ASSESSMENT OF PROFILE RELEASE OF PHEROMONES IN EVA FIBERS OBTAINED BY SOLUTION BLOW SPINNING

Silvana Pereira Rempel[1*], Gustavo Sganzerla Martinez[2,3,4], Cássia Virginia de Oliveira[1], Scheila de Avila e Silva[2,4] and Otávio Bianchi[1]

1 – Department of Materials Engineering (DEMAT), Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil silvana.rempel@ufrgs.br, otavio.bianchi@gmail.com

2 – Computational Biology and Bioinformatics Laboratory, University of Caxias do Sul (UCS), Caxias do Sul, RS Brazil

3 – Nucleix Laboratory – Tezpur University, Tezpur, AS, India

4 – Department of Biotechnology, University of Caxias do Sul (UCS), Caxias do Sul, RS Brazil

Abstract – The pheromones released from polymeric dispensers in the form of fibers is a viable and suitable alternative to control insect pests in agriculture, reducing the consumption of pesticides. This study reports the application of an artificial neural network (ANN) in comparison with simple linear regression (SLR), to predict the release behavior of the synthetic sex pheromones of the oriental fruit moth, Grapholita molesta and citrus leafminer Phyllocnistis citrella from the fibers of ethylene-vinyl acetate (EVA) produced by blow spinning. The release of pheromones occurred linearly over 10 weeks, as determined by thermogravimetry analysis (TGA). A high level of reliability of the predicted pheromone release curves was obtained due to an excellent agreement between the theoretical and modeled results. The applied methodology can be extended to other controlled release systems of active agents.

Keywords: *ANN, pheromone, polymers, linear regression, artificial neural network.*

Introduction

Micro/nanofibers represent a class of material with extensive application possibilities due to their specific properties, such as a large specific surface area, high aspect ratio, selective permeability, and surface adsorption properties. These are suitable properties for application as a support system for pheromone releasing crops for insect control and monitoring [1].

The biggest challenge of the next century will be to keep growth in global food production to match or exceed the projected doubling of the human population. Among the various restrictions on food production, the problems associated with chemical pest control seem to be of concern. Thus, alternative pest control methods have been created to reduce the use of these compounds, which in most cases are toxic to humans. In this context, the use of pheromones in the control of agricultural pests appears as an adequate alternative since they have high specificity and do not harm the environment. These substances are specific to each species of insects and allow the protection of plants in a highly selective way. The use of polymeric micro/nanofibers containing incorporated pheromones and their release in a controlled and homogeneous way in the control of agricultural pests presents itself as an adequate form of precision agriculture, as it allows a better dispersion of agricultural inputs in crops, increasing the productivity and reducing costs [1].

The release profile can be determined using gas chromatography (GC), thermogravimetry (TGA), and UV-Vis spectrophotometry. Thermogravimetry is the simplest and most used technique to evaluate the amount and release profiles of pheromones in different polymeric dispensers *in vitro* conditions [2,3].

Due to its ability to make predictions, pattern recognition, and modeling, the artificial neural network (ANN) has been applied in many aspects of research, especially in its ability to generalize problems. Specifically, ANNs are known as a powerful tool to simulate various non-linear systems and have been applied to several problems of considerable complexity in many fields, including engineering, psychology, medicinal chemistry, diagnostics, and pharmaceutical research [4,5].

Many studies have been conducted to develop new methodologies to study controlled release systems, especially related to drug release, due to the significant impact on modern therapy. These quantities can, primarily, be predicted by theoretical models to reduce the number of experiments required. In general, as the dependence on the number of parameters increases, the solution based on the least-squares adjustment becomes more complex. In this sense, alternative approaches must be studied, in such a way as to combine the advantages of conventional methods, which are established, with those of other techniques, such as ANNs [6,7].

In this context, the present study aims to apply the ANN approach to adjust the TGA curves to release pheromones from polymeric supports. In addition, the data were analyzed by simple linear regression (SLR) to provide a comparison with the ANN methodology. This new data processing methodology can be expanded to predict the release behavior of different active agents from different designs, reducing costs and analysis time.

Experimental

Materials

EVA copolymer (Braskem, HM 728, Triunfo, Brazil) with 28 wt.% of vinyl acetate content and melt flow index (190 °C/2.16 kg) of 6.0 g/10 min, the average molecular weight of Mn = 146,000 g mol^{-1}, and polydispersity index of Mw/Mn = 3.2 determined by TG and gel permeation chromatography measurements (GPC). The solvents used in the preparation of the solutions were chloroform (ACS) ($CHCl_3$, density: 1.48 g mL^{-1}, bp: 61.2 °C) and xylene (ACS) (C_8H_{10}, density: 0.87 g mL^{-1}, bp: 140 °C). The solvents were used as received and purchased from Dinâmica Química Contemporânea Ltda, Diadema, Indaiatuba, Brazil. The pheromones (Z,Z)-7,11-hexadecadienal and (Z,Z,E)-7,11,13- hexadecadienal from CLM (Phyllocnistis citrella Station) and the (E)-8-dodecenyl acetate, (Z)-8-dodecenyl acetate, and Z-8-dodecenol from G. molesta were purchased from Sigma-Aldrich (St. Louis, Missouri, USA) and donated by ISCA Tecnologias (Ijuí, Brazil).

Fiber-pheromone system

The fibers-pheromone system was produced in a commercial airbrush model BD- 134K, using a nozzle diameter of 0.3 mm. This device is attached to a flexible structure and connected to the compressed air network with a regulated pressure of 5 bar. A flat collector is positioned in front of the airbrush, at a distance of 25 cm. To evaluate the effect of the feed rate on the size of fibers, the feed rates varied from 0.3 to 5 mL min^{-1} at 45 °C. Due to the low evaporation rate of the solvents used in the solution blow spinning, a thermal blower with a temperature of approximately 120 °C and airflow of 12.2 m s^{-1} was positioned next to the spinning system, at 30° to the nozzle.

Pheromone release profile by SLR

The release profile of the fiber-pheromone system was evaluated by thermogravimetric analyses (TGA). The analyses were performed in a PerkinElmer 4000, using ~10 mg of the sample at a heating rate of 10 °C min^{-1} from 30 to 700 °C under a nitrogen atmosphere (50 mL min^{-1}). The profile, release rate, and amount of pheromone incorporated in the fiber were evaluated based on the determination of the amount of evaporated pheromone (23 ± 2 °C and 50 ± 5% relative humidity) at each week of measurement over 10 weeks.

Prediction of the pheromone release profile by ANN

The ANN fitting curves took place in the statistical programming platform R [8] through the usage of the *nnet* package [9]. The nature of ANNs enables the approximation of any function [10]. Hence, the curves were created by using the functions for computing the liberation of pheromones vs. days in CLM and Grapholita methods, respectively:

$$f(x) = -0.05 \times x + 19.97 \quad (1)$$

$$f(x) = -0.31 \times x + 24.06 \quad (2)$$

The following parameters were employed for the training of the ANN: *i*) five hidden neurons; *ii*) 60 and 70 training iterations (CLM and Grapholita, respectively), the epoch choosing process follows [11]; *iii*) the formula aimed to predict the pheromone liberation through the day by following functions 1 and 2; *iv*) the weight optimization algorithm implemented by *nnet* is the Broyden-Fletcher-Goldfarb-Shannon (BFGS) based on gradient descent; *v*) the activation function is logistic and finally; *vi*) the *nnet* function returns the sum of the square errors for the model residuals.

Results and Discussion

Pheromone release profile by ANN and SLR

The TG curves in the temperature range from 30 to 700 °C for the two release systems and are shown in Fig. 1 (a). Pure pheromone, pure fiber, and fiber/pheromone systems are presented at different weeks of release. The fiber + pheromone sample refers to the fiber with the pheromone after being spun, which has not been submitted through the release process. As shown in the mass loss curves, as the pheromone evaporation occurs, the mass loss is lower in the range up to 300 °C for the Grapholita. It is possible to quantify the amount that was incorporated during spinning. In the sample with CLM, the third loss of mass overlaps the EVA mass loss. EVA has 28 wt % vinyl acetate. Thus, it was possible to correct the initial amount of pheromone to ~6.8 wt % according to the mass differences, thus contributing to the incorporation of CLM in the fiber (not shown here). No residual material above 500 °C was observed for all fiber samples. The graphical inset in the temperature range of 100–350 °C illustrates the difference between the samples (pheromone, fiber + pheromone, and pure fiber) at the beginning and after five weeks of release.

By using a simple linear regression (SLR), it was possible to estimate the amount incorporated and the release of pheromones from fiber-pheromone systems. Fig. 2(a) shows the pheromone release curves for the Grapholita and CLM fiber systems. Both release curves showed a linear profile with coefficient correlations greater than 0.9. A linear adjustment was possible to estimate the amount of pheromone incorporated in the fibers and the release rate. For CLM, a release rate of 0.05 wt % per day was assessed, while for Grapholita the release rate was 0.31 wt %

per day. The initial amount incorporated in the fiber was 19.97 wt % ±0.30 for the CLM, whereas the Grapholita was 24.06 wt % ±0.57. The pheromone Grapholita showed a 17 wt % greater content incorporated when compared whereas than the CLM. The increase in pheromone incorporation in the fibers is related to the solubility parameter of this pheromone being closer to that of the polymer. Another critical parameter is that it is possible to estimate the total release time under controlled conditions (*in vitro*). For this, it is enough to extrapolate when the amount of pheromone tends to zero. The EVA/CLM system will reach full release in 399 days, and the EVA/Grapholita in 77 days.

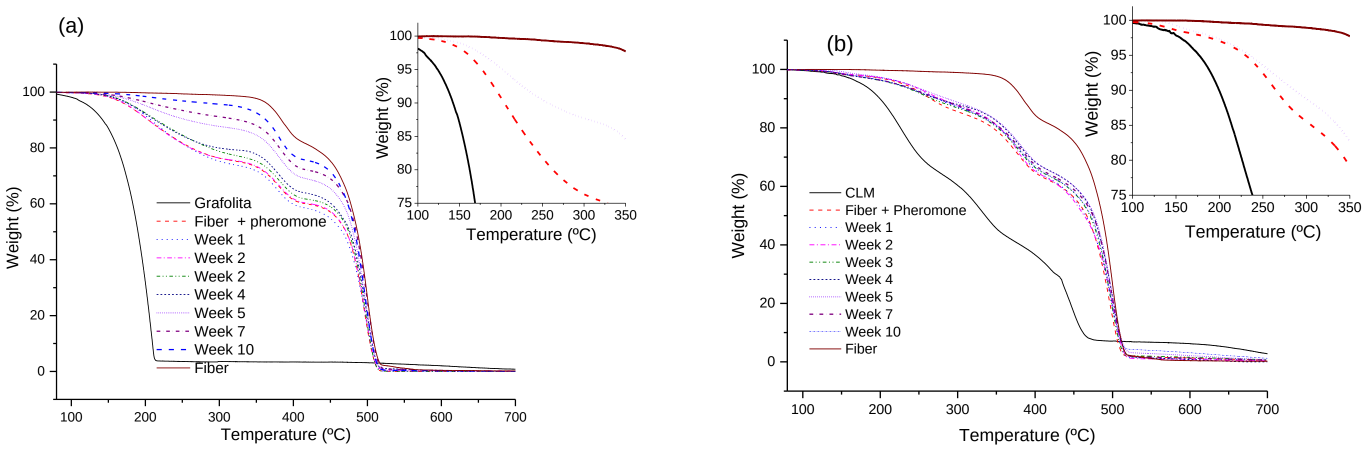

Figure 1 – TGA curves of the loss mass versus temperature for pheromone/fiber release systems (10°C min^{-1}) from Grapholita (a) and CLM (b) (inset graphic in the range of 100–350 °C) [1].

When observing the results obtained by ANN and for TGA/SRL, we noticed that the results for pheromone release are similar (Fig. 2 (a), since both models provide almost overlapping lines. Like the SRL, the ANN study also indicated a release profile of approximately 399 days for the Grapholita pheromone and 77 days for the CLM pheromone. The Loss Function graphs show a Mean Square Error (MSE) close to zero (Fig. 2 (b)), demonstrating that the desired outputs and ANN outputs for the training set have become very close to each other.

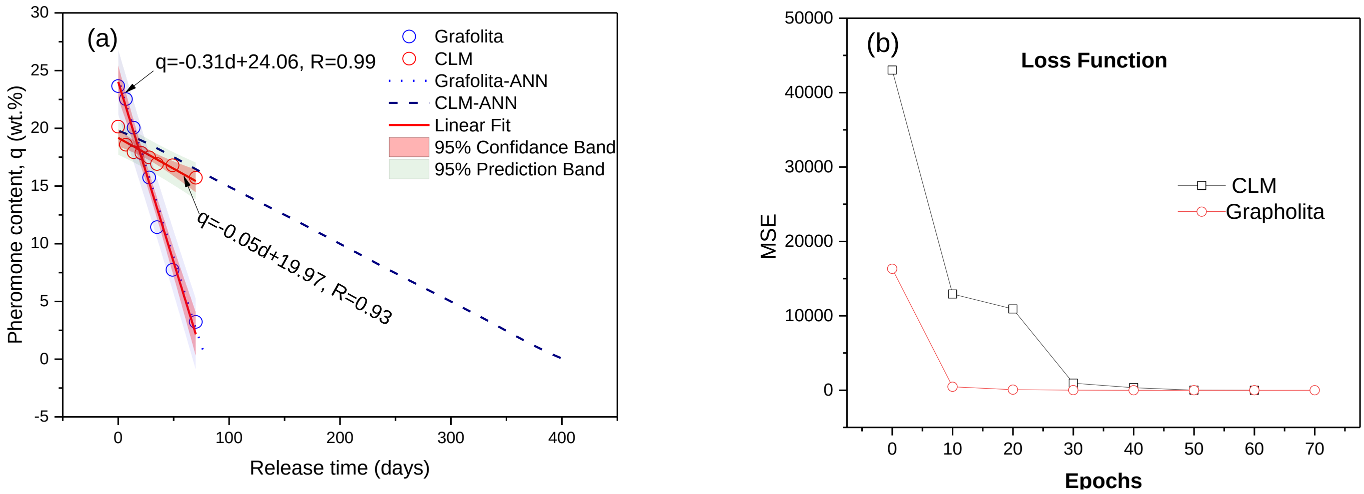

Figure 2 – (a) Comparison of the pheromone release profile between that observed by SLR and predicted by ANN and (b) loss function from CLM and Grapholita.

Conclusions

The release characteristics follow approximately linear kinetics, which is again very favorable for application in plant protection. A requirement for plant protection is that the release of pheromones during the growth period of the plants must be as constant as possible.

ANN proved to be an efficient tool to simulate and predict the release profile of pheromones from EVA fibers. The ANN and SLR models allow excellent predictive skills for any measured property since many experiments have been carried out previously.

The results obtained after the learning stage may be considered to predict the ideal experimental conditions quantitatively. This approach might be helpful for experimental analysis to simulate and design efficient systems for the controlled release of active agents.

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