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Using Neural Networks or Linear Models to Predict the Characteristics of Microcapsules Containing Phase Change Materials

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Summary: Microcapsules with large amount of PRS® paraffin wax encapsulated and narrow size distribution were prepared by shirasu porous glass (SPG) emulsification technique and a subsequent suspension like polymerization process and then examined by DSC, laser diffraction and SEM analyses. An experimental design approach, based on a central composite design, was used to determine quantitatively the effect of PRS® paraffin wax/styrene mass ratio (PRS/St), percentage of polyvinylpyrrolidone/styrene mass ratio (%PVP/St) and water/styrene mass ratio (H_2O/St) on the microparticles properties. The results were fitted using two black-box models. The empirical equations allow the prediction of the amount of the paraffin wax encapsulated and the mean particle size in number as a function of aforementioned synthesis variables.

It was observed that both models allowed to drawn the same conclusions. %PVP/St mass ratio was the most important parameter affecting the particle size distribution decreasing the average particle size with the increase of %PVP/St. On the other hand, PRS/St mass ratio has a direct influence on the latent heat of fusion.

Keywords: heat capacity; microencapsulation; neural network; paraffin wax; polystyrene

Introduction

Textiles containing phase change materials (PCMs) helps to combat both cold and heat, in general this effect can be called thermoregulation. The textile industry has been slow to react to the possibilities of microencapsulation, although in the early 1980s phase change materials were used by the US national aeronautics and space administration (NASA) with the aim of managing the thermal barrier properties of space suits.[1] Nowadays, there is a growing interest in the introduction of the thermoregulatory effect in sport, work and casual clothes. For use in textile materials, an appropriate particle size should range from 0.5 to 100 μm.[2] As a consequence, Colvin and Bryant (1998)[3] used microcapsules containing PCMs of 30 to 100 μm for textile fibers, composites and foams. Pause (2003)[4] made PCM microcapsules of 1 to 60 μm for nonwoven protective garments with thermo-regulating properties. Shin et al. (2005)[2] prepared microcapsules containing eicosane with a particle size of 0.1 to 10 μm for development of thermoregulating textile materials. In order to avoid changes in the texture of textile materials with the microcapsules incorporation, particle size and also its size distribution should be considered in the production process.

Paraffins waxes compared to other PCMs have high heat-storage capacities, are easily available and not expensive. Hawlader et al. (2003)[5] prepared microcapsules containing paraffin waxes with a

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latent heat of fusion between 145 and 240 J/g. Shin et al. (2005)[2] prepared microcapsules with a heat storage capacity of 134.3 J/g for thermoregulating textile materials. PRS® paraffin wax has been encapsulated in our research group by a polymer cover (polystyrene) by means of suspension like polymerization technique obtaining a maximum energy storage capacity of 153.5 J/g that makes them suitable for textile application.[6,7]

In this study, the original experimental set-up was modified in order to obtain microcapsules with narrow size distribution by means of a microporous membrane. In literature has been tested that this kind of membranes are suitable to prepared monodispersed polystyrene, polylactide, polystyrene-co-methylmethacrylate and polyurethane microspheres.[8]

Neural networks (NNs) can be a very useful tool for the modeling and prediction of performance of microencapsulation process. However, references concerning the estimation of number particle size and heat latent of microcapsules using an empirical approach based on neural networks have not been found up to date. On the other hand, the linear black-box polynomial model is the most simple and extended black-box model and it has been used for this purpose in a previous work.[9]

Two in-house softwares were developed to predict the latent heat and the average particle size in number of microcapsules containing PCMs as a function of the studied synthesis variables paraffin wax PRS® to styrene mass ratio (PRS/St), percentage mass ratio of polyvinylpyrrolidone to styrene (%PVP/St) and water to styrene mass ratio (H_2O/St).

PRS/St mass ratio was selected in order to improve the thermal storage/release capacity of the PCM microcapsules. This parameter has been varied from 0.25 to 1.11.[7] It is also known that the %PVP/St mass ratio and H_2O/St mass ratio have an important influence on particles size and size distribution.[10] Taking into account the previous works dealing with a suspension polymerization process,[11] %PVP/St mass ratio ranging from 4.09 to 11.31 and H_2O/St mass ratio from 4.09 to 11.31 have been evaluated. The arguments in which have been based the selection of the range of conditions can be found in Sánchez et al. (2008).[9]

For that reason, the aim of this work is to obtain empirical equations based on neural networks that allow to relate the initial conditions of a given experiment with the most important characteristic of the microcapsules, the mean particle size and the energy storage capacity per mass unit and finally, to compare the optimal values obtained with those attained using the linear black-box polynomial model.

Experimental Part

Suspension like polymerization reactions were performed in a 1-L double-jacketed glass reactor equipped with digital control of stirring rate and temperature, a reflux condenser and a nitrogen gas inlet tube. The experimental setup was described in a previous paper.[9] The synthesis process involves two phases: a continuous phase containing water and polyvinylpyrrolidone and a discontinuous phase one containing styrene, PRS® paraffin wax and benzoyl peroxide.

The continuous phase was transferred to a glass reactor with mild agitation during 10 minutes. After that, continuous phase was circulated during 3 minutes through the SPG membrane because the hydrophilic membrane used must be pre-wetted with the aqueous phase. As the initiator was already mixed with monomer and paraffin wax, these products were added into dispersion phase storage tank. Next, the discontinuous phase was permeated by nitrogen gas through the uniform pores of the SPG membrane into the continuous phase to form uniform droplets in situ at the membrane/continuous phase interface. In order to ensure a regular droplet detachment from the pore outlets, shear stress is generated at the membrane/continuous phase interface by recirculating

the continuous phase during 10 minutes using a low shear pump.

After every experiment, the used membrane was recovered by means of the following procedure. First of all, it was soaked in 2 wt.% solution of AOT in ethanol for 2 h. After that, it was rinsed and soaked in pure water. Next, it was immersed for 1 h in water solution of 2 M HCl at 70 °C and finally, it was rinsed and soaked in pure water for 30 min. This procedure fully recovers the initial hydrophilic state of the SPG membrane, which can be used in subsequent experiments.

The suspension like polymerization reactions were maintained under vigorous agitation (1600 rpm), the reaction media was bubbled with nitrogen and the temperature was set at 110 °C in the thermostat bath. Temperature and agitation were maintained in a fixed value during the experiments. The polymerization process was carried out for 6 h under a nitrogen atmosphere.

Next to polymerization process, 200 g of methanol were added into the glass reactor by mild agitation when its temperature was 70 °C. Methanol is used to improve the decantation procedure. Finally, the polymerized microcapsules were filtrated by pressure to remove paraffin wax has not been encapsulated and latex particles. The purified microcapsules were dried at room temperature.

Particle size and particle size distribution were determined on a Malvern Mastersizer Hydro 2000 SM light scattering apparatus in a diluted dispersion of the particles in methanol. Measurements of melting point and melting heats of different materials employed and obtained were performed in a differential scanning calorimetry model DSC Q100 of TA Instruments equipped with a refrigerated cooling system and nitrogen as the purge gas. These measurements were done varying the temperature in the range from -30 °C to 80 °C with a heating rate of 10 °C/min. Each sample was analyzed at least twice and the average value was recorded. Furthermore, the content of paraffin wax in the microcapsule can be estimated according to the measured melting enthalpy of different standards mixtures of polystyrene and paraffin wax. The experimental values obtained were fitted to a straight line with the following form:

$$\%\,\text{Paraffin wax content} = (\text{DeltaHm} - 7.2004)/1.921 \quad (1)$$

where DeltaHm is the enthalpy of analysed microcapsules (J/g)

The following materials were used in this study. Styrene (99 wt.%) was of reagent grade (Merck Chemical). Styrene was washed with sodium hydroxide to remove the inhibitor and calcium chloride as desiccant. Benzoyl peroxide (97 wt.%) was used as initiator (Fluka Chemical). PRS® paraffin wax (Mw 478 g/mol) was of commercial grade, this is a medium range vacuum distillate basically consistent in a mixture of hydrocarbons C_{19}-C_{27} produced and commercialized by the petrochemical company Repsol-YPF (Spain), and was used as core material; Polyvinylpyrrolidone (K30, Mw 40,000 g/mol) of reagent grade (Fluka Chemical) was used as stabilizer and methanol to pour the samples. All these reagents were used as received. Water was purified by distillation followed by deionization using ion-exchange resins. Nitrogen was of high-purity grade (99,999%). A tubular type Shirasu porous glass membrane with pores sizes of 5.5 μm was used to produce a narrow microcapsules size distribution. At the end of every experiment, the used membrane has been retrieved by a treatment with sodium dioctyl sulfosuccinate (AOT) (Fluka Chemical, 96 wt.%), ethanol (Panreac Chemical) and chloride acid (Prolabo Chemical) reagents.

Results

Table 1 shows the factorial design with three factors in two levels. 17 experiments including three central repeats, changing PRS/St mass ratio from 0.25 to 1.11, %PVP/St mass ratio from 4.09 to 11.31 and H_2O/St

Table 1.
Factor levels and experimental design.

Variable	Low (−)	High (+)	Centre (0)	Axial (-α)	Axial (+α)
PRS/St	0.36	1.00	0.68	0.25	1.11
%PVP/St	5.03	10.37	7.70	4.09	11.31
H_2O/St	5.03	10.37	7.70	4.09	11.31
		Exp.	PRS/St	%PVP/St	H_2O/St
		1	0.36	10.37	10.37
		2	0.68	7.70	11.31
		3	1.00	5.03	5.03
		4	0.68	4.09	7.70
		5	0.36	5.03	10.37
		6	0.25	7.70	7.70
Central composite design	2^3 factorial design + 3 central points	7	0.68	7.70	7.70
		8	1.00	10.37	5.03
		9	0.68	7.70	7.70
		10	0.68	7.70	4.09
		11	0.68	7.70	7.70
		12	1.00	5.03	10.37
		13	0.68	11.31	7.70
		14	0.36	10.37	5.03
		15	1.11	7.70	7.70
		16	1.00	10.37	10.37
		17	0.36	5.03	5.03

mass ratio from 4.09 to 11.31. The average particle size in number and the microcapsules latent heat were analyzed for each experiment obtaining an average particle size in number ($dpn_{0.5}$) ranging between 1.68 and 15.52 μm and a latent heat of microparticles ranging between 33.03 and 102.20 J/g.

The experimental results of the central composite design (CCD) were fitted using the NN strategy with a single neuron. The equations obtained for $dpn_{0.5}$ and the latent heat of microcapsules are the following:

$$dpn_{0.5} = 26.67 * (1/(1 + 1/EXP((0.24 \cdot PRS/St) - 0.27 \cdot (\%PVP/St) + 0.13 \cdot (H_20/St)))) \quad (2)$$

$$Latentheat = 93.97 * (1/(1 + 1/EXP((5.51 \cdot (PRS/St) + 0.16 \cdot (\%PVP/St) - 0.31(H_20/St)))) \quad (3)$$

In Figure 1 are shown the experimental and the predicted values obtained with the model.

A good fitting with an average error lower than 7% for the latent heat and around 20% for $dpn_{0.5}$. The fitting for latent heat seems to be similar to that obtained using the linear polynomial model with a medium error of 7%. Thus, in order to select a model for this purpose, the NN should be used as black-box model due to the lower number of parameters require for this fitting (6 parameters less). On the other hand, the average deviation for $dpn_{0.5}$ is higher than that found with the linear model (8%). The average deviation could be decreased doing a higher number of experiments in order to improve this fitting. It is also possible that increasing the number of neurons used in the neural network undergoes a better fitting but the number of parameters will be increased.

3D simulations from the NN equations are shown in Figure 2 for the $dpn_{0.5}$ and latent heat of microcapsules, respectively.

The 3D response surface at 7.70 of H_2O/St mass ratio (Figure 2a) clearly shows a decrease of $dpn_{0.5}$ with increasing the amount of suspension agent (%PVP/St). This could be attributed to the reduction of the interfacial tension between polymer and aqueous phase with the increase of the content of polyvinylpyrrolidone in the polymerization medium. On the other hand, the $dpn_{0.5}$ of the microcapsules increases when

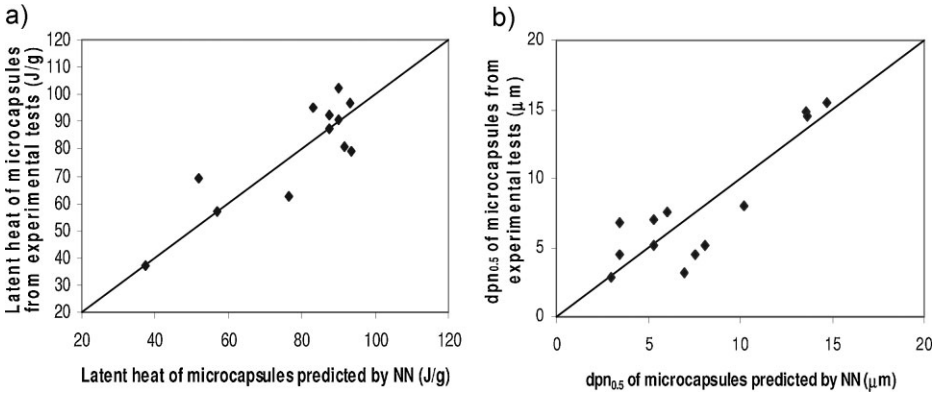

Figure 1.
Neural networks fitting. (a) Latent heat of microcapsules (J/g); (b) Average particle size in number (μm).

paraffin wax amount increases. This is in agreement with the results reported by Mlynek and Resnick (1972).[12] Nevertheless, the influence of H_2O/St mass ratio seems to be almost negligible unless the polyvinylpyrrolidone content will be very small. The same conclusions have been drawn using the linear polynomial model but the lower fitting exhibited by the neural network gives an overprediction of the average diameter in number mainly for the higher values of PRS/St and the lower values of %PVP/St.

Figure 2b shows the response surface plot for the latent heat of microcapsules at 7.70 of H_2O/St mass ratio. According to previous studies,[7] as the core to coating ratio increases, the amount of paraffin wax encapsulated increases passing through a maximum and then decreasing again. The maximum latent heat capacity obtained is reached using PRS/St of 1.02, %PVP/St of 7.69 and H_2O/St of 8.70. As it was expected for latent heat this point is quite close to the optimal point obtained using the linear model (PRS/St of 1.02, %PVP/St of 9.43 and H_2O/St of 8.23) because of the medium errors were equal.

Shin et al.[2] reached a 53 wt % of phase change material encapsulated using coacervation method. Xing et al. (2006)[13] reported the encapsulation of paraffin

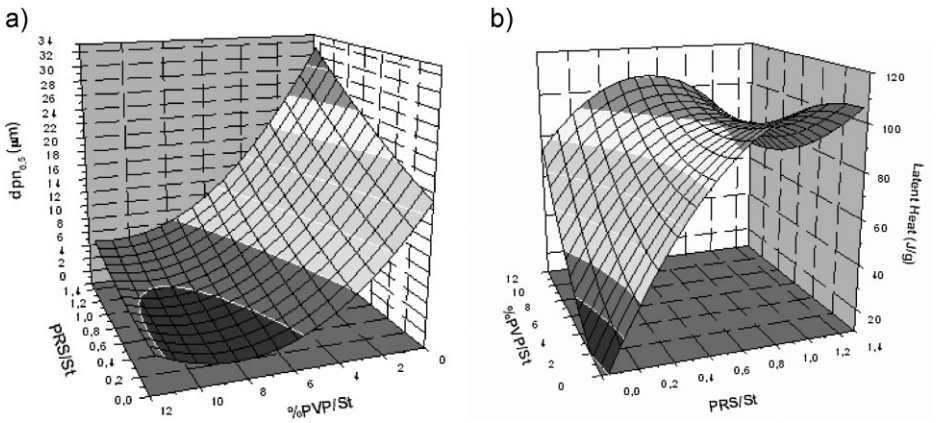

Figure 2.
Effect of PRS/St and %PVP/St mass ratios (a) on the $dpn_{0.5}$ and (b) on the latent heat of microcapsules at 7.70 of H_2O/St mass ratio.

around 70 wt% by in situ polymerization method. However, with reference to pure paraffin as PCM the percentage of paraffin encapsulated was not more than 20 wt% when paraffin is microencapsulated directly.[14]

Conclusion

It has been shown that both black-box models are able to fit the experimental data. A lower number of parameters can be found using neural networks for the latent heat. However, a large number of experimental data or the use of a higher number of the internal neurons are required for a suitable prediction of the average particle size in number using a model based on neural networks. Accordingly, in the case of low number of experimental data available the best alternative is carried out the fitting process by the linear polynomial model.

Taking into account the different response surfaces, both models allow to deduce the same conclusions. The average particle size is strongly influenced by %PVP/St mass ratio although changes of PRS/St and H_2O/St mass ratios produce variations of viscosity, interfacial tension and density of each different phase that have a strong influence on the particle diameter size. Furthermore, it was observed that the principal influence corresponds to changes in the mass ratio of PRS/St for latent heat of microcapsules.

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