

Modeling and Simulation of Monochlorotriazinyl- β -cyclodextrin Paper Grafting by Artificial Neural Network

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This study presents the neural network modeling of monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) grafting on paper supports. Neural networks are very efficient in predicting the evolution of a process, providing a good approximation of the studied grafting process, further used for the interpolation and extrapolation of the results beyond the experimental range. The grafting was realized by a pad-dry-cure treatment and the mathematical model has quantified the influence of the real independent variables (i.e. concentrations of MCT- β -CD and of the catalyst temperature) on the grafting degree as goal function. The treated paper samples were analyzed by FT-IR-ATR spectroscopy and SEM, in order to prove the grafting of the cellulosic support.

Keywords: artificial neural network, modeling and simulation, grafting, nanocoated paper

The heritage paper documents in libraries and archives are subject to the action of environmental conditions (heat, light, moisture, microorganisms, pollutants, dirt etc.), leading to aging phenomena - yellowing, loss of resistance [1]. In order to delay and even prevent the damaging activity of these factors, a non-invasive conservation technique - the treatment of the paper support with different protective coatings - has been used [2-7]. For the paper treatment with cyclodextrin derivatives there are a few literature reports [8, 9] and the results of our previous research work, realized on the other cellulosic supports (e.g. cotton, flax), concerning the development and diversification of highly performing advanced materials by using new compounds and technique, adequate for the protective nanocoatings [10-12] has encouraged the present study.

This completely original study represents a complex approach of the paper grafting problem, with serious conclusions which could be used in practice for the restoration and preservation of the cultural heritage papers. For this chemical modification, a reactive derivative was used, namely monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) and a cellulose Japanese veil was chosen as model, frequently used in the conservation of the archive documents and of other heritage objects (painted substrates, for example).

The development of this chemical complex system, as well as the laws leading it, is not known only partially. For this reason, and since the artificial neural networks (ANN) have the ability to efficiently approximate strong nonlinear complex functions [13, 14], it was established that the neural modeling of the studied process constitutes the main objective of this present paper. A few type MLP (Multi Layers Perceptron) neural networks have been used, among them, the optimal topology by means of successive trials method was determined. The MLP performances tested have been evaluated through the comparison of standard deviation, correlation between the experimental data and data obtained by predictions and percentage relative errors. In this respect, the obtained MLP patterns represent a good choice in order to achieve predictions at the variation of operation conditions, having the possibility to replace the

time and materials consumer experiments. The simulations realized with the established neural models, provided safe information concerning the grafting process evolution, highlighting the maximum possible, as well as the necessary running conditions. Some aspects related to the analysis of optimal values stability are established. The final results, obtained by neural modeling and simulation, provide the possibility of process knowing, in order to control leading the grafting process, under optimal conditions. Consequently, the efficiency of ANN used for new processes and systems is thoroughly proved in this case study.

Experimental part

Materials

Chemically modified cyclodextrin (monochlorotriazinyl- β -cyclodextrin with degree of substitution of 0.46 per anhydrous glucose unit), used as host, was purchased from Germany.

Sodium carbonate (as analytical reagent grade) was obtained from Romania.

As grafting substrate, a Japanese veil (with a thick of 25 microns and an areal density of 15 g/m²) was obtained from Romania.

Methods

Grafting of (MCT- β -CD) to paper substrates was realized by means of a pad-dry-cure treatment. Paper samples were dipped (impregnation method) or brushed (brushing method) with different concentrations of solutions of MCT (50-200 g/L) and Na₂CO₃ (20-100 g/L), at room temperature, without agitation. After the oven drying, the paper samples were cured at different temperatures (100-150°C), for 5, 10 or 15 min. Finally, the paper samples were washed under running water for 5 min and then with distilled water to remove non-reacted substances and again dried in vacuum at 80°C for 24 h.

The quantity of monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) bonded to the fibers was estimated gravimetrically as a percentage ratio between the difference of final and initial samples weights and the initial sample mass.

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Results and discussion

The treated paper samples were analyzed by FT-IR-ATR spectroscopy and SEM, in order to prove the grafting of the cellulosic support.

FT-IR-ATR analysis

FT-IR-ATR analysis was carried out on the Multiple Internal Reflectance Accessory (SPECAC, SUA) with KRS-5 (thallium bromide – iodide) ATR crystal, with 25 reflections, 250 scans and an investigation angle of 45 degrees, in the 1800 - 600 cm^{-1} range. This accessory was attached to the FTIR-IR Affinity-1 (Shimadzu- Japan) Spectrophotometer.

The absorption spectrum of the papers modified with the MCT- β -CD (C spectrum) compared with the spectrum of MCT- β -CD (A spectrum) has the same characteristic bands (fig. 1), for the triazinyl nucleus (i.e. stretching vibrations $\nu(\text{C}=\text{N})$) at 1575 and 1460 cm^{-1} for the functionalized papers, respectively at 1474, 1572 and 1602 cm^{-1} for MCT- β -CD. The small shifts of the characteristic bands for the triazinyl nucleus are due to substituent modification in the reaction between MCT- β -CD and cellulose (chloride atom has been replaced by O-Cel).

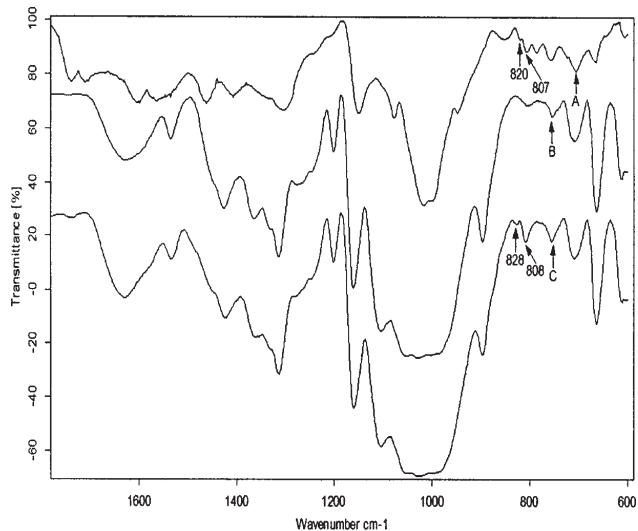


Fig. 1 FT-IR-ATR spectra for: A - MCT- β -CD, B - the Japanese veil, C - the Japanese veil functionalized with MCT- β -CD (impregnation method)

In the functionalized paper spectrum (C spectrum), two new absorption bands characteristic for the triazinyl nucleus too, as small shoulders, at 820 and 807 cm^{-1} will appear. The same time, the absorption band from 785 cm^{-1} , assigned to the stretching vibration $\nu(\text{C}-\text{Cl})$ from the reactive compound, which disappear after the grafting, is a prove that the reaction between MCT- β -CD and paper takes place.

That means the Japanese veil has indeed been functionalized with the reactive product monochlorotriazinyl- β -CD.

Scanning Electron Microscopy (SEM)

The SEM investigation was performed by means of a SEM QUANTA 200 3D scanning electronic microscope Holland. The microscope, entirely computer operated, contains an electron gun with tungsten filament with a potential between 200 V and 30 kV and a 3 nm resolution at 30KV, with a magnifying power between 13 and 1,000,000x in the resolution mode, a scanning speed between 200 ns and 0,1 ns per pixel. The working pressure is lower than 1×10^{-2} Pa.

Comparative SEM analysis of non-functionalized (fig. 2) and functionalized Japanese veil samples (fig. 3) has allowed the visualization of smooth micro deposits and continuous films of reactive product on the surface of modified cellulosic support. The same time, it can be noticed that, after the mild curing treatment during the grafting process, the fibers have not thermally degraded, the only heating effect being the thermal activation of the polymer surface with final superficial nanocoating.

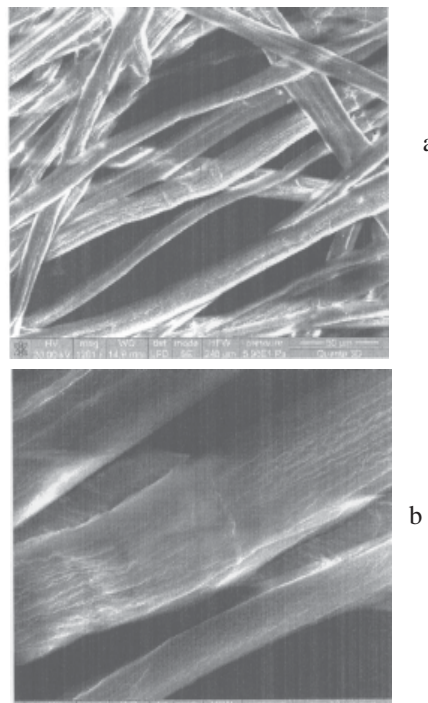


Fig. 2 SEM image of non-functionalized Japanese veil: a - (x 1200), b - (x 5000)

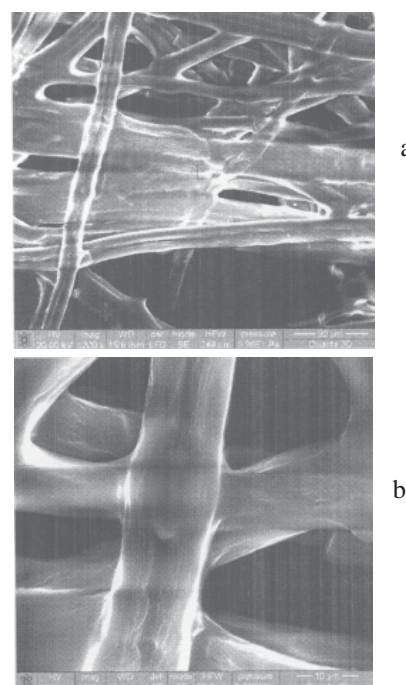


Fig. 3 SEM image of MCT- β -CD functionalized Japanese veil: a - (x 1200), b - (x 5000)

Mathematical modeling and simulation

The mathematical model has quantified the influence of the real independent variables (i.e. type of the paper

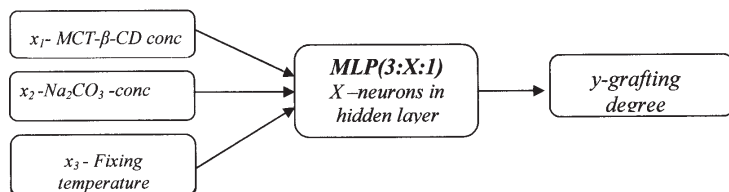
INPUT DATA
OUTPUT DATA


Fig. 4. Grafting degree modeling

Grafting degree, %	Neural model	MSE	r	$\bar{e}\%$
y_{A5}	MLP(3:5:1)	0.014117	0.998822	0.23
y_{A10}		0.05736245	0.997553	0.212531
y_{A15}		0.00048	0.999917	0.220343
y_{B5}		$2.04 \cdot 10^{-7}$	1	0.008252
y_{B10}		$8.68E-06$	1	0.038898
y_{B15}		$3.56E-07$	1	0.005856

Table 1
 TRAINING PERFORMANCES

Grafting degree, %	Neural model	MSE	r	$\bar{e}\%$
y_{A5}	MLP(3:5:1)	0.010700682	0.999124	0.591441
y_{A10}		0.256977	0.981858	0.613768
y_{A15}		0.003886	0.999486	0.199633
y_{B5}		$6.47 \cdot 10^{-6}$	0.999999	0.046941
y_{B10}		$1.07E-05$	0.999998	0.043342
y_{B15}		$2.33E-05$	0.999997	0.048495

Table 2
 VALIDATION PERFORMANCES

support, concentrations of MCT- β -CD and of the catalyst, temperature) on the grafting degree as goal function.

The type of artificial neural networks used in these applications is the multilayer perceptron, MLP (fig. 4) – a layered network in which signals are feed forwarded from a layer of input neurons through several further layers to a layer of output neurons [12].

For neural modeling there have been used: sigmoid axon transfer function, Levenberg Marquardt learning rule, maximum epochs of 10.000 and threshold of 10^{-16} .

The development of the neural model has involved the following steps: the collection of the experimental data (50 x 6 sets of experiments), grouped in two kind of sets: one for training and the other for testing (validation), determining of the neural network topology through the training of the network and validation of the neural model comparing the predictions of the network with unseen data (validation stage).

For the Japanese veil grafting, MLP(3:5:1) type models for 2 treating techniques have been obtained. The MLP architecture has been determined using the trying - error technique.

The adjustment of the neural network function to the experimental data (the training) is based on a non-linear regression procedure. The training has been realized by aleatory values assignment for the predominance of each neuron, the evaluation of neural network output and calculus of differences between the network output and known results (by means of experiments), through an objective error or function. If the error is too big, the predominances are adjusted, and the process is running again in order to evaluate the network output. This cycle is repeating until the error decreases below an imposed value, or a stop criterion is fulfilled.

Table 1 contains the topologies (neural models) made by training, as well as the performances recorded by them: MSE (Mean Square Error – Standard deviation), r (correlation coefficient between the experimental output and that belonging to the network) and $\bar{e}\%$ (percentage mean relative error).

The statistical results presented in table 1 indicate that the MLP (3:5:1) neural model is adequate because the

values of r are very close to unity and the models errors are insignificant.

The practical use of neural models depends upon the obtaining of some good results in the validation stage (table 2), in which new experimental data, other than the ones in the training stage, has been used.

The performances of the neural models for the validation stage, presented in table 2, have highlighted the existence of a very good correlation (0.999124 and 0.999999) between the experimental data and the predictions of the network, with a relative average error in the range 0.59% and 0.043%, and the value of MSE lower than 0.025. Therefore, the obtained models present a good capacity of generalization and can be used for predictions in other conditions than the experimental ones. In the present case, the obtained MLP have been used for predictions aiming at understanding (through simulation) the behaviour of the studied system outside the experimental domain.

The established neural models were used at the systems simulation studied in order to obtain information regarding the evolution of the grafting degree related to the input parameters (figs. 5 -10).

In the case in which the reagents have been applied by the impregnation and the squeezing of the samples, with an increase of the catalyst concentration and of the curing temperature, the grafting degree increases up to a limit of 9.3% for a time duration of 5 min (y_{A5} – fig. 5), 11.5% for a 10 min-duration (y_{A10} – fig. 6) and 13- 14% for 15 min (y_{A15} – fig. 7).

When the reagent solutions are applied by brushing the Japanese veil, with an increase of the catalyst concentration (30 - 90 g/L) and of the curing temperature (100 - 200°C), the grafting degree increases up to a limit of 10% for a time duration of 5 min (y_{B5} – fig. 8, y_{B10} – fig. 9), and 13 % for 15 min (y_{B15} – fig. 10).

The increase of the MCT- β -CD concentration from 90 to 150 g/L has a small influence on the grafting degree for both application variants, for short curing durations (5 min, figs. 5 and 8), but for longer durations (10 min- figs. 6, 7, respectively 15 min- figs. 9, 10), the increase of the grafting degree has been higher.

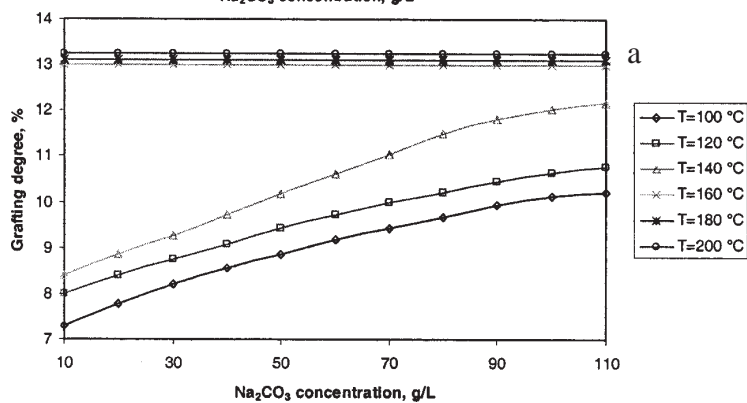
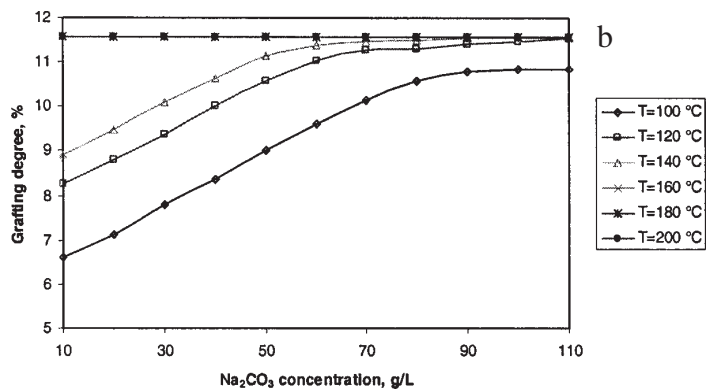
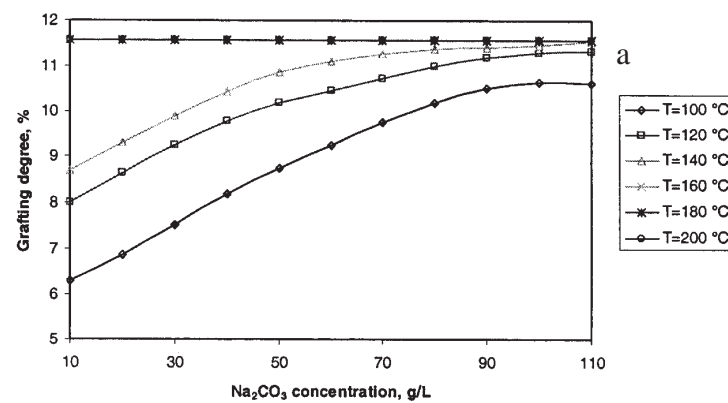
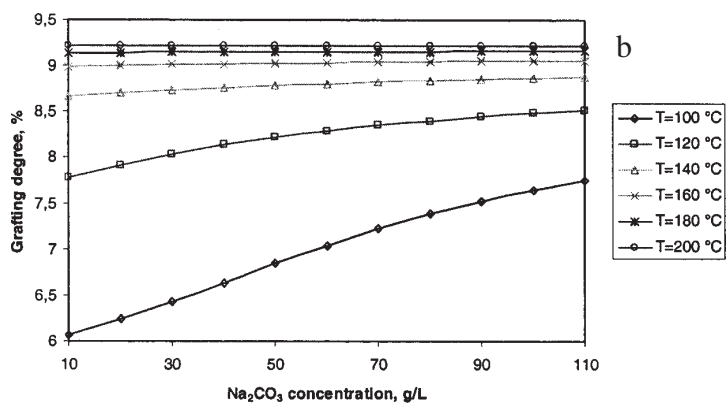
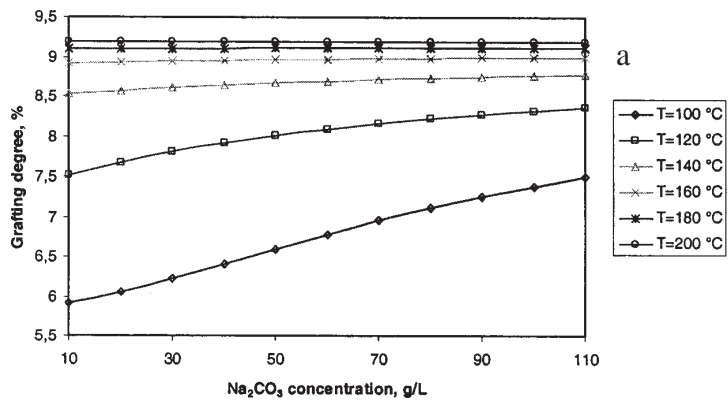


Fig. 5. The grafting degree (y_{A5}) versus Na_2CO_3 concentration (x_2) for the concentrations of 90 (a) and 150 g/L (b) $\text{MCT-}\beta\text{-CD}$ (x_1), at different curing temperatures $x_3 \in [100-200^\circ\text{C}]$

Fig. 6. The grafting degree (y_{A10}) versus Na_2CO_3 concentration (x_2) for the concentrations of 90 (a) and 150 g/L (b) $\text{MCT-}\beta\text{-CD}$ (x_1), at different curing temperatures $x_3 \in [100-200^\circ\text{C}]$

Fig. 7a. The grafting degree (y_{A15}) versus Na_2CO_3 concentration (x_2) for the concentrations of 90 (a) 150 g/L (b) $\text{MCT-}\beta\text{-CD}$ (x_1), at different curing temperatures $x_3 \in [100-200^\circ\text{C}]$

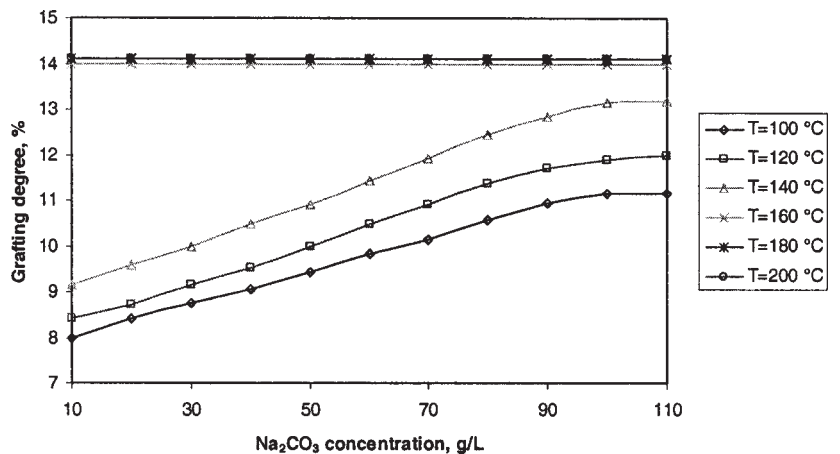


Fig. 7b. The grafting degree (y_{A15}) versus the Na_2CO_3 concentration (x_2) for the concentrations of 90 (a) 150 g/L (b) *MCT*- β -CD (x_1), at different curing temperatures $x_3 \in [100-200^\circ\text{C}]$

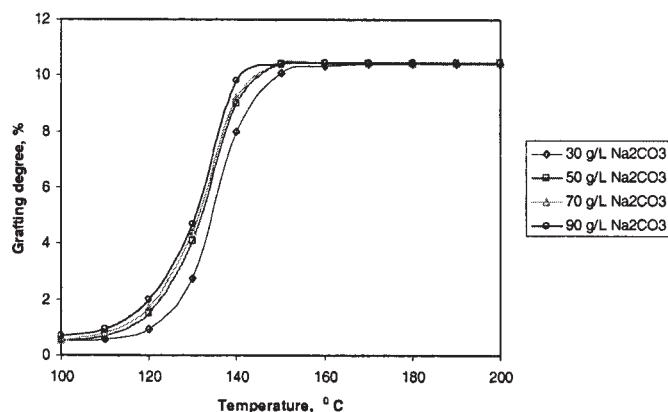
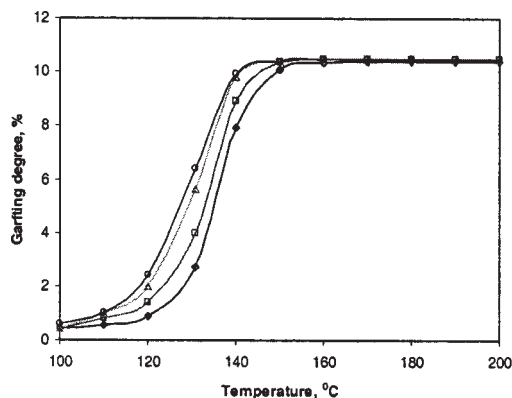


Fig. 8 The grafting degree (y_{B5}) versus the curing temperature (x_3) for the concentrations of 90 (a) and 150 g/L (b) *MCT*- β -CD (x_1), at different concentrations of Na_2CO_3 ($x_2 \in [30-90 \text{ g/L}]$)

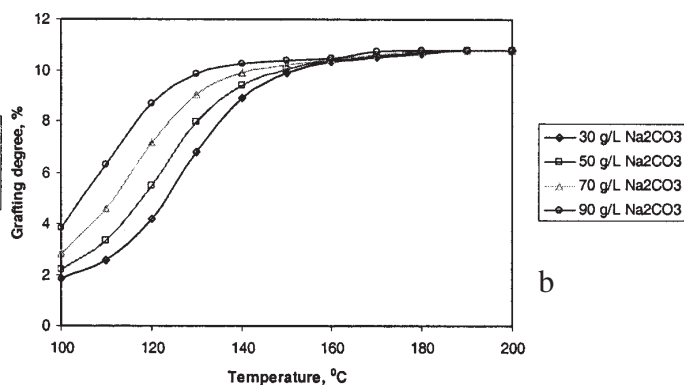
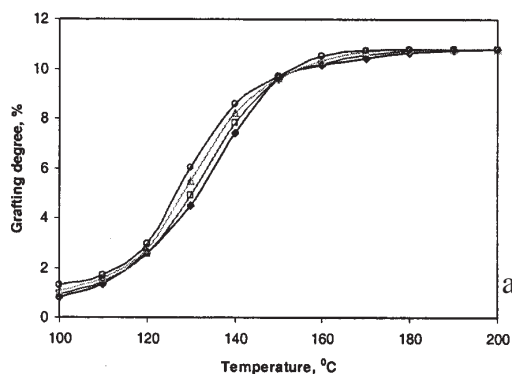


Fig. 9 The grafting degree (y_{B10}) versus the curing temperature (x_3) for the concentrations of 90 (a) and 150 g/L (b) *MCT*- β -CD (x_1), at different concentrations of Na_2CO_3 ($x_2 \in [30-90 \text{ g/L}]$)

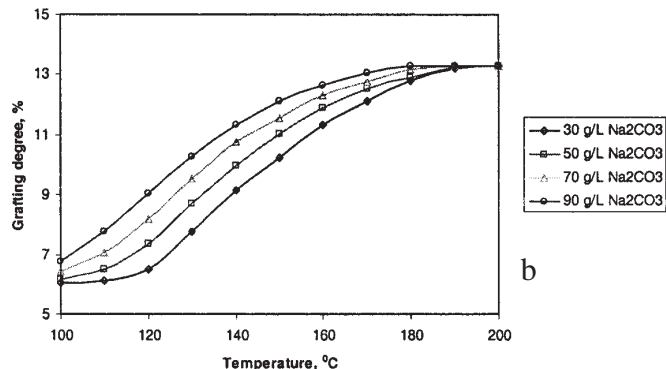
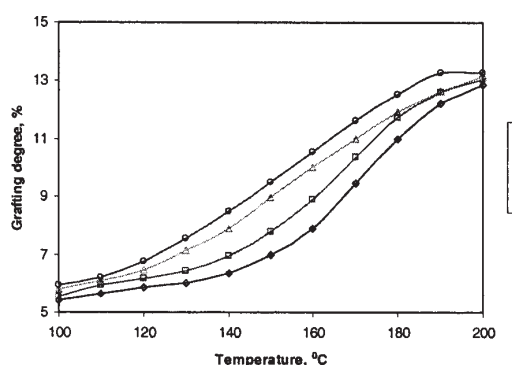


Fig. 10 The grafting degree (y_{B15}) versus the curing temperature (x_3) for the concentrations of 90 (a) and 150 g/L (b) *MCT*- β -CD (x_1), at different concentrations of Na_2CO_3 ($x_2 \in [30-90 \text{ g/L}]$)

These results have led to the conclusion that both variants of reagents application (impregnation and brushing) are adequate from the point of view of the final grafting degree (approx. 13-14%), the optimum curing

duration being of 15 min, the *MCT*- β -CD concentration of 150 g/L and the catalyst concentration - 90 g/L. But, from a practical point of view, the most advantageous application is the brushing because it protects the paper documents

against the mechanical strains during the squeezing process that accompanies the impregnation.

The results obtained by simulation on determined neural models are in accordance with the technological/practical possibilities for the studied procedures. The use of the neural models has the advantage that these, due to their capacity of generalization, confirmed by the results at validation, have allowed the extrapolation of experimental data. Therefore, the resulting predictions have permitted a more thorough analysis of the studied systems with the determination of the best application conditions.

For further application of our researches in the field of heritage documents conservation, the superficial grafting of MCT- β -CD on papers was utilized to provide hosting nanocavities that have included a wide variety of chemicals as follows: cinnamic derivatives (ferulic acid - (*trans*) [3-(4-hidroxi-3-methoxyphenyl)-2-propenoic acid]), urea derivatives (allantoin-5-ureidohydantoin) or ketonic derivatives (4,4'-bis(dimethylamino) benzophenone - Michler's ketone) for specific protective effects (antibacterial, UV protective, antistatic finishes etc.). These results have been reported in other researches [15-17].

Conclusions

Analyses by FT-IR-ATR and SEM characterization techniques have indeed proved that the paper samples were functionalized with monochlorotriazinyl- β -CD.

For every studied case, the MLP type neural models adequate by means of the analyses of statistics indicators values and by comparison of their performances with new experimental data were established. The chosen neural models have been used at grafting processes simulation for different operation conditions.

The simulation results have highlighted the optimal operation conditions necessary for control leading of the grafting process (the final grafting degree: 13-14%) on the studied systems: the optimum curing duration - 15 min, the MCT- β -CD concentration - 150 g/L and the catalyst (sodium carbonate) concentration - 90 g/L.

The present study shows the efficiency of artificial neural networks use, in order to graft the Japanese tissue with monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) leading to important savings of: time, energy, material resources, by avoiding the experiments, an extremely important issue for the cultural heritage field, where the work techniques should be as non-destructive as possible.

The neural network modeling of monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) grafting on Japanese veil is very

efficient in predicting the evolution of a process, providing a good approximation of the studied process, further used for the interpolation and extrapolation of the results beyond the experimental range.

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