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Isosorbide-based microcapsules for cosmeto-textiles

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ABSTRACT

New microcapsules based on renewable materials and containing perfume were designed for cosmeto-textile application. Such microcapsules contained the neroline fragrance as core material and a bio-based polyurethane as wall material. The polymer wall was synthesized by interfacial polycondensation of isosorbide and methylene bis(phenyl isocyanate). The chemical structure of the microcapsules was confirmed by IR and ^{1}H NMR spectroscopies. The encapsulation efficiency of perfume was determined using ^{1}H NMR analysis technique accounts for 30%. Microcapsules of spherical shape and 27 μm diameter consisted of a liquid core and a polymer wall, as revealed by means of small-angle light scattering measurements and scanning electron microscopy (SEM) observations. Neroline-loaded microcapsules were impregnated on polyamide textile substrate. The impregnation yield was about 80%. The presence of microencapsulated perfume and the durability of the impregnation effect were tested by SEM, UV–visible spectroscopy and gas chromatography. The polyamide knitting finished with microcapsules slowly released its microcapsule content and the neroline remained until twentieth washing cycles.

1. Introduction

Microencapsulation of various materials is an effective method that aims at two major purposes:

(i) the control over the delivery rates into the surroundings leading to sustained release properties;

(ii) the stabilization of functional agents by their protection against reactions with moisture, light and oxygen (Benita, 1996; Mercadé-Prieto and Zhang, 2012; Park et al., 2001; Vandamme et al., 2007). Microencapsulation of solid, liquid or gaseous materials results in a solid powder form that is advantageous in many applications. In particular, immobilization of liquid compounds onto solid supports often requires their encapsulation as prerequisite to their deposition onto solid surface as an adhesive and durable coating. This technique has been early applied to carbonless copy paper (Green, 1957; White, 1992) and it has currently found applications in many technical domains such as, food, adhesives, cosmetics, pharmaceutics, phytosanitary products, medicine, liquid crystals labels, phase-change materials (Bouchemal et al., 2004; Glenn et al., 2010; Matsunami and Ichikawa, 2002; Suryanarayana et al., 2008; Tseng et al., 2005; Whateley, 1992).

Encapsulation processes have been introduced in the textile industry for the implementation of specific properties to textile materials by coating them with various active substances (Monllor et al., 2007). Such application takes advantage of the solid powdered form of microencapsulated liquids for an easy deposition onto the textile fibers. Fabrics having long-lasting fragrance release properties are manufactured by coating fibers with microcapsules loaded with perfumes (Delaye, 2004; Madene et al., 2006; Monllor et al., 2007; Nelson, 2001; Pena et al., 2012; Rodrigues et al., 2009; Specos et al., 2010a,b; Tzhayik et al., 2012; Zhang and Rochefort, 2012).

The microcapsules can be applied by stamping works, exhaustion dyeing, impregnation, spraying and coating. Besides, microcapsules can be incorporated in the fiber directly without modifying its touch and color (Monllor et al., 2007; Nelson, 2002; Roxana et al., 2008).

Polyurethane is an appropriate candidate for microcapsule-shell in textile application owing to its good adhesive properties and compatibility with skin (Cordeiro et al., 1997; Dieterich, 1981; Fenouillot et al., 2010; Gaudina and Sintes-Zydowicz, 2008; Saihi et al., 2006; Shuklay et al., 2002; Varke and Sreekumar, 2010).

Microencapsulation processes rely on several chemical methods such as in situ polymerization, coacervation (Jyothi et al., 2010).

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Interfacial polymerization is a widely used method that allows the manufacture of microcapsules from an o/w emulsion by the formation of thick polymer walls around liquid droplets (Arshady, 1992; Frère et al., 1998; Hong and Park, 1999; Jabbari, 2001; Mirabedini et al., 2012; Pearson, 1985; Salaün et al., 2011; Wagh et al., 2009; Yan et al., 1993). Encapsulation methods based on in situ polymerization are open to health concerns coming either from residual monomers in case of their incomplete conversion, or the formation of hazardous degradation products during the life cycle of the materials. A well-known example of such potential health hazard is bisphenol A contained in polycarbonate. In order to remedy such concerns, the substitution of harmful reagents by alternative monomers is a definite progress toward safety. Sustainability of the manufacture processes also requires the utilization of bio-based materials from renewable sources. Attractive diol monomers to be used in polycondensation in place of bisphenol A are dianhydrohexitols such as isosorbide (Fenouillot et al., 2010).

The present work aims at the development of microcapsules based on materials taken from sustainable renewable sources. Since polyurethane is widely used as a wall materials of microcapsules prepared by interfacial polycondensation, and considering the large body of work devoted to polyurethane materials using diols from natural sources (Fenouillot et al., 2010), the preparation and properties of isosorbide-based polyurethane microcapsules have been investigated. Microcapsules loaded with the neroline perfume were prepared by interfacial polymerization using the bio-based isosorbide as a diol in place of the conventional diols often used in polycondensation (Rodrigues et al., 2009). The substitution of such diols for isosorbide kept the main favorable characteristics of polyurethane microcapsules. The microcapsules were characterized for their chemical composition and morphology. Finally, the behavior of such microcapsules for polyamide textile finishing was investigated so as to assess them with regards to their application for cosmeto-textiles.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

4,4′-Methylene bis (phenyl isocyanate) (MDI, Aldrich 98%), isosorbide (Acros 98%), Polysorbate 80 (Tween^{TM} 80, Aldrich 98%), dibutyltindilaurate (SnDBDL, Aldrich 95%). In order to bond the microcapsules to the polyamide knitting, an acrylic cross linking agent (RESACRIL BD CONC; supplied by Prochimica Novarese SPA, Italy) was used. 2-Ethoxynaphthalene (neroline) was synthesized by O-ethylation of β-naphthol with ethyl bromide (Azizi et al., 2011). Microencapsulation processes were carried out in a thermostated double jacketed 1 L glass reactor, (Sovirel), equipped with an anchor blade mixer, a digital control of stirring rate and an oil thermostat bath. The emulsion was maintained by a homogenizer Ultra-Turrax T 25 Basic equipped with a S25N 25F shaft rotating at 12,000 rpm.

2.1.2. Methods

^{1}H NMR spectra were recorded on a Bruker AV300 spectrometer. IR analyses were carried out in transmission mode with a Shimadzu FT-IR spectrometer on KBr pellets with sample concentration of 1 wt%. Optical microscopy pictures of microcapsules were taken with a Leica DMLM microscope equipped with Color view camera and soft imaging system. A drop of the aqueous suspension placed between a glass plate and a cover slip was observed in transmission mode. scanning electron microscopy (SEM) analyses of the surface morphology were performed using a Jeol JCM 5000 microscope operating at 10 kV acceleration under moderate vacuum, thus avoiding the need for metallization of the samples. An aqueous suspension of microcapsules was cast on aluminum stubs and dried before observation by SEM. Particle size distribution was studied by small-angle light scattering using a Coulter 13320 laser-diffraction particle size analyzer. UV–vis absorption spectra were recorded with a Cary 50 Probe spectrophotometer of Hellma quartz cuvettes in 10 mm optical path.

2.2. Microcapsules preparation

Isosorbide-based polyurethane microcapsules were prepared by interfacial polycondensation method using the dibutyltindilaurate catalyst according to previous reports (Giraud et al., 2005; Rodrigues et al., 2009). The polyurethane synthesis reaction is shown in Fig. 1. The synthesis process starts with an o/w emulsion involving two phases: a continuous phase containing 225 mL of water and 0.63 mmol of Polysorbate 80 (solution I); and a dispersed phase containing neroline and 7.08 mmol of MDI in 45 mL of cyclohexane (solution II). 7.08 mmol of isosorbide and 0.4 mL of SnDBDL were dissolved in 35 mL of the solution I, to form the solution III.

The solution II was stirred with 190 mL of solution I in the reactor at room temperature for 5 min. Agitation was regulated, by a homogenizer Ultra-Turrax T 25, at a speed of 12,000 rpm in order to prepare an o/w emulsion. Then, the solution III was added and the speed was decreased to 500 rpm. The temperature was maintained at 60 °C during 6 h (Azizi et al., 2011). The obtained microcapsules were separated by centrifugation (Gyrozen 416G) at a speed of 3000 rpm for 20 min, rinsed with cyclohexane to eliminate the residual monomer and non-encapsulated neroline and dried under vacuum. In order to study the shell structure, polyurethane microcapsules were prepared following the same procedure, without introducing neroline in organic phase (dispersed phase) and characterized with ^{1}H NMR and IR spectroscopies. ^{1}H NMR (300 MHz, DMSO-*d6*, δ in ppm from TMS): 9.64–9.562 (m, NH urethane); 8.4 (s, NH urée); 7.09–7.39 (m, Ar-H) 5.16–3.6 (H isosorbide + Ar-CH2-Ar).

IR (cm-1): 3325 (m, N—H asymmetric bending), 3050 (m, aromatic C—H stretching); 2872 (s, aliphatic C—H stretching); 1720 (m, C=O stretching); 1410 (m, C=C stretching); 1530 (s, C—N bending); 1230 (m, C—O stretching).

2.3. Application of microcapsules to textile finishing

Impregnation was chosen as the most suitable process to apply neroline-loaded polyurethane microcapsules on textile fibers. Pure polyamide knitting (203 g m^{-2}) was impregnated with encapsulated active product (Jing et al., 2011; Rodrigues et al., 2009). Microcapsules were suspended in bath containing acrylic cross-linking agent (RESACRIL BD CONC, 50 g L^{-1}). Fabric was impregnated in the bath for 15 min. The impregnated textile was dried for 5 min at 100 °C and thermally fixed at 120 °C during 5 min.

3. Results and discussions

3.1. Preparation of the neroline-loaded microcapsules

The preparation process of microcapsules consisted in two steps, as a first step, the organic phase containing the neroline perfume and the hydrophobic monomer (MDI) in cyclohexane was emulsified in water at room temperature. The Polysorbate 80 surfactant added in the aqueous phase is a hydrophilic emulsifier (HLB = 15) that causes the formation of an emulsion of the oil-in-water type (o/w). The full oil phase was stable with respect to coalescence. Creaming was prevented by keeping stirring at a low rotation rate. The second step is the polycondensation reaction that was