	MNN (7 : 20 : 10 : 2)	0.002027	0.9609	9.8828
4	JEN(7:42:14:2)	0.000231	0.9992	1.2311

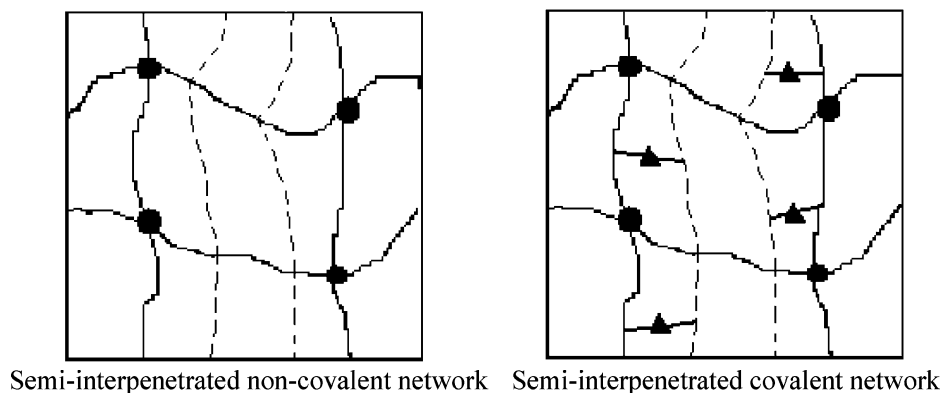


Fig. 3. Structure of semi-interpenetrated networks.

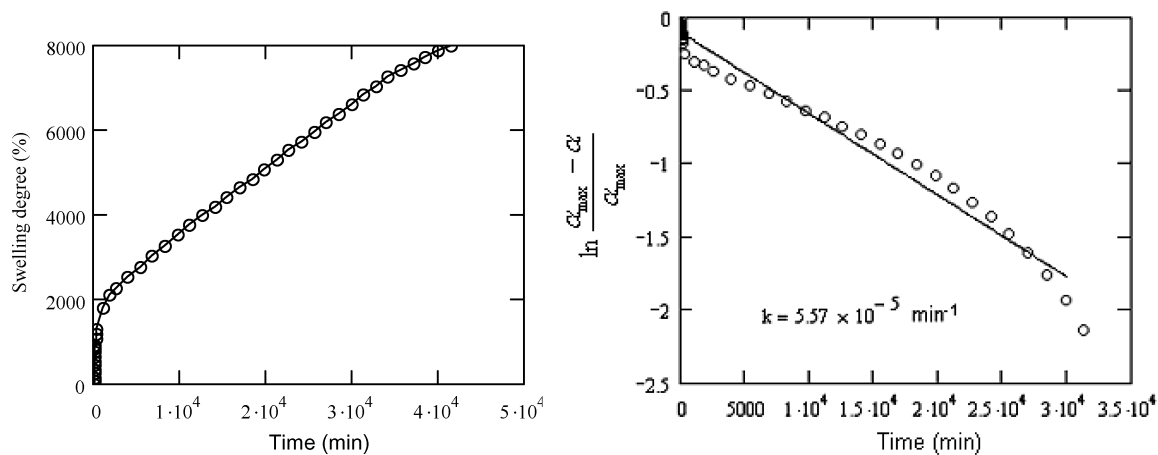


Fig. 4. Typical swelling kinetic curves for mono-component networks (sample No. 8, Table 1).

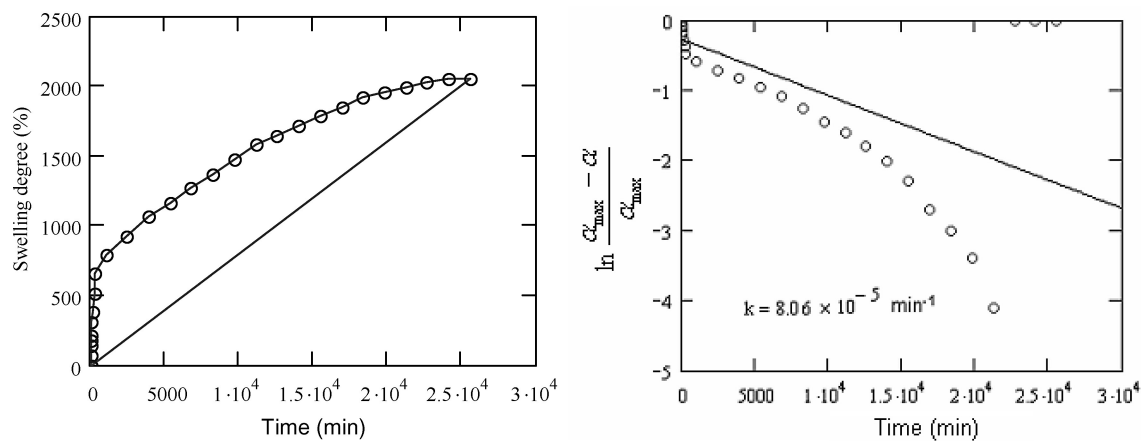


Fig. 5. Typical swelling kinetic curves for bi-component networks with starch (sample No. 6, Table 2).

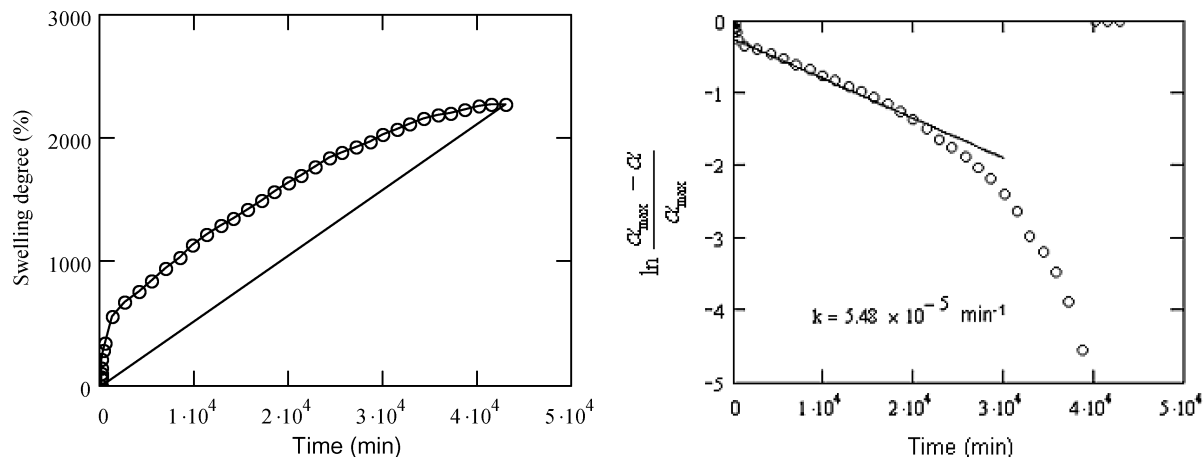


Fig. 6. Typical swelling kinetic curves for bi-component networks with PVA (sample No. 8, Table 3).

of network were trained, considering different activation functions, in different combinations. It appears that the best combination was Integrator Axon for context units, Tangent Hyperbolic Axon for the two hidden layers and Sigmoid Axon for the output layer. In these conditions, the training performance for JEN(7:42:14:2) becomes: $MSE = 0.0000872$, $r = 0.9997$ and $E_p = 0.9764$. Consequently, an adequate combination of the transfer functions in the neural model represents a way of improving the performances of the network.

3 Results and Discussion

A simultaneous polymerization/crosslinking procedure was applied for the preparation of polyacrylamidic hydrogels to obtain polymers with different network densities and morphologies. The synthesis was carried out in presence of some natural (starch and gelatin) or synthetic (PVA) polymers with high biodegradability and yielded

semi-interpenetrated non-covalent or covalent networks. The most probable structures are of non-covalent type, without excluding the formation of more or less important interpenetrated domains (Figure 3).

The presence of these domains is due to the covalent bonds appearing through the interactions of the functional groups of the included polymers, those from PAAm and from the crosslinking agent.

The use of the inclusion polymers was intended to increase of the biodegradation capacity of PAAm, a polymer characterized by a reduced biodegradability, both in physiological and environmental conditions.

The obtained experimental data show that the synthesized networks, mono-component and multi-component, present a high hydrosorption capacity. It appears that, in all cases, monomer and initiator concentrations, temperature and polymerization /crosslinking duration influence the yield of the crosslinked polymer up to maximum value of 50%. The relatively low yields are due to the formation of PAAm homopolymer that doesn't participate to

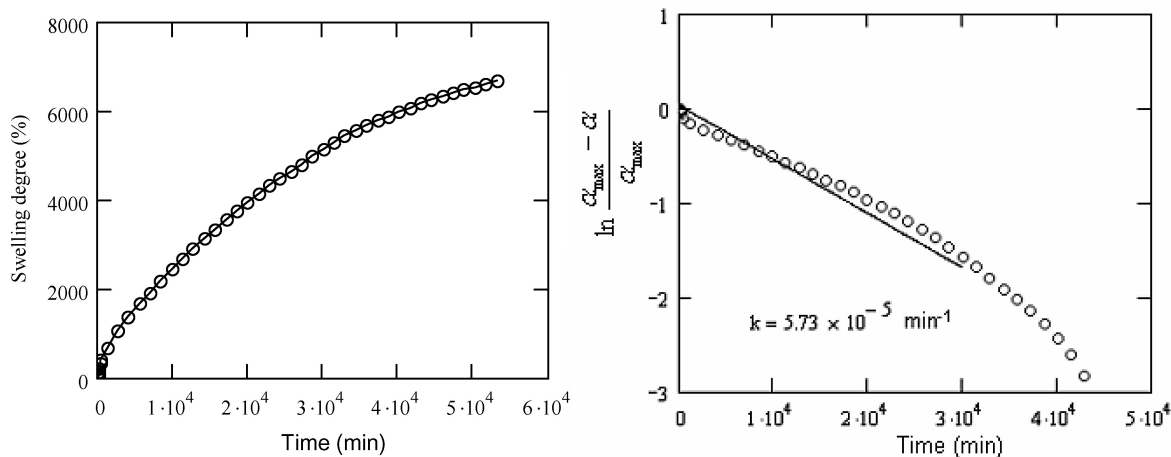


Fig. 7. Typical swelling kinetic curves for bi-component networks with gelatin (sample No. 7, Table 4).

Table 6. Experimental and predicted polymer yield in the validation phase for JEN(7:42:14:2)

Type	C_M [mol/l]	C_I [% weight]	C_A [mol/l]	T [°C]	t [h]	PI [g]	η [%]	α [%]	η [%] JEN	E_r [%]
1	1.68	0.5	12.33	50	5	0	23.5	6950	21.90	6.8085
1	3	0.47	12.33	50	5		41.1	1211	43.90	6.8646
1	3	0.5	4	50	5		69.9	4256	65.70	5.9816
1	3	0.5	12.33	54	5		42	9986	45.50	8.2817
1	3	0.5	12.33	50	6		44.2	6263	42.80	3.1893
2	1.4	0.5	12.33	50	5	1	19.3	2575	20.70	7.1428
2	3	0.21	12.33	50		1	29	1791	27.20	6.2392
2	3	0.5	4	50		1	24.1	3882	24.20	0.4983
2	3	0.5	12.33	57		1	34	1565	36.80	8.1716
2	3	0.5	12.33	50		1.3	30.8	1582	29.90	2.7958
3	0.92	0.5	12.33	50	5	1	12.8	2030	13.10	2.0249
3	3	0.31	12.33			1	19.2	7640	18.40	4.3659
3	3	0.5	6			1	21.9	3195	20.00	8.6757
3	3	0.5	12.33			1	19.3	2275	18.60	3.8262
3	3	0.5	12.33			0.8	21	3380	22.80	8.4681
4	1.75	0.5	12.33	50	5	1	24.5	5214	22.30	9.0909
4	3	0.18	12.33			1	28.6	6203	26.30	8.0097
4	3	0.5	2			1	49.9	1475	47.10	5.6679
4	3	0.5	12.33			1	29.2	6658	27.80	4.7619
4	3	0.5	12.33			0.5	27.1	6820	29.20	7.6299

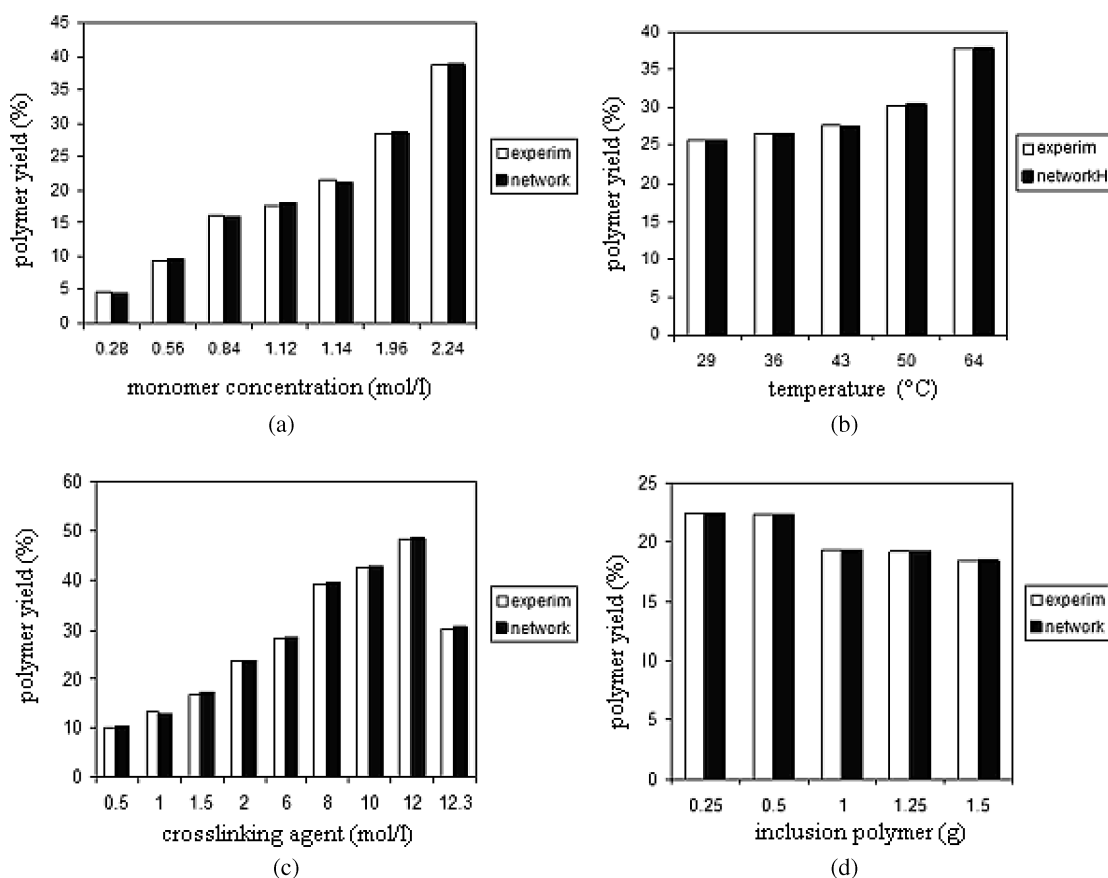


Fig. 8. Experimental data and JEN(7:42:14:2) results obtained for polymer yield in different reaction conditions: (a) $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 0$ g, type 1 (no polymer added); (b) $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $t = 5$ h, $PI = 1$ g, type 2 (starch); (c) $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 1$ g, type 2 (starch); (d) $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 1$ g, type 3 (PVA).

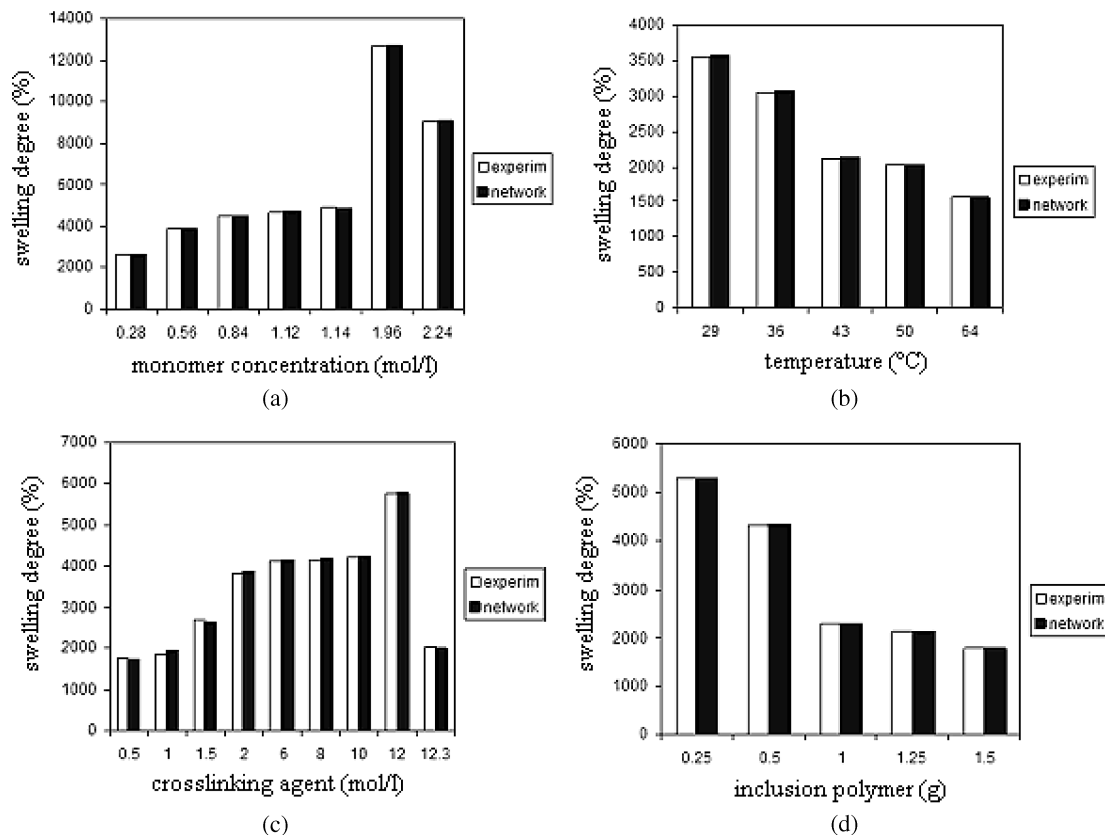


Fig. 9. Experimental data and JEN(7:42:14:2) results obtained for swelling degree in different reaction conditions: **(a)** $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 0$ g, type 1 (no polymer added); **(b)** $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $t = 5$ h, $PI = 1$ g, type 2 (starch); **(c)** $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 1$ g, type 2 (starch); **(d)** $C_M = 3$ mol/l, $C_I = 0.5\%$ weight, $C_A = 12.3$ mol/l, $T = 50^\circ\text{C}$, $t = 5$ h, $PI = 1$ g, type 3 (PVA).

the crosslinking process and it is removed from the system during the purification.

The results also show that polymer yield depends mainly on monomer concentration, in agreement with literature results (5, 6). As expected, the yield in crosslinked polymer increases with monomer concentration (Tables 1–4). The bi-component networks PAAm-starch or PAAm-gelatin attained yields comparable to those of the mono-component networks, while the PAAm-PVA networks were obtained in much smaller yields. This is due to the complexity of the processes that compete for the formation of mono- and multi-component networks (modification of the viscosity of the reaction mixture and of the reaction rate). The forming of the networks and their characteristics are influenced by the differences existing between the used inclusion polymers (structure and reactivity).

The presence of the inclusion polymers induces a different swelling behavior. For mono-component networks, the maximum swelling degrees exceed 10000%, while the multi-component networks swell up to 8000%. These differences are due either to the clogging of the three-dimensional networks with the inclusion polymers, or to the forming of high density covalent interpenetrating networks.

The processing of the data on swelling kinetics of the obtained hydrogels in different experimental conditions led to the curves presented in Figures 4–7.

The artificial neural network architecture, training method, training rates and activation functions were determined using a trial and error approach. Several attempts were made until the proper parameters were reached and, after them, the selected neural network configuration produced the minimal errors in both training and testing data. The trial and error method has as main disadvantage the time consumed for testing manually many possibilities concerning the type and topology of the network, number of epochs (training time), training method, activation function etc. On the other hand, an advantage of this technique could be the flexibility of the method which allows the user to favorably combine different modeling characteristics and to take into accounts the particularity of the studied case.

The results of the training procedure for reaction yield and swelling degree were very successful. Figures 8 and 9 show a good match between the measured and calculated output parameters that means the neural model learned well the behavior of the process.

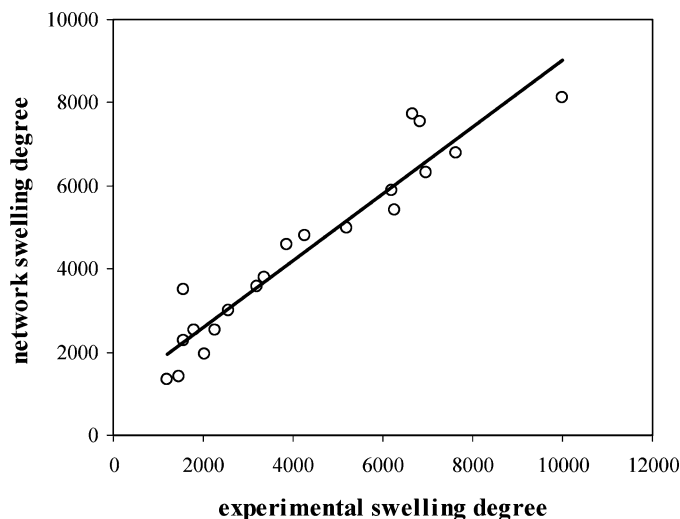


Fig. 10. The validation phase for swelling degree predicted with neural model JEN(7:42:14:2).

The main advantage of a neural network consists of the capacity of generalization from the training examples to other inputs that were not seen yet. As a general rule, the model is sought from experimental available sets of data that clearly contain a number of very interesting relationships, feature correlations and other information which cannot be deduced in a straightforward manner from the first principles, by theoretical calculations or even with numerical methods.

The validation results are presented in Table 6 for the polymer yield and in Figure 10 for the swelling degree. Generally, a good agreement was obtained when compared experimental data not used in the training the neural network with neural network predictions. Relative errors (E_r) in Table 6 were calculated using the formula:

$$E_r \% = \frac{|\eta_{exp} - \eta_{net}|}{\eta_{exp}} \cdot 100 \quad (4)$$

where indices *exp* and *net* denote experimental and network yields.

One can notice that the validation relative errors are below 9% for polymer yield and a little higher for swelling degree, with a maximum of 12%. The satisfactory results obtained with the neural model JEN(7:42:14:2) prove that it can be used to make predictions under different reaction conditions, substituting the experiments which are time and material consuming.

Generally, compared to the mechanistic model of a polymerization process, a neural network based model is built more easily and provides accurate results. This is due to the empirical character of this type of modeling. The versatility of the neural network approach allows us to render faithfully experimental data used for training. One still needs to understand that the neural network approach does

not clarify the reaction mechanism itself and does not answer the great question “why?”. So, one should consider that both approaches – mechanistic and neural – are nicely complementary. One side is represented by the mechanistic model which renders chemical and physical laws and can supplies, sometimes, less accurate results; the other side is the neural network model with an empirical character and, generally, accurate results. The utility of the neural modeling becomes evident when phenomenological models are not available as, for instance, for polyamide based hydrogels synthesis.

One can conclude that the neural network modeling methodology gives a very good representation of polyamide based hydrogels synthesis. It is a general technique that can be easily applied to other polymerization processes.

4 Conclusions

A simultaneous polymerization/crosslinking procedure was applied for the preparation of polyacrylamide hydrogels to obtain materials with different swelling capacities and morphologies. The synthesis was carried out in the presence of some natural (starch and gelatin) or synthetic (PVA) polymers with high biodegradability and yielded semi-interpenetrated networks, without excluding the formation of more or less important interpenetrated domains.

The dependence between reaction conditions (amount of monomer, initiator, crosslinking agent, inclusion polymer, temperature and reaction time) and yield and swelling degree in crosslinked polymer was evaluated with artificial neural networks.

The paper emphasizes a general methodology of modeling based on neural networks. This technique has as main goal to develop an optimum network configuration that could lead to accurate predictions. It includes the stages described below.

- The analysis of the problem takes into account the 177 experimental data, available for the preparation of the multi-component hydrogels based on polyacrylamide. The experiments were designed to cover uniformly the variation domain of the parameters, this being an important requirement for obtaining a credible mathematical model. The chosen inputs variables of the network were the reaction conditions which influence the polymer yield and swelling degree.
- The data were split into training and validation sets, approximately 10-15% being reserved for the testing phase. The validation data do not participate to the training phase and they were selected from different points of the experimental domain.
- The establishment of the neural model supposes the use of a trial and error method. Different types of neural networks (MLP, GFF, MNN, JEN) were tested in order to identify the adequate configuration for the approached

case study. The combination of different transfer functions for context units, hidden and output layers was a possibility to improve the performance of the model.

The most adequate neural model for the approached process was JEN(7:42:14:2) which provides accurate results in training and testing phases of the modeling methodology.

The presented modeling algorithm is quite general and can be also applied for different chemical processes, with high chance to provide accurate results and useful information for experimental practice.

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