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Enhanced photoprotection for photo-labile compounds using double-layer coated corn oil-nanoemulsions with chitosan and lignosulfonate

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ABSTRACT

With the aim to establish a novel nanocarrier system with relatively high payload and high photoprotection capacity for photo-labile active compounds, in this work, deltamethrin (photo-labile compound) was encapsulated into corn oil-nanoemulsions (NE) by a hot high pressure homogenization technique followed by coating with chitosan as the first coating layer (CH-NE) and lignosulfonate as the second coating layer to form a double-layer coated NE (L-CH-NE). The optimal conditions for preparation of NE, chitosan coating and lignosulfonate coating were investigated. The results indicate that polymer coating and the number of coating layers significantly affected the release profile and photoprotection capacity of nanocarriers. In particular, after coating, the release rate became slower and photoprotection capacity became higher. Moreover, in the case of L-CH-NE after 24 h of UV exposure in direct photolysis and 2.5 h of UV exposure in indirect photolysis, the non-degraded amount of deltamethrin was approximately 4.5 times and 2.1 times, respectively, higher than that of the free-from deltamethrin. In the future, this novel nanocarrier system will show great potential and be widely applied to many fields related to protection of photo-labile compounds against photo-degradation.

1. Introduction

Photodegradation has become an essential topic in people's daily lives due to the worldwide decrease of the ozone layer [1]. Photodegradation is one of the most common degradative processes causing lost of activity of photo-labile antibiotics, drugs, cosmetic compounds and pesticides [2–4]. Therefore, to maintain a concentration level above the minimal effective concentration (MEC), a larger amount of these compounds has to be used which would result in a decrease in commercial profit [3]. In addition, harmful photodegradation products may be formed from this process and released to the surrounding environment, causing toxicity in the ecosystem including humans [3,5]. Many strategies have been developed to reduce the effect of photodegradation on photo-labile compounds such as chemical structure modification for pesticides or use of UV absorbers as additives in cosmetic formulations [1,6]. However, these methods have some drawbacks. For example, the improvement of photostabilization without changes in biological activity or target specificity of pesticides may not be achieved merely by structural alterations [3]. Moreover, the use of UV absorbers as sunscreens in cosmetic formulations can cause photoallergies, phototoxic reactions and skin irritations [1]. Therefore, a suitable strategy for photoprotection is still required.

Nowadays, nanocarriers have been widely investigated for their diverse industrial applications, including cosmetic, agriculture, pharmaceutical and food industries, to control the release, enhance enzyme activity and improve biodistribution of the encapsulated active compounds [7,8]. However, the application of nanocarriers for photoprotection has still not been attended. Although some studies have mentioned that solid lipid nanoparticles (SLN) possess photoprotection ability, SLN has a limited payload, rapid leakage of encapsulated compounds and low photoprotection capacity [9,10]. Therefore, a novel nanocarrier system with high payload and high photoprotection capacity is necessary.

Lignosulfonate is a derivative of lignin, which is produced through the sulfite pulping process as a by-product in the production of cellulose [11]. Application of lignosulfonate is mainly based on its dispersive, stabilizing, binding and complexing nature [11]. Lignin itself is an insoluble polymer, while lignosulfonate has a

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good solubility in aqueous solutions [12]. In addition, lignosulfonate is a polyanion and exhibits photoprotection properties [12,13]. Besides, chitosan is a biocompatible, biodegradable, non toxic cationic polysaccharide and has been used in pharmaceutical, biotechnology, food and agricultural industries [14,15]. With the ability of UV absorption, chitosan can be used as a UV protective material [3]. In particular, a study of Fredheim indicated that lignosulfonate can interact with chitosan at pH 4.5, a condition in which they are oppositely charged [12]. Corn oil has a melting point of about −18 °C, thus it exists in liquid form at room temperature. Corn oil contains α-tocopherol, γ-tocopherol and a relatively high concentration of polyunsaturated fatty acids, thus possessing a high antioxidant capacity [16,17]. Therefore, corn oil is capable of protecting against UV-B radiation [18,19].

Deltamethrin, [(*S*)-α-3-phenoxybenzyl-(1*R*)-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylate], is a synthetic type II pyrethroid insecticide and is widely used in veterinary products to control lice, flies, and ticks on cattle, sheep and pigs, as well as in agricultural formulation to control numerous insect pests on fruits, vegetables and field crops [20]. However, deltamethrin can be quickly degraded by photo-degradation because the chemical bond of pyrethroids can be cleaved by wavelength below 380 nm [21]. In addition, in the natural environment, deltamethrin is photo-degraded at a faster rate than its rate of biodegradation and hydrolysis [21]. Therefore, in this work, deltamethrin was proposed to be used as a photo-labile core material.

With the objective of establishing a novel nanocarrier system with relatively high payload and high photoprotection capacity for photo-labile active compounds, a photo-labile active compound (deltamethrin) was first encapsulated into a corn oil-nanoemulsion (NE) by a hot high pressure homogenization technique. Secondly, the resulting NE was coated with chitosan as the first coating layer and subsequently coated with lignosulfonate as the second coating layer. Following this, the optimal conditions for preparation of primary NE, the optimal conditions for chitosan coating and lignosulfonate coating were investigated. Furthermore, the release rate, photoprotection capacity of NE, NE coated with chitosan (CH-NE) and NE double-coated with chitosan and lignosulfonate (L-CH-NE) were also compared.

2. Materials and methods

2.1. Materials

Lecithin from soybean (Junsei Chemical, Tokyo, Japan) and Tween-80 (Samchun Pure Chemical, Seoul, Korea) were used as surfactants. Corn oil (Sigma–Aldrich, St. Louis, MO, USA) was used as a liquid lipid. Deltamethrin (98%) was obtained from Kyung-Nong (Kyungju, Kyungsangbuk-do, Korea). Chitosan (molecular weight 30,000 Da, degree of deacetylation: 90–94%) was obtained from Biotech (Mokpo, Jellanam-do, Korea). Sodium lignosulfonate was obtained from Tokyo Chemical Industry (Tokyo, Japan). All other chemicals were of analytical grade.

2.2. Preparation of corn oil-nanoemulsions (NE)

NE was prepared by a hot high pressure homogenization technique [22]. Briefly, corn oil (3%, w/w) and deltamethrin (1.4%, w/w) were heated to 85 °C, followed by mild stirring to dissolve the deltamethirn. At the same time, a mixture of soybean lecithin and Tween-80 (ratio 1:1, w/w) was added to distilled water and stirred at 85 °C for 45 min. The surfactant mixture solution was heated to 85 °C and poured into the corn oil containing deltamethrin. The lipid phase was emulsified in the aqueous phase using Ultra-Turrax® T 25 basic homogenizer (IKA®-Werke, Staufen, Germany) at 19,000 rpm for 5 min. The formed pre-emulsion was homogenized using a high pressure homogenizer of Microfluidics, model M-110P (Newtown, Massachusetts, USA) at different pressures and cycles. The resulting dispersion was dispersed in 4 °C cooled water at a ratio of 1:9 (v/v) with stirring at 500 rpm to form primary NE.

2.3. Preparation of chitosan coated NE (CH-NE)

Different amounts of chitosan were dissolved in 0.5% (v/v) acetic acid aqueous solution by stirring at room temperature to form a range of chitosan concentrations from 0.1% to 0.5% (w/v). The chitosan solutions were added drop-wise to primary NE dispersions at a ratio of 1:10 (v/v) with stirring at room temperature.

2.4. Preparation of double-layer coated NE with chitosan as the first coating layer and lignosulfonate as the second coating layer (L-CH-NE)

Different amounts of lignosulfonate were dissolved in acetate buffer solution of pH 4.5 by stirring at room temperature to form a range of lignosulfonate concentrations from 0.1% to 0.5% (w/v). After coating with chitosan, the CH-NE dispersion was simultaneously centrifuged at 16,000 rpm, 4 °C for 1 h using a high speed refrigerated centrifuge, model CR-21G (Hitachi Co., Ltd., Japan). The supernatant was removed and the pellet was re-dispersed into acetate buffer of pH 4.5. After this, the lignosulfonate solutions were added drop-wise to the resulting dispersions at a ratio of 1:10 (v/v) with stirring at room temperature.

2.5. Measurement of particle size and zeta potential

The mean size, polydispersity index (PDI) and zeta potential of nanocarriers (NE, CH-NE and L-CH-NE) were determined by a nanosize analyzer (Malvern Zeta sizer, Nano Z-S; Malvern Instruments, Malvern, UK). Briefly, the samples were diluted 40 times with distilled water (pH 5.6–5.9). This dispersion was added to a polystyrene latex cell. Measurements were carried out at 25 °C with a detector angle of 90°.

2.6. Encapsulation efficiency and payload

After preparation, the nanocarrier dispersions were filtered using a cellulose ester membrane with a 1 μm pore size to remove the unencapsulated deltamethrin that had precipitated in the solution [10]. The dispersions after filtration were diluted 5 times with distilled water followed by dissolving in tetrahydrofuran at a ratio of 1:3 (v/v). The encapsulated deltamethrin was determined using reverse-phase high performance liquid chromatography (HPLC) with a model 2690 pump (Waters, Milford, MA, USA), a model 996 photodiode array detector (Waters) and a Kromasil C18 column (250 mm× 4.6 mm) (EKA Chemicals AB, Bohus, Sweden), packed with particles of 5 μm in diameter. The mobile phase was a mixture of acetonitrile and water (90:10, v/v). The flow rate was 1 mL/min at room temperature. Detection wavelength and retention time of deltamethrin was 230 nm and 6.2 min, respectively [10]. Encapsulation efficiency and payload were calculated based on the following equations:

$$\text{Encapsulation efficiency}(\%) = \frac{\text{Deltamethrin in nanoparticles(mg)}}{\text{Initial added deltamethrin(mg)}} \times 100 \tag{1}$$

$$\text{Payload}(\%) = \frac{\text{Deltamethrin in nanoparticles(mg)}}{\text{Amount of nanoparticles(mg)}} \times 100 \tag{2}$$