Particuology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Modeling and optimization of the parameters affecting the in-situ microencapsulation process for producing epoxy-based self-healing anti-corrosion coatings

Ali Ebrahiminiya [a], Mohammad Khorram [a,*], Shadi Hassanajili [a], Mehdi Javidi [b]

[a] School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran
[b] Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran

ARTICLE INFO

Article history:
Received 22 May 2016
Received in revised form
21 December 2016
Accepted 9 January 2017
Available online xxx

Keywords:
Urea–formaldehyde
Response surface methodology
Central composite design
Ultrasonic homogenization
Linseed oil
Self-healing coating

ABSTRACT

Micro/nanocapsules of urea–formaldehyde resin loaded with linseed oil, which are a self-healing agent in glass flake epoxy anti-corrosion paint, were prepared using a combination of ultrasonic homogenization and in-situ polymerization. The main objective of this study was to model and optimize the microencapsulation process. Five-level central composite design was used to design, model, and optimize the microencapsulation process. A quadratic model was constructed to show the dependency of the percentage of encapsulated linseed oil and capsule size, as model responses, on the studied independent variables (the rotational speed of the agitator and the power and duration of sonication). Analysis of variance showed that all of the variables have significant effects on the encapsulated linseed oil percentage, while the rotational speed of the agitator and sonication time is effective variables for controlling the capsule size. Under the determined optimum conditions, a maximum encapsulated linseed oil percentage (ELO%) of 93.9% and a minimum micro/nanocapsule size of 0.574 μm were achieved at 594 rpm agitation, 350 W sonication power, and 3 min sonication time. Validation of the model was performed. The percentage relative errors between the predicted and experimental values of the ELO% and micro/nanocapsule size are 1.28% and 3.66%, respectively. The efficacy of the optimum micro/nanocapsules in healing cracks in a glass flake epoxy paint and corrosion protection was investigated by the salt spray test and Tafel polarization technique.

Introduction

Microencapsulation of active materials in hollow spheres is an attractive subject in various fields, such as controlled release systems (Möbus, Siepmann, & Bodmeier, 2012), preservation of flavor (Gharsallaoui et al., 2012), biotechnology (Nazzaro, Orlando, Fratianni, & Coppola, 2012), and food additives (Otálora, Carriazo, Iturriaga, Nazareno, & Osorio, 2015). Recently, the use of microcapsules containing self-healing agents for healing cracks generated in polymeric coatings and paints has attracted considerable interest (Liu, Zhang, Wang, Wang, & Wang, 2012; Sauvant-Moynot, Gonzalez, & Kittel, 2008; Suryanarayana, Rao, & Kumar, 2008). These capsules loaded with a self-healing agent are incorporated in the coating. The microcapsules rupture and release the self-healing agent during crack formation. The released self-healing agent reacts with a catalyst dispersed in the polymeric coating or undergoes oxidative polymerization and drying, leading to crack repair.

The most important techniques for preparing microcapsule-loaded active agents are interfacial polymerization, in-situ polymerization, coacervation, and meltable dispersion (Karger-Kocsis, 2010). Among the above-mentioned methods, in-situ polymerization is a popular method to prepare microcapsules for self-healing applications. However, in standard emulsion microencapsulation methods, the lower limit of the capsule diameter is approximately 10 μm (Blaiszik, Sottos, & White, 2008). To prepare sub-micrometer and nanoscale capsules, some researchers have combined ultrasonic homogenization and in-situ encapsulation techniques (Blaiszik et al., 2008; Kouhi, Mohebbi, Mirzaei, & Peikari, 2013). In this combination technique, some parameters, such as the rotational speed of the agitator and the power and time of sonication, have a strong effect on the size of the prepared capsules and

* Corresponding author. Fax: +98 71 36473748.
E-mail addresses: ali_ebrahiminiya@yahoo.com (A. Ebrahiminiya), mkhorram@shirazu.ac.i, khorram_m@hamoon.usb.ac.ir (M. Khorram), ajili@shirazu.ac.ir (S. Hassanajili), mjavidi@shirazu.ac.ir (M. Javidi).

http://dx.doi.org/10.1016/j.partic.2017.01.010
1674-2001/

the percentage of encapsulated self-healing agent. The capsule size and loading percentage of the active agent have important effects on the self-healing properties of the coating. For a microcapsule-based self-healing coating, the size of the microcapsules strongly influences the self-healing performance. The microcapsule diameter affects the amount of released healing agent in the cracked area (Sun, Zhang, Tang, & Yang, 2016). A smaller microcapsule diameter results in better compatibility with the coating matrix (Samadzadeh, Boura, Lochab, Kumar, & Roy, 2010). Rule, Sottos, and White (2007) investigated the influence of the microcapsule diameter on the performance of self-healing materials. They investigated the relationship between the microcapsule size, healing agent delivery, and healing performance by the fracture test. They demonstrated that the amount of healing agent delivered is determined by the product of the microcapsule weight fraction and the microcapsule diameter. Matsuda et al. (2016) investigated the effect of the particle size of pH-sensitive microcapsules produced by water-in-oil emulsion polymerization. They found that smaller size microcapsules showed better corrosion inhibition properties. The core content is one of the most important characteristics of microcapsules and their self-healing performance. Sharma, Shukla, Lochab, Kumar, and Roy (2014) investigated the effect of the concentration of the encapsulating polymer on the core content. They demonstrated that the core content can be increased by decreasing the encapsulating polymer concentration in the feed solution.

Optimization of the process parameters affecting microencapsulation using the in-situ polymerization method has been investigated by several researchers. Gil, Cuenca, Romero, Valverde, and Sánchez-Silva (2014) optimized the synthesis procedure of microparticles containing gold. They studied the effects of the amount of organic solvent and the gold precursor to polymer mass ratio (Au/PUF) on the properties of the prepared microcapsules. The obtained results showed that increasing the amount of organic solvent leads to a decrease of the gold encapsulation efficiency and an increase of the average diameter of the encapsulated gold microparticles. Increasing the Au/PUF ratio also increased the particle size. Kouhi et al. (2013) prepared microcapsules filled with healing agents using in-situ polymerization of urea–formaldehyde. They investigated the effect of the agitation rate on the average diameter of the microcapsules and their self-healing performance. Their results showed that increasing the agitation rate leads to a decrease of the mean diameter of the microcapsules and improves the performance in self-healing applications. Ollier, Penoff, and Alvarez (2016) optimized the synthesis conditions of epoxy resin microencapsulation. They analyzed the emulsification conditions (time, and agitation method and rate), viscosity of the core phase, stirring speed, core/shell mass ratio, and drying process. They found that microcapsules prepared at the optimized reaction conditions have a satisfactory size (below 150 μm). In another study (Hatami Boura, Peikari, Ashrafi, & Samadzadeh, 2012), the effect of the rotational speed of the agitator on the microcapsule size was the only investigated process parameter, and the process parameter was optimized. All of the above-mentioned studies have been performed by investigating one variable at a time. This ignores the interactions between affecting factors and does not reflect the actual responses.

To optimize the process conditions and minimize the number of experiments, response surface methodology (RSM) can be used. RSM is an efficient mathematical and statistical tool for constructing empirical models that describe the effects of the studied parameters and their interactions on the response (Myers, Montgomery, & Anderson-Cook, 2009). Khoee, Payandeh, Jafarzadeh, and Asadi (2016) modeled and optimized in-situ polymerization microencapsulation of epoxy resin in poly(urea–formaldehyde). To model and optimize the microcapsule size and its core content, the central composite design (CCD) method was used. The agitation rate, surfactant concentration, and sonication time were the parameters analyzed.

Table 1
Experimental ranges and levels of the independent variables.

Independent input parameter	Levels and the actual values of parameter				
	−2	−1	0	1	2
Agitation speed, X_1 (rpm)	300	400	500	600	700
Power of sonication, X_2 (W)	200	250	300	350	400
Duration of sonication, X_3 (min)	0	3	6	9	12

The main objective of this study is to model and optimize the effects of the rotational speed of the agitator, sonication power, and sonication time on the micro/nanocapsule size and percentage of encapsulated healing agent in capsules prepared by the combined method of ultrasonic homogenization and in-situ polymerization. The shell of the prepared micro/nanocapsules was composed of urea–formaldehyde and its core material was linseed oil as a healing agent owing to its film-forming ability by atmospheric oxidation. RSM in conjunction with CCD was used to determine the optimal experimental conditions for minimizing the capsule size and maximizing the percentage of encapsulated healing agent.

Experimental

Materials

Urea, ammonium chloride, poly(vinyl alcohol) as a surfactant, and resorcinol as a cross-linking agent were purchased from Daejung Co. (Gyeonggi-Do, South Korea). Pure linseed oil as a healing agent was obtained from Sigma-Aldrich Co. (St. Louis, USA) and formaldehyde was obtained from Merck Chemicals Co. (Darmstadt, Germany). Glass flake epoxy and hardener were procured from Firoozeh Paint Co. (Shiraz, Iran).

Experimental design and statistical analysis

To investigate the effect of the rotational speed of agitation, sonication power, and sonication time on the diameter of the micro/nanocapsules and the linseed oil content in the micro/nanocapsules, a three factor CCD was used. The agitation speed (X_1), sonication power (X_2), sonication time (X_3) were chosen as the three independent factors for investigation (Table 1). The other parameters that normally affect the in-situ polymerization process were set at fixed values. As shown in Table 1, five levels of the numerical factors were considered. The number of experiments determined by CCD is $N = k^2 + 2k + c_P$, where k is the number of factors and c_P is the center point replicate number. In the present study, the number of independent variables is three and hence $N = 20$ for five repetitions in a center point experiment. The parameter that indicates the upper and lower levels of the independent variables in the experiment design, α, is two for this design, because there are three independent variables. The test factors were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X_i}, \quad (1)$$

where X_i is the independent variable, X_0 is the real value of the independent variable in the center point of the independent variable, and x_i is the code value of the independent variable, and ΔX_i is the step change.

Please cite this article in press as: Ebrahiminiya, A., et al. Modeling and optimization of the parameters affecting the in-situ microencapsulation process for producing epoxy-based self-healing anti-corrosion coatings. *Particuology* (2017), http://dx.doi.org/10.1016/j.partic.2017.01.010