Micro/nanoencapsulation of citriodiol with ethyl cellulose for repellent textile finishing

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INTRODUCTION AND OBJECTIVE

Functional textiles have been developed to satisfy the needs of comfort and safety of consumers. The most studied applications include insects' repellency, antimicrobial finishing, phase change materials, fire retardants, among others. The need for long-term durability of functionality has brought about the introduction of microencapsulation techniques. In particular, natural derived repellents have been microencapsulated using different wall materials and applied to textile substrates to control their release (Specos 2010). Citriodiol is one of the biopesticides tested and registered by the EPA, and included in the European Biocidal Products Directive 98/8/EC. We have previously encapsulated citriodiol by complex coacervation, applied it to cotton textiles and demonstrated its higher efficacy compared to citronella essential oil (Hermida 2011). However, these functional textiles do not withstand using conditions, particularly laundry.

Ethyl Cellulose (EC) is a biocompatible polymer commonly used as wall material for microencapsulation. Its covalent grafting to cotton through esterification in the presence of polycarboxylic acids and catalyzers has been previously reported (Badulescu 2008). The aim of this work is to compare EC citriodiol-contaning micro and nanoparticles intended for cotton fabrics finishing. Both particles and treated textiles have been characterized to select the most suitable for further repellency assays.

MATERIALS AND METHODS

Preparation and characterization of microparticles
Citriodiol containing microparticles (MP) were prepared by an emulsion-solvent evaporation technique using low viscosity EC (7 cps). Briefly, citriodiol and EC (1:1) were dissolved in CH_2Cl_2 (solids: 5% w/w). This oily phase was added to aqueous 1% PVA, homogenized and the solvent was evaporated under constant agitation. Solidified MP were washed, filtered and air dried. MP were observed by dual-beam scanning electron microscopy (DB-SEM) and their size determined by laser diffraction (LD). An aqueous suspension of freshly prepared MP was further used for textile treatment.

Preparation and characterization of nanoparticles
Nanoparticles (NP) were prepared from EC 7 cps by a nanoprecipitation technique. Briefly, citriodiol and EC (1:1) were dissolved in acetone (solids: 5.8% w/w). This oil phase was slowly added to water under constant magnetic stirring. The solvent was evaporated under agitation and NP were paper filtered to eliminate big polymer agglomerates. NP were observed by DB-SEM and their size determined by dynamic laser spectroscopy (DLS).

Textile treatment and characterization
Cotton fabrics were treated with MP or NP suspensions by different procedures (Table 2): (i) fabrics were padded through an aqueous finish bath containing 8% MP or 4% NP and dried for 3 min at 60ºC; (ii) the finish bath contained MP, citric acid (CA) and sodium hypophosphite (SH) as catalyst at a ratio 8:6:3 and the fabrics were dried at 60ºC or dried at 60ºC and cured at 160 ºC; (iii) fabrics were first padded through 4% NP suspension, then padded through 6:3 CA-SH solution and finally treated as described in (ii). The finishing procedure was modified for NP to prevent massive agglomeration which was observed upon incubation with CA-SH. In another set of assays, textiles were previously treated with chitosan (CHI) with the aim of creating a positive layer onto cotton. In this case (iv), fabrics were first padded through 1.5:10:2 CHI-CA-SH solution, dried at 60ºC, cured at 130ºC, rinsed with water and further treated with MP and NP suspensions as previously described. Cotton samples were conditioned at 21ºC and 65% RH and mass gain was registered after each step. Textiles were analyzed by SEM and ester linkage formation was assessed by ATR-FTIR.

Citriodiol content was determined in treated textiles or MP by incubation in acetone upon sonication for 5 min (EC solubilization). After fabric/MP filtration, the polymer was precipitated with hexane. The filtered solutions were analyzed by gas chromatography coupled to a mass detector (GC-MS). The major repellent components of citriodiol, (cis and trans p-Menthane-3,8-diol, PMD) were quantified. Results were expressed as mg citriodiol per g fabric.

RESULTS AND DISCUSSION

MP presented very low citriodiol encapsulation (Table 1), due to its release towards surfactant solution. On the other hand, NP's high encapsulation was inferred from low citriodiol water solubility (0.03% w/v), as no surfactant was included during prepartion. NP suspension was monodisperse and presented a negative charge (Table 1, Z-Pot<<0).

Table 1: MP/NP characterization

Type of particle	Mean Size	Z-Pot (mV)	Solid yield %	% EE
MP	42 μm (3.1)[a]	ND	56	7.5
NP	151 nm (0.085)[b]	-38 mV	85	98

%EE: % Encapsulation efficiency ND: non determined; [a] Span (LD); [b] Polydispersity Index (DLS)

Both MP and NP were spherical and presented smooth surfaces (Fig.1). MP SEM images showed small microparticles which aggregated like grape bunches in accordance with mean size determination (Table 1).

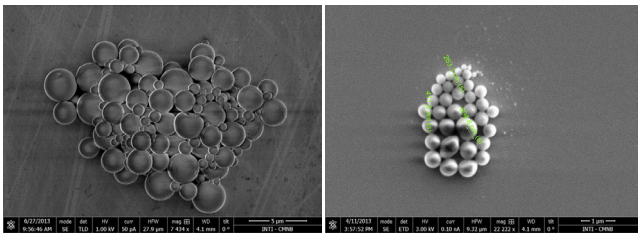

Figure 1: DB-SEM images of MP 7400x (left) and NP 22000x (right)

Once applied to fabrics, MP could be profusely observed in between the fibres (Fig.2, left). On the other hand, NP could not be observed.

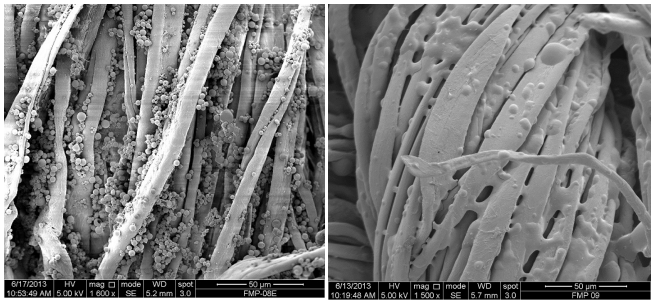

Figure 2: SEM images of MP-CASH-60 (left) and MP-CASH-60-160 (right)

Table 2 shows the characterization of cotton treated with citriodiol-containing MP and NP. NP suspension dried at 60°C (NP-60) was undoubtedly the most efficient finishing treatment to obtain high citriodiol content in fabrics, probably due to NP's high encapsulation efficiency. This is in contrast with their low mass gain. On the other hand, any treatment intended to graft NP (CASH) or increase NP loading (CHI) decreased citriodiol contents. In the first case (CASH), NP may have reacted with crosslinker and lost content. Moreover, curing at 160°C produced a complete citriodiol loss. In the second (CHI), the decrease was not so significant and was attributed to lower NP loading, but the desired attraction effect by opposite charges was not observed.

Table 2: Treated textiles characterization

Sample	Mass gain (%)	mg Citriodiol / g fabric
MP-60	8.6	1.12 ± 0.09
MP-CASH-60	20.6	0.54 ± 0.04
MP-CASH-60-160	15.4	< 0.01
CHI-CASH-60-160-MP-60	16.1 (9.5+6.6)*	0.61 ± 0.02
NP-60	2.2	4.04 ± 0.45
NP-CASH-60	6.0	0.28 ± 0.02
NP-CASH-60-160	4.4	< 0.01
CHI-CASH-60-160-NP-60	11.1 (9.3+1.8)*	2.05 ± 0.21

*(CHI mass gain+MP or NP mass gain)

A similar behaviour was observed for MP, though the loss after CASH treatment at 60°C was not so marked. However, citriodiol was also completely lost after curing at 160°C. Figure 2 (right) shows how the treatment alters MP morphology which actually melted onto the fibres. ATR-FTIR results demonstrated grafting of NP and MP at 160°C, while the linkage at 60°C was achieved at a low percentage (data not shown).

CONCLUSIONS

Citriodiol nanoparticles padded on plain cotton were the most effective finishing treatment for future repellency assays. Further assays will be performed to develop new methods for NP fixation to cotton, either at lower temperatures or using alternative catalysts and/or crosslinkers.

REFERENCES

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