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Quaternized carboxymethyl chitosan/organic montmorillonite nanocomposite as a novel cosmetic ingredient against skin aging

Kaihang Chen [a], Binzhao Guo [a], Jiwen Luo [a,b,*]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China
[b] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

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ABSTRACT

It is of technical and economic importance to develop an effective cosmetic ingredient against skin aging through low-cost and facile production. This study developed a polymer/layered silicate nanocomposite as cosmetic ingredient against skin aging. Firstly, quaternized carboxymethyl chitosan (QCMC)/organic montmorillonite (OMMT) nanocomposite (QCOM) was fabricated via solution-induced intercalation. QCOM with different mass ratios of QCMC to OMMT were studied by various characterizations as well as moisture-adsorption and retention activities and UV-protection capacity. QCOM was then added into a cosmetic formulation to prepare a cosmetic cream. And the evaluation of its efficacy about skin care was conducted. The results showed that the optimal QCOM had better moisture-adsorption and retention behaviors than hyaluronic acid, and QCOM solution displayed good UV-protection ability. Furthermore, the QCOM-containing cosmetic cream meets the hygienic standard for cosmetics; it has negligible dermal irritation and a prominent moisture-retention efficacy on human stratum corneum.

1. Introduction

Skin aging is one of the most frequent dermatologic concerns, characterized by wrinkling, dryness, sagging and incremental laxity of the skin (Leonida & Kumar, 2016). Skin aging is a consequence of both intrinsic aging that occurs as time passes, and extrinsic aging that stems from environmental factors. The primary environmental factor that leads to skin aging is solar ultraviolet (UV) radiation. This UV-induced skin aging, so-called photoaging (Fisher et al., 2002; McCullough & Kelly, 2006), may cause a decrease in the elasticity and hydration of skin, giving rise to wrinkles and/or hyperpigmentation.

Cosmetic products involving creams, powders and emulsions are developed and prepared for aesthetic skin care. In general, cosmetics are expected to embellish or modify physical appearance, and even preserve the physico-chemical conditions of skin, *i.e.*, sustain a hydrated skin without wrinkles and blemishes (Carretero & Pozo, 2010; Libio, Demori, Ferrão, Lionzo & da Silveira, 2016). There are already some anti-aging cosmetics in the market. The active ingredients in these cosmetics are often synthetic chemicals. Long-time use of such chemicals likely brings about side effects including irritant contact dermatitis, allergic contact dermatitis, phototoxic and photo-allergic reactions (Mukherjee, Maity, Nema & Sarkar, 2011). Natural products such as curcumin, aloin, epicatechin, ginsenoside, hyaluronic acid (HA), etc. are therefore receiving tremendous attention. Particularly, HA is perhaps the best moisturizing substance in the nature. However, the extraction of these natural products from raw materials can be much expensive. Thus it is necessary to develop an effective ingredient for anti-aging cosmetics through low-cost process, which would be beneficial to popularization.

Chitosan is a biodegradable, biocompatible and non-toxic polysaccharide (Fan et al., 2016; Philippova et al., 2001), which could be easily obtained from the naturally abundant chitin derived from the exoskeleton of crustaceans. Chitosan has a backbone similar to HA, implying that it could be metabolized by endogenous enzymes (Hamed, Özogul & Regenstein, 2016). It is reported that chitosan with high molecular weight can decrease transepidermal water loss, in turn, preserving the elasticity and softness of skin (Jimtaisong & Saewan, 2014; Leonida & Kumar, 2016). Its film-forming properties may endow skin with smoothness and protection against harsh environmental conditions. Interestingly, chitosan also do benefits to the sunscreen formulations by increasing their water resistance (Jimtaisong & Saewan, 2014; Leonida & Kumar, 2016). However, the poor solubility of chitosan in

* Corresponding author at: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China.
E-mail address: holdit@126.com (J. Luo).

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neutral water, in some degree, hinders its further applications. Hence, Chemical modification of chitosan is proposed to address this problem. For example, water-soluble chitosan derivatives can be obtained by grafting quaternary ammonium or/and carboxymethyl groups onto the molecular chain of chitosan.

Minerals are widely used in cosmetic industry as active ingredients or excipients (Silva, Oliveira, Farias, Fávaro & Mazzilli, 2011). When they serve as active ingredients, the therapeutic activity is determined by their physical and physico-chemical properties as well as their chemical composition. For instance, minerals with high refractive index can function as solar protectors while those with high sorption capacity and specific surface area can utilized as creams, powders and emulsions (López-Galindo, Viseras & Cerezo, 2007). Montmorillonite (MMT) is one of the most significant layer clay minerals. With non-toxicity, good biocompatibility and high sorption ability, it can be employed in cosmetic formulations to impart opacity, remove shine and cover blemishes. Adhering to skin, it can also take up grease and toxins (Carretero & Pozo, 2009, 2010).

Notably, MMT after organically modified shows dramatic improvements in sorption performance, including removing grease and heavy metals (Patel, Somani, Bajaj & Jasra, 2006). Modified MMT has a layer structure with enlarged interlayer spacing, which facilitates the intercalation of polymer, like chitosan. The combination of modified MMT and polymer would create a nanocomposite with enhanced properties compared to initial materials (Dawson & Oreffo, 2013; Zheng, Li & Yao, 2002). Such a nanocomposite with desirable characteristics may provide promising prospects for cosmetic industries.

In this study, chitosan was chemically modified by grafting quaternary ammonium and carboxymethyl groups to acquire a water-soluble chitosan derivative, quaternized carboxymethyl chitosan (QCMC). MMT was organically modified by Gemini surfactant to prepared organic MMT (OMMT). Through the solution-induced intercalation method, the polymer/layered silicate nanocomposite, QCMC/OMMT (denoted as QCOM) was fabricated. Structure and morphology characterizations of QCOM as well as moisture-adsorption and retention activities and UV protection ability were investigated. QCOM nanocomposite was then incorporated into a cosmetic formulation to prepare a QCOM-containing cosmetic cream. Chemical and microbiological tests, dermal irritation assay and moisture-retention measurement on human stratum corneum were performed to evaluate this novel cosmetic cream contained QCOM.

2. Materials and methods

2.1. Materials and apparatus

Chitosan (molecular weight $\approx 2.0 \times 10^5$ g/mol and degree of deacetylation $\approx$ 85%) was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd. (China). Chloroacetic acid was procured from Aladdin Industrial Co., Ltd. (China). 2, 3-epoxypropyltrimethyl ammonium chloride (ETA) was supplied by Dongying Guofeng Fine Chemical Co., Ltd. (China). Sodium-montmorillonite commercialized with cation exchange capacity of 87 mmol/100 g was purchased from JianRong Mineral Refining Plant (China). Gemini surfactant ($C_{43}H_{92}N_2Cl_2$, Formula weight: 707; Chemical structure was shown in Fig. 1S) used to modify montmorillonite was obtained from DaoChun Chemical Technology Co., Ltd. (China). All other chemicals employed were of analytical grade and used as received. Nanosized zinc oxide (ZnO) with particle size of 30 ± 10 nm and titanium dioxide (TiO_2, anatase) with particle size of 5–10 nm were provided by Shanghai Macklin Biochemical Technology Co., Ltd. (China). All aqueous solutions or suspensions were prepared using ultrapure water with a resistance of 18.2 MΩ cm.

Table 1
Composition of QCOM cosmetic cream.

Ingredient	w/w%
QCOM 2-1	0.56 ± 0.05
Stearic acid	11.2 ± 0.1
Hexadecanol	3.4 ± 0.1
Potassium hydroxide	0.56 ± 0.05
Ultrapure water	84.3 ± 0.1

A XH-100B microwave synthesis equipment was supplied by Beijing XiangHu Science and Technology Development Co., Ltd. (China). It transmitted continuous microwave irradiation with a frequency of 2450 MHz.

2.2. Fabrication of QCOM nanocomposite

The preparation procedure of QCMC was reported in our previous study (Chen et al., 2016). Briefly, the carboxymethylation of chitosan was performed using chloroacetic acid under microwave irradiation (800 W and 70 °C) for 25 min. Subsequently, the quaternization reaction was conducted with ETA under microwave irradiation (800 W and 75 °C) for 70 min. Finally, QCMC was obtained after dialysis and lyophilization. Note that the molecular weight of QCMC was 1.3×10^5 g/mol, determined by gel permeation chromatography.

OMMT was synthesized on the basis of reported procedure (Liu, Sun & Wang, 2011). Briefly, MMT was reacted with Gemini surfactant under microwave irradiation (800 W and 85 °C) for 1 h. Next, the resulting product was rinsed by 50% isopropanol. OMMT was obtained after being lyophilized and ground.

QCOM was prepared as follows: Firstly, 1% (w/v) OMMT suspension was prepared and swelling for 24 h. Two different concentration QCMC solutions of 0.5% and 3% (wt.) were prepared, respectively. OMMT suspension was reacted with QCMC solution (0.5% wt.) under microwave irradiation (800 W and 85 °C) for 10 min and then another QCMC solution (3% wt.) was added dropwise. The reaction was continuously executed under microwave irradiation for 70 min. The product was purified by dialysis and QCOM was finally obtained by lyophilization at −50 °C. Different QCOM were prepared according to the mass ratios of QCMC to OMMT. Sample with QCMC: OMMT = 1: 2 (w/w) was labeled as QCOM 1-2. Analogously, other samples were designated as QCOM 1-1, QCOM 2-1, QCOM 4-1 and QCOM 8-1.

2.3. Characterization

X-ray diffraction (XRD) measurements were carried out on a D8 Advance X-ray diffractometer (Bruker, Germany). The microstructures of OMMT and QCOM were analyzed using a JEM-2010HR transmission electron microscopy (TEM) (JEOL, Japan). UV–vis spectra were recorded on a TU-1810 UV–vis spectrometer (PGeneral, China). Fourier transform infrared spectroscopy (FT-IR) of samples was measured by a Tensor 27 (Bruker, Germany) under dry air at room temperature through a KBr pellet method.

2.4. Preparation of cosmetic cream

The formulation of cosmetic cream containing QCOM was listed in Table 1. Hydrophilic and hydrophobic substances were heated using water bath, respectively. With vigorous stirring, hydrophilic substances were added into hydrophobic substances to obtain a complex of uniformity. Cooled down to ambient temperature, the QCOM cosmetic cream was obtained.