Effects of Silane Coupling Agent on Casein-based Silica Composite Leather Finishing Agent

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Abstract

Silane coupling agents are recognized as efficient coupling agents extensively used in composites and adhesive formulations. In this paper, casein-based silica nanocomposite latex was prepared via double-in-situ method. The latex was mainly characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and Thermogravimetry (TGA). Effects of the silane coupling agent KH570 on the structure and performance of the latex and film, as well as the application performance were discussed systematically. Results show that the introduction of KH570 increases the silica-shell uniformity due to the improvement of the compatibility between the organism and the inorganic particles. In addition, existence of KH570 could endow the hybrid films with enhanced mechanical strength, water resistance and heat resistance. Based on the leather finishing application results, the as-prepared composite emulsion in the presence of KH570 may endow finished leather samples with the preferred wet and dry rub resistance, water resistance and tensile strength. Finally, latex particles formation mechanism was proposed.

Keywords: Casein; silane coupling agent; Leather finishing; Double-in-situ

1. Introcuditon

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] (Wang 2004), which could restrict its practical applications. Chemical modification of the casein structure or blending with other materials, including cross-linkers[2] (Barreto 2003), polymers[3] (Syed 2006) and layered silicates[4] (Pojanavaraphan 2010)have been attempted to correct its deficiencies. Modified casein has been widely used as a film-forming material in leather finishing, papermaking, printing, coating and other industries[5-7] (Ghosh 2009; Yuntao 2007; Liangdong 2006).

Nano silica has been widely studied and used due to their thermal and electronic stability in the past decades[8] (Stober 1968). In our previous study, we have prepared casein-based composite 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] (Qunna 2011). Although the tensile strength and hydrophobic property improves 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, thus 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.

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 function 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[10-12] (Nihei 2008; Kominar 1994; Gupta 1983). Consequently, silane coupling agents are frequently used since they can form stable chemical bonds with both inorganic and organic materials [13] (Wu 2007). In our previous study, various kinds of methacryloxy propyl trimethoxyl silanes were used in preparing polyacrylate-based silica nanocomposite, separately, and the effects of methacryloxy propyl trimethoxyl silane types on the resultant emulsion performance were investigated systemically Results showed that the introduction of methacryloxy propyl trimethoxyl silane could endow the emulsion with uniform distributed particles size, superior mechanical properties and thermal stability [14](Hu 2009).

In this study, methacryloxy propyl trimethoxyl silane (KH570) was adopted in preparing casein-based silica nanocomposite latexes, and effects of KH570 on properties and the structures of the composite were mainly investigated.

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. All the chemicals used were analytically pure grades.

2.2 Preparation of Casein Based Silica Nano-composite

The polymerization was conducted as follows. Firstly, a specific amount of casein was added to a certain dosage of triethanolamine solution 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℃. When the temperature was raised to 75℃, a specific amount of caprolactam dissolved in a specific volume of distilled deionized water and a certain dosage of KH570 (different dosages were used) was dropwise added to the flask with an appropriate dropping rate, respectively. When KH570 was completely fed, a specific amount of TEOS was dropwise added into the system, and the reaction was allowed for 2.0 h. A specific amount of BA and MMA and APS solution 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 nano-composite was obtained. In order to further investigate the effects of KH570 on the performance of casein-based composite, the control sample in the absence of KH570 was also prepared.

2.3 Characterization and Testing

TEM characterization was performed on a H-600 transmission electron microscope at an accelerator voltage of 75 kV. DLS measurements were carried out on a BT9300Z laser-scattering particle size distribution analyzer. FTIR characterization was conducted on an IR Prestige-21 FTIR spectrometer. TGA experiments were carried out on a Q500 TGA thermogravimetric analyzer with a heating rate of 20 °C min^{-1} from 35 °C to 600 °C in an air atmosphere. According to QB/T 2710-2005 and GB/T 4689.21-2008, Mechanical and water-resistant properties of films and the leather samples after finishing were tested, respectively. Mechanical property testing was performed on an AI-3000 universal tensile testing machine.

3. Results and Discussion

3.1 Effects of silane coupling agent on film water-resistance

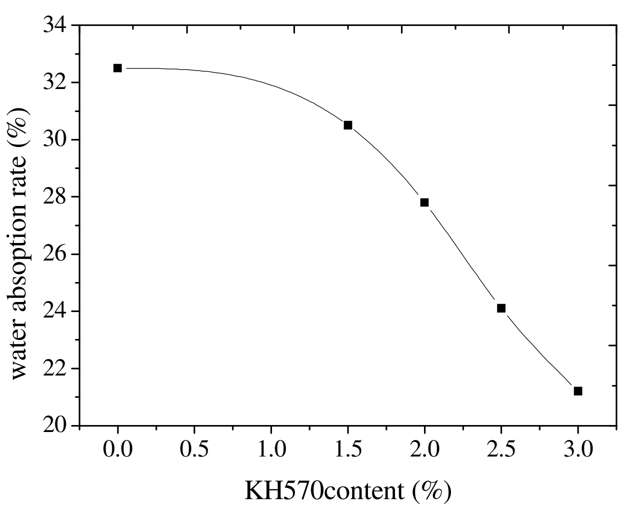

Fig.1 Film water-resistance as a function of KH570 content

As shown in Fig. 1, the water absorption of the film decreases as the silane coupling agent KH570 dosage increases, suggesting that the introduction of KH570 into the matrix improves the film water resistance. As is known to us, after the hydrolysis of the silane coupling agent, one end reacts with silanols on nano-SiO_2 surface, thus connected with the inorganic phase; the other end reacts with the double bond of acrylate monomers, thus connected with the polymer phase. In other words, KH570 playes a role connecting bridge between the organic phase and inorganic phase. In this case, the existence of nano-SiO_2 helps the formation of a relatively compact composite film a net-working structure, which could inhibit penetration and spreading of the water molecules through the composite film. In addition, KH570 could function in modifying the surface of the generated nano-SiO_2 particles by condensing with the hydroxyl groups on them, thus reducing the hydrophilic of the particles.

3.2 Effects of silane coupling agent on film mechanical properties

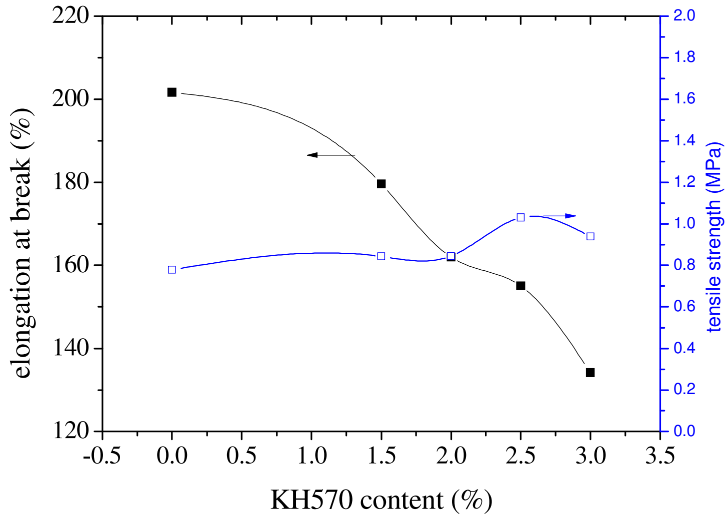

Fig.2 Film mechanical property against KH570 content

In Fig. 2, it's noted that the variation in KH570 dosage significantly changes the mechanical properties of the composite film. In general, as the KH570 dosage increases, the film elongation at break decreases while tensile strength increases. This result is basically in accordance with those reported by B. Chmielewska [15](Chmielewska 2006) and Quankun [16] (Quankun 1998). The reason for this phenomenon is that a compact composite film with net structure has formed. As depicted above, nano-SiO_2 particles play crosslinking points in the hybrid film. Consequently, the rigidity or strength of the film could be improved. However, the formation of the net-structure could restrict the relative movement of the molecular chains, thus reduce the film flexibility.

3.1Application performance

Tab. 1 Effects of silane coupling agent on the application performance

Latex sample*s*	In the absence of KH570	In the presence of 2% KH570
Tensile strength(MPa)	5.23	5.78
Elongation at break (%)	62.31	57.53
Air permeability (($mL/cm^2 \cdot h$)	8.40	3.56
Moisture permeability($mg/(10cm^2 \cdot 24h)$)	532.97	445.05
Dry rub resistance(class)	4	4-5
Water absorption rate for 24 h (%)	231.76	199.90

In order to investigate the effect of the silane coupling agent on the application performance of the composite emulsion, emulsion in the presence of 2%KH570 and in the absence of KH570 were applied in leather finishing process, separately. The application performance of these emulsion samples were listed in Tab.1. Through analysis, it was found that introduction of KH570 helps improve tensile strength, dry rub resistance and water resistance of the finished leather. However, hygiene performance (air permeability and water vapor permeability) and flexibility reduced to some extent. In short, the effecting laws of KH570 on application results are basically consistent with those on the film performance regarding water-resistance and mechanical properties. With regard to the reduced hygiene performance in the presence of KH570, it can be also attributed to the relatively compact inorganic- organic hybrid film with net structure, which hinders the infiltration or penetration of the air molecules and the water vapor molecules.

3.2 Film thermal stability

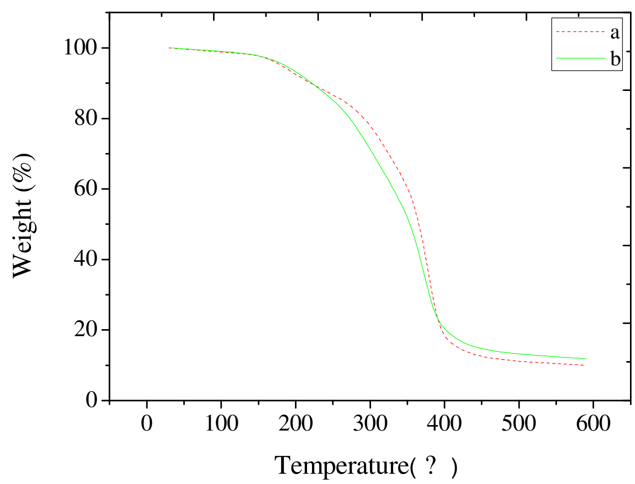

Fig.3 TG curves of the films obtained from the emulsion (a) in the presence of 2% of KH570 and (b) in the absence of KH570

The thermal decomposition behavior of dried casein-based silica composite films was investigated at a heating rate 10℃/min under air flow, as illustrated in Fig. 3. It is seen from Fig.3 that the fastest thermal decomposition temperature of the film in the absence of KH570 and in the presence of KH570 is around 373.4℃ and 378.39℃, respectively, which reflects that the latter one has enhanced thermal stability. In this case, it could be concluded that the introduction of the silane coupling agent could endow the composite film with strong resistance to heat. In the system, KH570 acts as a bridge connecting the inorganic and organic phases, which could increase the crosslinking degree of the composite film. In the same time, the coupling agent is involved in the coupling reaction, which makes the structure of the film change form linear to the three -dimensional structure [17] (Radhakrishnan 2004), thus improves the heat resistance of the material. This is also explicable in terms of both the formation of -Si–O–Si-polymer bonds with high bond energy on the film surface to improve the thermal stability and the increase of thermal stability with increasing silica content of casein-based composite films[18](Wenbo 2011).

3.4 Particle morphology, size and distribution

Tab.2 Effects of silane coupling agent on particles size and its distribution

Latex samples	Average diameter(nm)	PDI	Zeta potential(mV)
In the presence of 2% KH570	141.3	0.361	-22.5
In the absence of KH570	147.2	0.378	-19.8

In order to investigate the effect of KH570 on the particle morphology, size and distribution, the latex in the presence of 2% KH570 and that in the absence of KH570 was characterized by DLS and TEM methods, separately, as revealed in Tab.2 and Fig.5. From the results, it's noted that the average diameter and PDI of composite latexes decrease slightly after introducing KH570 into the matrix. In addition, the introduction of KH570 helps to obtain a more stable colloidal particle since the absolute value of zeta potential is larger. Furthermore, it's obvious that the encapsulation extent on the core layer becomes more efficient under the action of KH570.

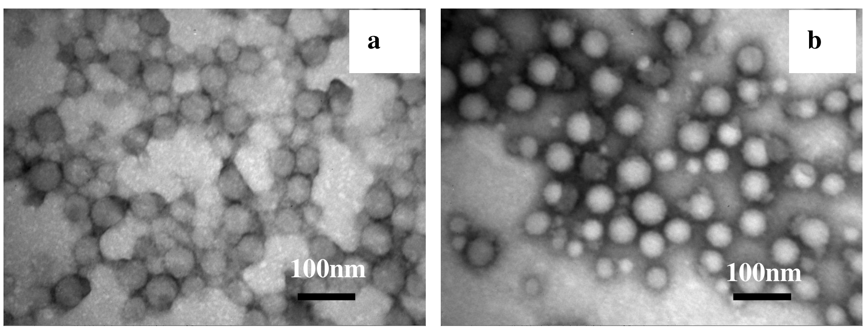

Fig.5 TEM images of the composite latexes (a) in the presence of 2% of KH570 and (b) in the absence of KH570)

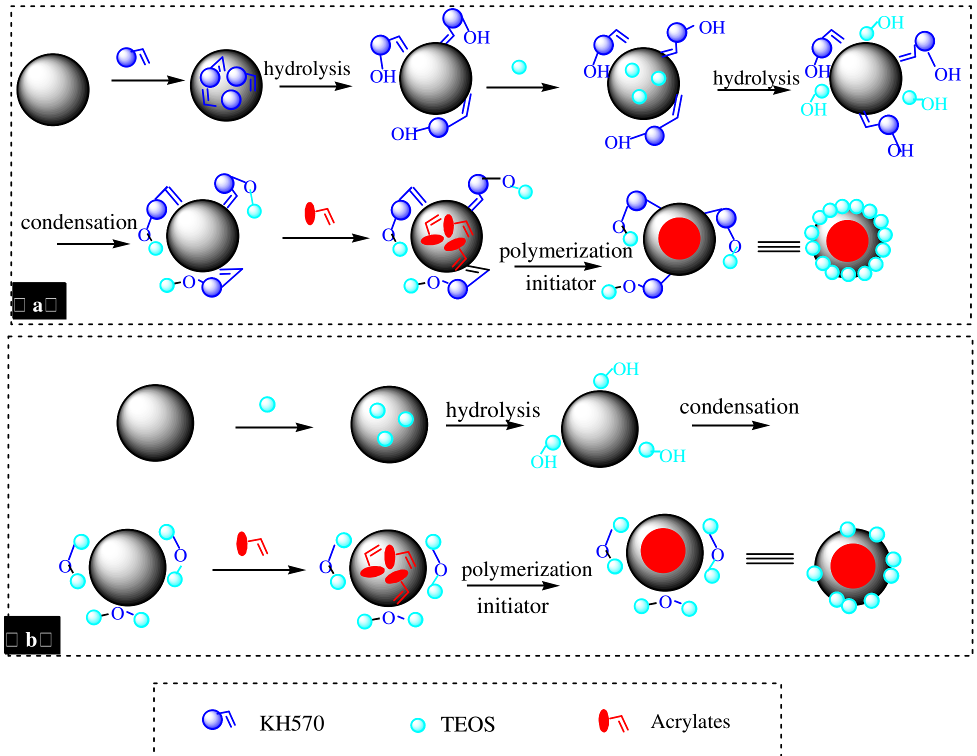

Fig. 6 formation mechanism for the composite latexes (a) in the presence of KH570 and (b) in the absence of KH570)

From this phenomenon, we could conclude that the existence of silane coupling agent is favor for decreasing the particle size thus increase the emulsion stability. On one hand, KH570 could adsorb on the surface of silica particles, which form a mesh structure covered the particle surface and prevent the particle gathering larger [19](Jinliang 2013). On the other hand, KH570 is beneficial for enhancing the binding force between the organic core layer and inorganic shell layer, thus improving the uniformity of the shell thickness.

Combination of the above experimental results shows that KH570 has significant effects on latex and film performances. In order to further clarify the effect of KH570 on latex structure and its formation process, a simple discussion about casein-based silica nanocomposite latex particle formation mechanism for latex in the presence of KH570 and that in the absence of KH570 is proposed, separately. As depicted in Fig. 6 (a) and (b) , the hybrid latexes all exhibit evident core-shell structures. Differently, the latex in Fig. 6 (a) has a more uniform shell thickness that that in Fig. 6 (b). As mentioned above, silane coupling agent is beneficial for enhancing the binding force between the organic core layer and inorganic shell layer, thus improving the uniformity of the shell thickness.

4 Conclusions

Effects of the silane coupling agent KH570 on the structure and performance of casein-based silica nanocomposite latex and its film, as well as the application performance were discussed systematically. Results show that the introduction of KH570 increases the silica-shell uniformity due to the improvement of the compatibility between the organism and the inorganic particles. In addition, existence of KH570 could endow the hybrid films with enhanced mechanical strength, water resistance and heat resistance. Based on the application results for leather finishing, the emulsion in the presence of KH570 may entitle leather sample after finishing the preferred resistance to wet and dry rub resistance, water resistance and strength.

Acknowledgements

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