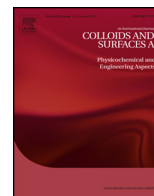




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Effectiveness of grafting modes of methoxycinnamate sunscreen onto silica particles



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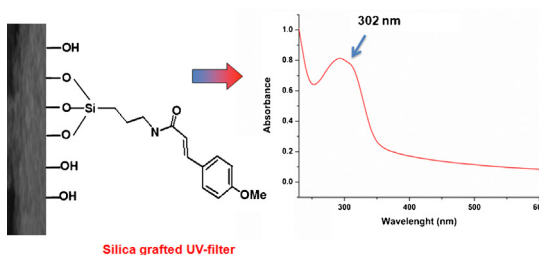
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HIGHLIGHTS

- Immobilization of modified *p*-methoxycinnamic acid onto silica particles.
- New grafting routes of UV filter onto silica surface.
- High grafting degree of UV-filter.
- Maintaining of UV-absorbing ability after immobilization of UV-filter.

GRAPHICAL ABSTRACT



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ABSTRACT

Immobilization of *p*-methoxycinnamate onto silica particles has been performed following two synthesis routes differing by the nature of the coupling agent used for the grafting of UV molecule to silica surface. Different coupling agents, triethoxysilane (TES) in the first route or 3-aminopropyltriethoxysilane (APTS) in the second route, were used. In the first route, the UV molecule was attached to silica by means of a short (C2) or a long (C10) alkyl spacer to study their effect on grafting degree. All synthesis methods led to successful grafting. The grafting degree of UV-filter onto silica particles was two-fold larger in the case of short spacer chains. Better water dispersion was obtained for the material synthesized using the first route. The water dispersion particles remained stable for 40 days. UV-absorbing ability was retained after immobilization of UV-filter molecules onto silica particles in all samples.

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1. Introduction

Sunscreen products are extensively used in order to prevent harmful effects of excessive sunlight exposure, such as causing sunburn, sultan, acceleration of aging and carcinogenic effects of UV-radiation [1–4]. Organic compounds such as *p*-methoxycinnamic acids and their esters are excellent compounds that are widely used as UV-filters, which absorb UV radiation in the

shorter wavelength region (290–320 nm) of the solar UV spectrum, especially UV_B, to reduce the dose of solar radiation that reaches the skin [5,6].

However, some studies have reported that UV-absorber undergoes a chemical degradation when exposed to sunlight [7,8] and likewise is unstable under irradiation in solution [9–11]. The latter reaction not only decreases the sunscreen UV-protective capacity during use [12–14], but can also lead to toxic or allergenic degradation products causing irritation [15,16]. Also, UV-filter can penetrate the deep layers of skin, possibly reaching the more vulnerable viable epidermis and dermis layers causing further damages [17]. Sunscreen products should be confined to the surface

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of skin and should not diffuse into its inner layers. Penetration of sunscreen ingredients to the dermis allows them (and their metabolites) to pass into the systemic circulatory system [18]. Organic UV-absorbers are aromatic molecules, some of them showing mutagenic properties [19]. Allergic contact dermatitis of organic UV-absorbers reported in a significant number of instances [20] involves uptake by the skin immune system at the level of the viable epidermis.

Various methods are used to remedy such troubles. It has been demonstrated that the use of mesoporous silica protects UV-filter molecules from sunlight effects. For instance, the encapsulation of UV-filter in mesoporous silica using in situ sol-gel polymerization of tetraethyl orthosilicate (TEOS) led to stabilization of the UV-filters [21]. In addition, Scalia et al. [22,23] demonstrated that the photodegradation of the UV_B sunscreen agent, *trans*-2-ethylhexyl-*p*-methoxycinnamate was reduced by inclusion inside the hydrophobic cavity of hydroxypropyl-β-cyclodextrin, although this effect was more significant in solution than in emulsion formulations. Likewise Martini et al. showed that UV-absorbers exhibited an increased skin accumulation when the free molecules were formulated in emulsions [24]. On another hand, encapsulation inside nanoparticle of poly(D,L-lactide-co-glycolide) improves the photochemical stability of the sunscreen agent, *trans*-2-ethylhexyl-*p*-methoxycinnamate [25]. The proposed solutions to this problem may be the confinement of organic UV-filter in nanospaces of inorganic materials or formation of inclusion complex in cyclodextrin to avoid direct contact of organic molecules with skin. Furthermore, because the encapsulation inside emulsion droplets or as inclusion complexes was unstable over time, penetration through the skin still might take place.

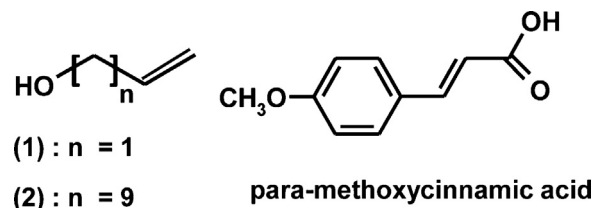
In the present work the *p*-methoxycinnamate used as UV-filter molecule has been attached to the surface of silica particles. Hence, grafting of UV-absorbers to silica particles have been investigated for the purpose of a validation of the concept. The chemistry involved in chemical grafting of silica is well-documented. Grafting organic molecules to titanium dioxide or zinc oxide solid particles would be more suitable since such solid particles are commonly used as 'physical' UV-blockers in sunscreen formulations. Chemical grafting such inorganic materials is much more difficult to achieve and the chemical stability of the linkage has been questioned [26].

A large grafting density of sunscreen molecules is required in order to reach a high enough concentration of UV-absorbers while keeping a not too high silica concentration. A silica material of large specific area (200 m² g⁻¹) was used and an efficient grafting process was investigated for that purpose. The present paper reports the grafting of methoxycinnamate esters as an alternative to the UV_B sunscreen octylmethoxycinnamate. Two grafting processes have been investigated for the grafting of methoxycinnamate: a three-steps grafting process and a one-step process using a silylated sunscreen ready to be grafted were investigated. The UV-absorption properties of the obtained materials will be studied in order to check whether the UV-absorbing properties of sunscreen are maintained upon their immobilization on silica surface.

2. Materials and methods

2.1. Reagents

Prop-2-enol (1), 10-undecylen-1-ol (2), triethoxysilane (TES), 3-aminopropyl triethoxysilane (APTS), and *trans*-methoxycinnamic acid (4-phenylpropenoic acid) (MCA) (Scheme 1) were purchased from Sigma-Aldrich. Fumed silica Cab-O-Sil with an average size of primary particles is 12 nm and a specific area of 200 m² g⁻¹ was obtained from Cabot Corporation (Tuscold, IL). The porous silica surface contains 3.5–4.5 hydroxyl groups per nm² according to the



Scheme 1. Chemical formula of allyl alcohol and *p*-methoxycinnamic acid.

technical information from the manufacturer. The OH density was checked by TGA.

2.2. Methods

¹H and ¹³C NMR spectra were recorded with a Bruker DRX300 spectrometer working at 300 MHz and 75 MHz Larmor frequencies for ¹H and ¹³C respectively. Solutions in acetone-*d*₆ or chloroform-*d*₁ containing tetramethylsilane as internal standard for chemical shifts. The abbreviations used are: s (singlet), d (doublet), t (triplet) and m (multiplet). Infrared spectra of each sample were recorded with a Perkin Elmer 1000 FTIR spectrometer in absorption mode between wave numbers 400 and 4000 cm⁻¹. Thermogravimetric analyses were conducted with Setaram SETSYS 175 over a temperature range 25–1000 °C, with a scan rate of 10 °C min⁻¹ under nitrogen flux of 100 mL min⁻¹. Elemental analyses were performed on a HORIBA carbon sulphur analyzer. UV absorbance measurements were carried out in quartz cuvettes of 10 mm optical path with a spectrophotometer Jasco V-530. Dispersions of silica powders at 10% (w/w) in water were prepared using an ultrasound disperser Sonics Vibracell 75042 equipped with a 3 mm shaft. Those dispersions were used for stability studies and UV absorbance measurements. Granulometric analyses were carried out by means of dynamic light scattering using a Malvern NanoZS instrument. The 10% silica dispersions were diluted so as to meet the concentration range requirement of dynamic light scattering where the count rate of the instrument is around 200 kHz.

2.3. Synthesis

2.3.1. First grafting route: using TES as coupling agent

In this route the grafting of UV-filter molecule to silica surface was made using TES as coupling agent. TES is first attached to the UV-filter molecule via hydrosilylation reaction [27,28] between Si–H group of TES and the vinyl group previously added to the UV-filter. For this purpose, the UV-filter molecules were first modified to provide a terminal vinyl function by esterification with either allyl alcohol or undecylenic alcohol. These two alcohols differing by the length of their alkyl chain were used in order to study their effect on the grafting degree.

2.3.2. Addition of vinyl function: formation of esters (E1, E2)

p-Methoxycinnamic acid (MCA) (1.78 g, 0.01 mol) was mixed together with 0.01 mol of allyl alcohol (1) or 10-undecylen-1-ol (2) (Scheme 2) in 15 mL of toluene, in presence of *p*-toluene sulfonic acid as catalyst [29]. The mixture was stirred under reflux at 110 °C for 48 h. The products were purified in a silica gel 60 column using *n*-hexane:ethyl acetate (80:20, v/v) as eluent.

The E1 ester was obtained with 83% yield.

¹H NMR (acetone-*d*₆) δ(ppm): 7.65 (d, 1H, –CH–Ar); 7.60 (d, 2H, H–Ar); 6.95 (d, 2H, H–Ar); 6.4 (d, 1H, CH=CH–C=O); 6.0 (m, 1H, CH₂=CH–CH₂–O); 5.35 (q, resulting from splitting, 1H, CH₂=CH–CH₂–O); 5.24 (dd, 1H, CH₂=CH–CH₂–O); 4.68 (d, 2H, CH₂=CH–CH₂–O); 3.82 (s, 3H, –O–CH₃).

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