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# Facile synthesis of casein-based silica hybrid nano-composite for coatings: Effects of silane coupling agent

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Silane coupling agents are recognized as efficient coupling agents extensively used in composites and adhesive formulations. In this paper, casein-based silica nano-composite latex for coatings was prepared via double-in situ method stabilized by methyl propyl trimethoxy silane (KH570) – a kind of silane coupling agent. The latex was mainly characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and thermogravimetry (TGA). Effects of KH570 on the structure and performance of the latex and film, as well as the application performance were discussed systematically. The results showed that the presence of KH570 increased the silica-shell uniformity due to the improvement of the compatibility between the organism and inorganism. Existence of KH570 could endow the hybrid film with enhanced mechanical strength, water resistance and heat resistance. The as-prepared composite may also give finished leather with preferred wet/dry rub resistance, water resistance and tensile strength. Latex particle formation mechanism was proposed accordingly.



## 1. Introduction

As a natural polymer, casein is a completely biodegradable raw material and has certain film-forming properties, such as good adhesive force and strong resistance high-temperature. However, casein film has less extensibility and water resistance due to its structure [1], which could restrict its practical applications. Chemical modification and blending with other materials, including cross-linkers [2], polymers [3] and layered silicates [4] for the casein have been attempted to correct its deficiencies. Modified casein has been widely used as a coating material in leather finishing, papermaking, printing, coating and other industries [5–7].

Nano-silica has been widely studied and used due to their thermal and electronic stability in the past decades [8]. In our previous study, casein-based composite was prepared by introducing acrylate monomers and commercially available nano-silica powders into casein matrix under the action of ultrasonic dispersion, and investigated its application performances [9]. Although the tensile strength and hydrophobic property improved through introducing nano-silica particles, the storing stability of the composite emulsion needs to be further improved due to the generation of sediment during long-time storing. In order to strengthen the interface interaction of the hybrid latex particles to improve the stability of the composite, tetraethoxysilane (TEOS), the precursor of silica was employed instead of silica powder in this study. This synthesis route was called double-in situ method. In our previous study, the results demonstrated that double-in situ is a possible route to prepare biodegradable casein-based silica composite emulsion for coatings and drug carriers [10,11].

During the process of composite synthesis, silane coupling agents are known to play important roles in connecting the interfaces of organic and inorganic phases since they can be functional at the interface to create a chemical bridge between the reinforcement and matrix, thus improving the stability, adhesion, strength or wear resistance of the composite [12–14]. Consequently, silane coupling agents are frequently used since they can form stable chemical bonds with both inorganic and organic materials [15]. In our research team, polyacrylate-based silica nano-composites for leather coatings were prepared by using various kinds of silane coupling agents separately, and the effects of silane types

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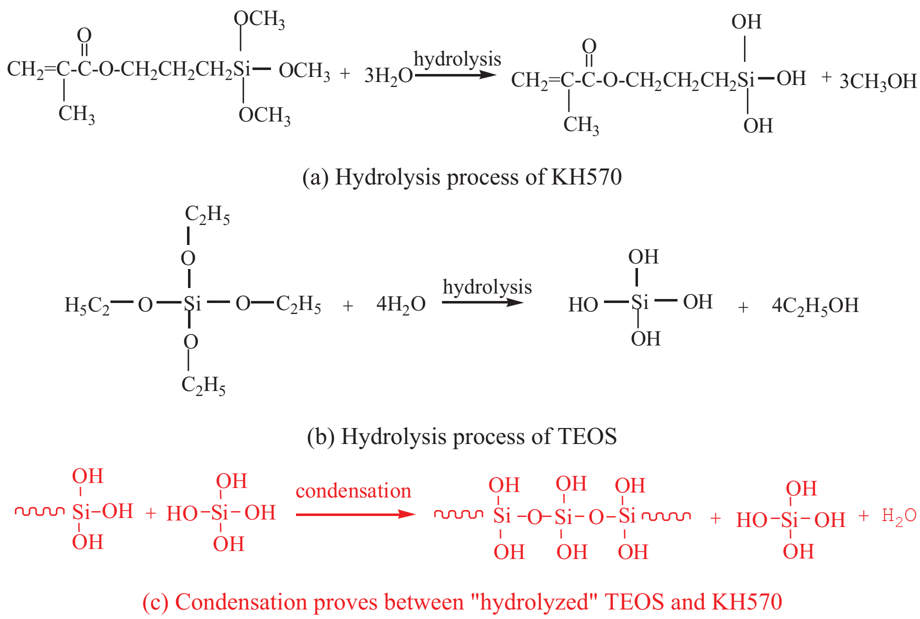


(a) Hydrolysis process of KH570

(b) Hydrolysis process of TEOS

(c) Condensation proves between "hydrolyzed" TEOS and KH570

**Fig. 1.** The hydrolysis and condensation process of TEOS and KH570.

on the resultant emulsion were investigated systemically. Results revealed that the introduction of double bond contained methyl propyl trimethoxy silane (KH570) could endow the emulsion with uniformly distributed particles size, superior mechanical properties and thermal stability [16]. Up to now, the effects of silane coupling agent on natural product-based composite emulsion, especially casein-based silica hybrid nano-composite has been rarely reported.

In this study, KH570 was adopted in preparing casein-based silica nano-composite latexes for coatings via emulsifier-free polymerization and double-in situ method. During the polymerization, KH570 was expected acting as a bridged linkage, which could join the organic and inorganic phase organically (hydrolysis and condensation process between TEOS and KH570 is given in Fig. 1). As a result, the stability and compatibility of the hybrid composite would be further guaranteed.

## 2. Experimental

### 2.1. Materials

Casein was purchased from Zhejiang Huatian Co. Ltd., Caprolactam, was supplied by Shanghai Guoyao Chemical Reagents Co. Ltd., Acrylates, ammonium persulfate and tetraethoxysilane were all provided by Tianjin Kemiou Co. Ltd., Tetraethoxysilane (TEOS) and silane coupling agent KH570 (γ-methacryloxypropyltrimethoxysilane) were all purchased from Tianjin Fuyu Co. Ltd. All the chemicals used were analytically pure grades.

### 2.2. Preparation of casein-based silica nano-composite

The polymerization was conducted as follows. Firstly, 11 g of casein was added to 3 g of triethanolamine dissolved in 87 mL of distilled deionized water in a 250 mL three-necked round-bottom flask fitted with a digital electric stirrer, a reflux condenser, a thermometer and a constant pressure dropping funnel. This solution was stirred for 2 h at 65 °C. When the temperature was raised to 75 °C, 5 g of caprolactam dissolved in 18 mL of distilled deionized water and 2 g of KH570 was dropwise added to the flask with an appropriate dropping rate, respectively. When KH570 was completely fed, 4 g of TEOS was dropwise added into the system, and the reaction was allowed for 2.0 h. 3 g of BA, 10 g of MMA and initiator solution of 1 g APS dissolved in 10 g of distilled deionized water were simultaneously fed to the system, and the reaction was allowed for 2.0 h. Finally, the obtained latex was cooled to room temperature and the casein-based hybrid nano-composite for coatings was obtained. In order to investigate the effects of KH570 on the performance of casein-based hybrid composite, the control sample in the absence of KH570 was also prepared.

### 2.3. Characterization and testing

The morphology of latex particle was investigated by an H-800 transmission electron microscope (Hitachi, Japan) operated with an acceleration voltage of 75 kV. The samples were diluted with distilled water and stained with 2% phosphotungstic acid solution. DLS measurements were carried out on a BT9300Z laser-scattering particle size distribution analyzer. TG experiments were carried out on a Q500 TG thermogravimetric analyzer (TA, USA) with a heating rate of 20 °C/min from 35 to 600 °C in an air atmosphere. AFM was performed using a SPA-400 AFM (Seiko Instruments Inc., Japan). Images were acquired under ambient conditions in tapping mode using a nano-probe cantilever. For AFM measurements, the corresponding hybrid emulsions (1 wt% solid content) were cast onto freshly cleaved glass plates and then dried at room temperature. SEM analysis was performed on a S4800 SEM instrument (Hitachi, Japan). Before testing, films of about 3 mm thickness were frozen dried and coated with a thin layer of gold using a vacuum sputter at an acceleration voltage of 5 kV.

The as-prepared casein based latex was applied as coating material in leather finishing process, and the application properties were measured. According to light industrial standard, e.g., QB/T 2710-2005 and GB/T 4689.21-2008, mechanical, water-resistance and sanitation properties of films and the finished leather samples after finishing were tested. Prior to analysis film properties, they must be conditioned under standard atmospheric conditions for 24 h. Mechanical property testing was performed on an AI-3000 universal tensile testing machine (Gotech, China). For water absorption of the films and leather samples after finishing, it was determined as