Powder Technology 284 (2015) 237–244

Contents lists available at ScienceDirect

Powder Technology

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

Sol–gel microencapsulation of oil phase with Pickering and nonionic surfactant based emulsions

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ARTICLE INFO

Article history:
Received 9 May 2015
Received in revised form 23 June 2015
Accepted 27 June 2015
Available online 3 July 2015

Keywords:
Oil-in-water emulsion
Pickering emulsion
Sol–gel encapsulation

ABSTRACT

Sol–gel polycondensation was used to encapsulate two different kinds of core with a silica shell, i.e. castor oil which is considered as a model active agent, and bisphenol A bis(diphenyl phosphate), an insoluble liquid fire retardant. The influence of the nature of the emulsifier was also studied, i.e. Pickering emulsion based on the interface stabilization performed by the organization of solid nanoparticles was compared to a classical emulsion process using a non-ionic surfactant. The influence of both cores and emulsifiers on the stability of emulsion was studied by granulometric analysis, optical microscopy and macroscopic morphology (from nacked-eye observations). The sol–gel encapsulation efficiency was assessed by Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analysis. Finally, thermal stability of microcapsules was evaluated by thermogravimetric analysis (TGA). Results show that both Pickering and classical emulsions processing allow successful sol–gel encapsulation of castor oil and bisphenol A bis (diphenyl phosphate) with a satisfying thermal stability for textile application. However, the use of Pickering emulsion with nanoparticles provides more highly stable emulsions and promotes silica shell formation.

1. Introduction

Textile structures are widely used in various applications such as clothing, insulation, absorption, or filtration due to their remarkable properties combining flexibility, low weight and mechanical behavior. It can be however interesting to bring further functionalities to these textiles in order to increase their added value. In this context, specific ennobling or finishing operations allow to add colors, water repellent or antimicrobial properties for example. Nevertheless, some active agents are very sensitive to the environment, or are in the liquid state and so unable to be linked efficiently on textile surfaces. In order to avoid any interaction with the environment, limit the reactivity and overcome volatility, the active agent can be encapsulated. The handling is then facilitated by transforming liquid products into solid powders allowing the release when necessary [1].

Encapsulation consists in coating small droplets or particles of active agents in order to entrap it as a core material with a protective natural or synthetic polymeric shell. A wide range of applications including cosmetics, drugs, perfumes, pesticides release or fire retardancy can be achieved by microencapsulation in various textile fields [2]. Fire retardant properties are particularly requested in numerous textile applications because of the high flammability, corrosive and toxic gases liberation of most synthetic polymers during combustion, and because of the more drastic safety standards. Active capsules or particles can be fixed on textiles by various ways in order to provide a durable functionalization. They can be blended with the polymer during spinning [3] or incorporated onto the manufactured textile by conventional finishing process such as padding [4] or coating without modification of the intrinsic properties of the support material [5].

For environmentally friendly purpose, a new dry powder impregnation technology for nonwoven structures by functional microcapsules is used [6]. It consists in the dispersion of microcapsules by an alternative electrostatic field in order to avoid water utilization and pollution by binders and capsules, and to reduce thermal energy consumption due to water evaporation after binding. To efficiently implement this process, capsules need to reach some particular specifications. They have to be within the size of 10 to 100 μm to allow particle mobility and migration through the textile pores of the nonwoven. Then, they need a satisfying thermal stability in order to stay undamaged during the fixation on the fibers which is performed around 150 °C. Regardless the impregnation process, capsules need to have sufficient mechanical properties to resist stressing during utilization. Silica shells or matrices are frequently used to encapsulate various types of active agents such as dyes [7], drugs [8], enzymes [9], bacteria [10] or fire retardant [3], and are widely used in cosmetics formulation because of their biocompatibility and limited toxicity [11]. Moreover, they exhibit high mechanical properties [12], excellent chemical and thermal stabilities with limited release of toxic gases during decomposition. This is due to the

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http://dx.doi.org/10.1016/j.powtec.2015.06.055
0032-5910/

excellent thermal stability and to the high heat resistance of Si—O—Si chains and of the relative crosslinked matrix [13]. Thus, silica particles are often used alone as fire retardant fillers [14]. As encapsulation shell, it offers a thermal insulation layer and a protective screen from further thermal degradation of the polymer residue, even at high temperature, and participates to char formation. It also improves thermal behavior of fire retardants as ammonium polyphosphate by delaying the pyrolysis process in polyurethanes [15], exhibits enhanced fire resistance and improved thermal stability encapsulating Bisphenol A bis (diphenyl phosphate) (BDP) in polyethylene terephthalate matrix [16]. Furthermore, sol–gel synthesis has the advantage of being carried out in very mild conditions i.e. in aqueous solution, at low temperature, and under atmospheric pressure.

In this study, two different actives (castor oil and BDP) have been encapsulated by silica shell. Castor oil, a renewable natural oil, has been encapsulated as a model compound. BDP is a halogen-free aryl phosphate effective fire retardant used increasingly because of environmental and/or regulatory issues. It is widely used as a copolymer during polymerization because of its good thermal and hydrolytic stability. The low volatility allows long term stability and aging [17], even if it tends to exude at high concentrations [18]. In this study, the purpose is the encapsulation of BDP to provide fire resistance to previously manufactured nonwoven textiles. Indeed, sol–gel encapsulation of this highly viscous colorless fluid improves polyethylene terephthalate thermal behavior and displays good flame retardancy for charring polymers as polycarbonates [3,19].

A classical emulsion process, using a common surfactant reducing the interfacial tension and facilitating the droplets division is compared to Pickering emulsion which is based on the utilization of nanoparticles with a strong anchoring at the interface and limiting the coalescence of the droplets to stabilize the oil-water interface. Polyoxyethylene (20) sorbitan monolaurate (Polysorbate 20 or Tween®20) is a non-ionic hydrophilic surfactant with a hydrophilic-lipophilic balance of 16.7. It is used as an oil-in-water emulsifier for its good stability and relative non-toxicity in many detergents and emulsification formulations from domestic to food or pharmaceutical applications. Aerosil R816 is a spherical powder of fumed silica particles with an average diameter of 12 nm. It corresponds to Aerosil 200 hydrophilic particles treated with hexadecylsilane. After high temperature treatment, particles are partially hydrophobic due to the grafting of dimethylsilyl groups on silica particles surface [20]. This strong Si—O—Si linkage presents excellent thermal and chemical stability [21]. Getting of oil-in-water or water-in-oil emulsions depends on the hydrophilic/lipophilic groups ratio modifying their wettability [22]. These particles are usually used in water-based coating systems or cosmetics and can be used for oil-in-water emulsification [23]. Emulsions based on nanoparticles are prepared in the same way than classical emulsion, and are known to have an improved stability, longer than several months [24,25]. In addition to their high stability performances, Pickering emulsion is used in this work to insulate the interface between the two phases and to avoid any material transfer as proved by Arditty [26]. In addition, it improves the shell rigidity and acts as an interfacial barrier against deformation [20].

The aim of this study is to encapsulate one FR compound, the BDP for textile functionalization. To handle the functionalization process, capsules need to be ranged between 10 and 100 μm and to support temperature higher than 150 °C. To manage this Pickering emulsion is combined with sol–gel process.

2. Materials and methods

2.1. Materials

BDP (Devan Chemicals, Belgium), castor oil (Sigma Aldrich, France) and cyclohexane (Sigma Aldrich) are used respectively as fire retardant, inert and removable core. Tetraethylorthosilicate (TEOS) (Sigma Aldrich) is used as shell material. Polyoxyethylene (20) sorbitan monolaurate (Tween®20) (Sigma Aldrich) is employed as an emulsifier and Evonik Aerosil R816 (Safic Alcan, France) is employed as a solid emulsion stabilizer for Pickering emulsions. Cetyltrimethylammonium bromide (CTAB) (Sigma Aldrich) is used as a structure-direction agent combined with Pickering emulsion. Formic acid and sodium hydroxide purchased from Aldrich are used as pH control agents. All products are used without any further purification before use.

2.2. Preparation of microcapsules

Both castor oil and BDP are non-soluble in water and primarily dispersed into an aqueous solution during the emulsion process thanks to emulsifiers. Emulsification is performed by an important mechanical stirring leading to the shredding of the oil into small droplets. Preliminary tests have been performed in order to confirm castor oil and BDP droplets stabilization by Aerosil R816, to determine the particle content, and to confirm the extended stability with this system. For both core (castor oil or BDP), emulsions have been prepared with 10 wt.-% of core and 0.5, 1 and 3 wt.-% of dried particles by mechanical stirring at 1000 rpm performed with a four titled blades propeller.

The preparation of microcapsules is illustrated in Fig. 1. The emulsion of 10 g of the core material is firstly prepared by mechanical stirring using a four titled blade propeller running at 1000 rpm into 100 ml of an aqueous phase containing 1 g of Tween®20 or 0.1 g of Aerosil R816 silica particles. 0.5 g of CTAB is added after the emulsion in the case of silica particles to promote hydrolysed silanol migration at the droplets surface [27]. 100 ml of 10 wt.-% tetraethoxysilane (TEOS) solution, previously hydrolyzed at pH 2.8, is then added dropwise in the emulsion. The mixture is kept under stirring at 45 °C during 24 h to initiate silane condensation. Sodium hydroxide aqueous solution (10 wt.-%) is gradually added up to pH 6, close to neutralization, in order to speed up the condensation and to shape a thick shell around the active substance. Capsules are then matured for 1 h, filtered, rinsed with water and dried 24 h at 50 °C. A thin powder is then obtained.

Cyclohexane, a highly volatile solvent, has been encapsulated by the same preparation method and evaporated one night at 80 °C to be used as blank for FT-IR comparison and TGA analysis.

2.3. Analytical methods

2.3.1. Particle size analysis and morphological characterization

Particle diameters were characterized with a laser-light blocking technique (AccusizerTM, model 770, Particle sizing systems, Santa Barbara, CA, connected to C770 software version 2.54). The particle size distribution, in number, was obtained one particle at a time, by comparing the detected pulse heights with standard calibration curve, obtained from a set of uniform particles of known diameter. Measurements were performed directly in the prepared solution at room

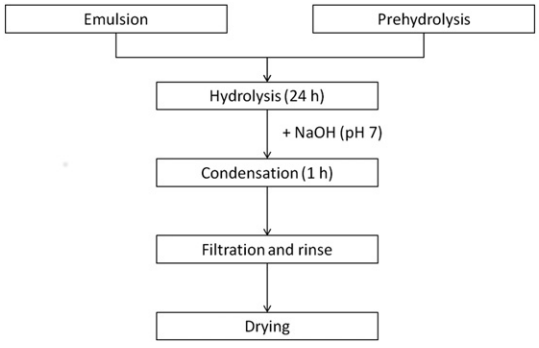

Fig. 1. Overview of the preparation of microcapsules. Preferred magnification: single column.