



Study of Surface Modification of Ultra-Fine CaCO₃ With Different Coupling Agent†

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To compare the superficial capacity of ultra-fine calcium carbonate powder, the coupling agents of γ -aminopropyl triethoxyl silane (KH550), γ -methacryloxypropyl trimethoxy silane (KH-570), vinyltrimethoxy silane (SG-Si 171) and di(dioctylpyrophosphato)ethylene titanate (NDZ-311) were used as modifiers to modify its surface activity. The structural changes and properties of the unmodified and modified ultra-fine CaCO₃ powder were characterized by Fourier transform infrared spectroscopy, contact angle measuring instrument (CAMI) and sedimentation stability experiment. The results showed that the coupling agent bonds covalently onto the surface of CaCO₃ particles and forms an organic coating layer. Contact angle measuring instrument indicated that the coupling agent molecules were absorbed or anchored on the surface of CaCO₃ particles, which facilitates to hinder the aggregation of CaCO₃ particles.

Key Words: Ultra-fine CaCO₃, Silane coupling agent, Surface modification.

INTRODUCTION

During the past decade, extensive research efforts on the preparation of polymer-inorganic nanocomposites have been reported in the literature from both the academic and industrial communities, due to improved mechanical and thermal properties, gas permeability and fire retardance compared to the pure polymer¹⁻⁵. However, the dispersion of nanoparticles and fabrication remains an unsolved or tough problem. It is possibly due to the particle agglomeration and immiscibility between the inorganic particles and the polymer matrix, which leads to the deterioration of polymer properties.

As one of most important nano-fillers, ultra-fine CaCO₃ particles have been widely studied and utilized in academic and industry society because of its commercial availability and the substantial improvement in properties of polymers⁶⁻⁸. Furthermore, due to the super mechanical properties and high thermal stability, CaCO₃ nanoparticles are filled in many kinds of polymers by *in situ* polymerization and blend methods^{9,10}. However, the foremost challenge of using CaCO₃ in polymers is to achieve its uniform spatial distribution in matrix due to their incompatible interface, which leads to the deterioration of polymer properties. What is more, nanoparticles tend to aggregate together since they have a large specific surface area and high surface tension. It is extremely difficult to homogenize polymer matrix with CaCO₃ nanoparticles just relying on the shearing force in melt-blending. In order to obtain a

homogeneous dispersed polymer/inorganic nanocomposites, several processing methods have been used^{11,12}. Surface modification of nanoparticles is an effective way to reduce their surface tension and increase the compatibility between them and polymer matrix.

In this study, in order to compare surface activity of ultra-fine CaCO₃ particles, KH-550, KH-570, SG-Si171 and NDZ-311 were used to modify ultra-fine CaCO₃. On the one hand, silanols or titanate as the side group [-Si-OCH₃ or -Ti-OO-] on the main chain of coupling agent may react with -OH which are on the surface of ultra-fine CaCO₃ particles containing active hydrogen. On the other hand, the main chain of coupling agent has the similar structure or polarity with BR, NR, NBR, *etc.* and provides them great compatibility.

The dispersion of coal powder particles as well as the mechanism of stable colloidal dispersion was discussed in anhydrous ethanol. The surface hydrophobicity and using efficiency of coupling agent as a modifier were also studied.

EXPERIMENTAL

Ultra-fine CaCO₃ was obtained from Henan Keli New Materials Co. Ltd., in china, average particle diameter 254 nm. G-aminopropyl triethoxyl silane (KH550), γ -methacryloxypropyl trimethoxy silane (KH-570), vinyltrimethoxysilane (SG-Si171) and di(dioctylpyro-phosphato) ethylene titanate (NDZ-311) were purchased from Nanjing Shuguang Chemical

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Group Co. Ltd., in China. Other reagents were of analytical grade and used as received.

Surface modification of ultra-fine CaCO₃: The ultra-fine CaCO₃ about 1 g were dispersed in 50 mL ethyl acetate with the aid of ultrasonic agitation and a certain amount of coupling agent (10 wt % of CaCO₃) was added into the flask, mixing round with high speed at 75 °C for 5 h, then reaction product was filtered and washed using ethyl acetate and vacuum drying for 20 h.

Instrumental analysis: FTIR and contact angle measuring instrument were performed to characterize the structures and properties of modified ultra-fine CaCO₃. FTIR spectras were carried out on spectrometer (Nicolet Co., Nexus-870, USA) with a resolution of 4 cm⁻¹ for which the samples were palletized with KBr powder. Surface hydrophilicity of ultra-fine CaCO₃ was investigated by contact angle measuring instrument (Kino Co., SL 200C, USA) at the room temperature, water was dropped on the sample surface and the angle values was taken as its contact angle.

Dispersion stability of ultra-fine CaCO₃ in ethyl acetate: Sedimentation stability experiment was achieved in sedimentation tubes. Typically, 0.1 g modified ultra-fine CaCO₃ was allowed to disperse in 100 mL ethyl acetate at room temperature. After a definite time, the stability of dispersion was estimated from photographs of dispersed CaCO₃ particles after standing.

RESULTS AND DISCUSSION

FTIR analysis: It can be seen from Fig. 1(a) that from coupling agent, the 3000-2800 cm⁻¹ correspond to the -CH₂-, -CH₃ absorption peaks and 1200-800 cm⁻¹ correspond to Si-O-C absorption bands of KH550, KH-570 and SG-Si171. The 1640 cm⁻¹ is attributed to C=C absorption peak of KH-570, SG-Si171 and NDZ-311, the 1650-1500 cm⁻¹ correspond to -NH absorption bands of KH550 and 1730 cm⁻¹ is attributed to C=O absorption peak of KH-570, the 1150 cm⁻¹ and 1038 cm⁻¹ correspond to -Ti-O-C absorption bands of NDZ-311.

Fig. 1(b) shows FTIR spectra of modified ultra-fine CaCO₃, modified ultra-fine CaCO₃ with SG-Si171 and KH-550, the 1050 cm⁻¹ and 1130 cm⁻¹ correspond to Si-O-C absorption bands, 1640 cm⁻¹ correspond to C=C two double bonds absorption peak of SG-Si171. The FT-IR spectra of modified CaCO₃ with KH-570^{10,12,13}. From the FT-IR spectra we can see that the detection of strong absorption peak at 1730, 1640, 1180 and 1080 cm⁻¹ are attributed to -C=O, C=C and -Si-O-C groups of the presence of KH-570, respectively. Furthermore, absorption of two double bonds of the presence of KH-570 in modified CaCO₃ was found. From the FT-IR spectra of modified CaCO₃ with NDZ-31, the absorption at 3000-2800 cm⁻¹ correspond to the -CH₂-, -CH₃ groups of NDZ-311. The Ti-O-C absorption bands are observed at 1150 cm⁻¹ and 1038 cm⁻¹, which coincide with -Si-O- absorption bands of silane coupling agent¹⁰⁻¹⁴. These indicate that the surface groups of CaCO₃ have changed from -OH to -Si-O-C or -Ti-O-C. These prove that the coupling agents are tightly absorbed at the surface of CaCO₃ particles by chemisorption.

Analysis of contact angle: Surface hydrophilicity of CaCO₃ particles was investigated by contact angle measurements as shown in Fig. 2. The contact angle of modified CaCO₃

by SG-Si171, KH-570 and NDZ-311 increase from 18.89° to 49.94°, 78.86°, 92.74° and 104.37° in water, respectively, suggesting the increasing surface hydrophobicity and the decreasing surface free energy of coal powder. Thereinto, the efficiency of modification with KH-550 and SG-Si171 is inferior to KH-570 and NDZ-311. These changes are likely due to the carbon backbone of coupling agent which is hydrophobic. It can be inferred CaCO₃ particles modified with coupling agent can be dispersed in polymer materials more easily than native CaCO₃ particles^{12,15-17}.

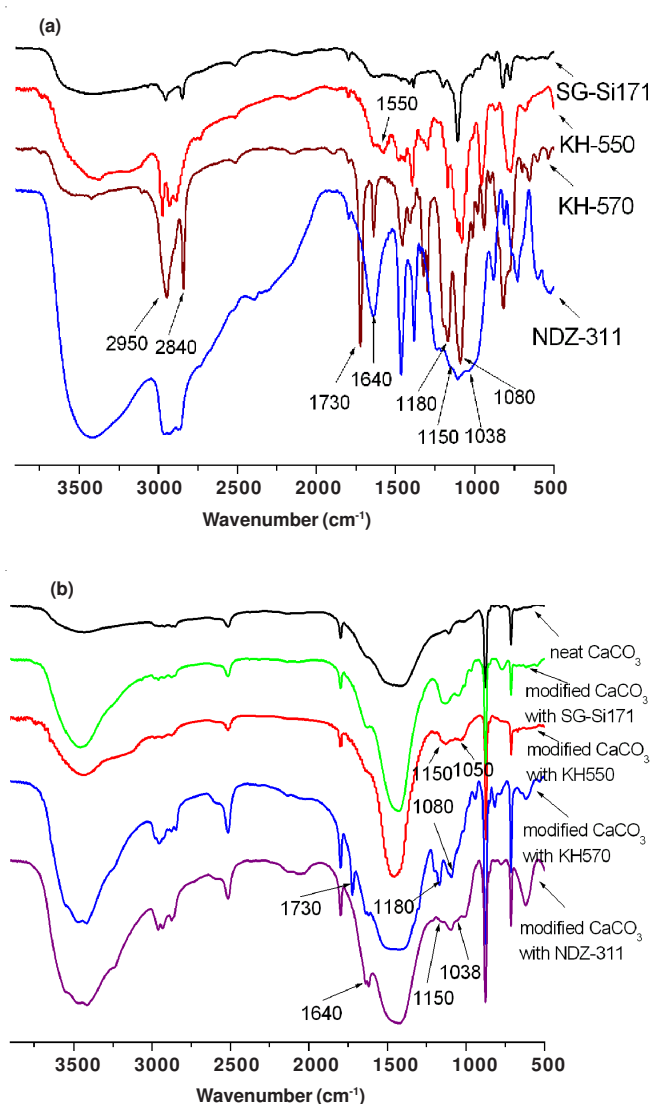


Fig. 1. IR spectra of (a) different coupling agents and (b) unmodified and modified CaCO₃

Stability of ultra-fine CaCO₃ dispersion in ethyl acetate: The dispersion stability of modified CaCO₃ by different coupling agent in ethyl acetate is compared with neat CaCO₃ as shown in Fig. 3. It can be seen that neat CaCO₃ particles, modified CaCO₃ by SG-Si171 and KH-550 have been completely precipitated for about 3 days, while the modified CaCO₃ with KH-570 and NDZ-311 have a stable colloidal dispersion in ethyl acetate.

The hydroxyl groups (-OH) from CaCO₃ particles can interacted with silanols (-Si-OCH₃) or titanate (-Ti-OO-)

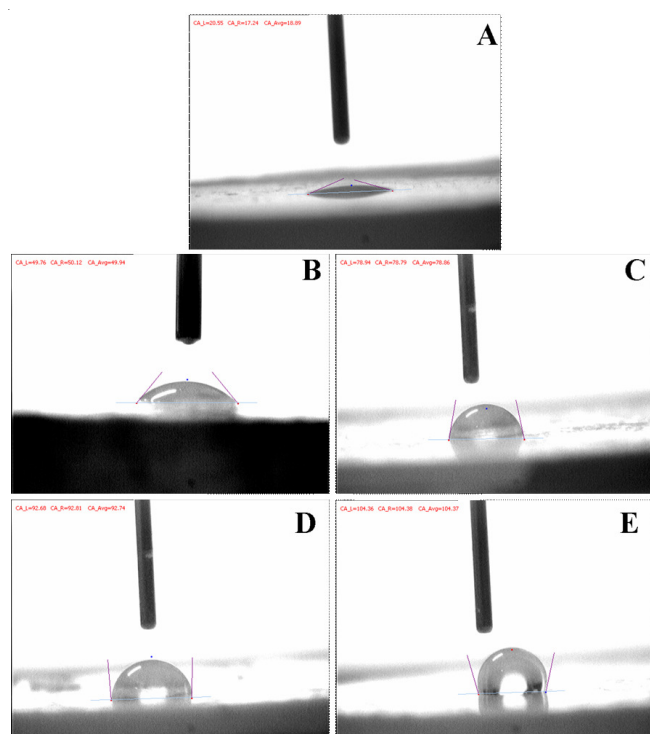


Fig. 2. Contact angle images of (A) neat CaCO_3 ; (B) modified CaCO_3 with SG-Si171; (C) modified CaCO_3 with KH-550; (D) modified CaCO_3 with KH-570 and (E) modified CaCO_3 with NDZ-311

groups from coupling agent to form (coupling agent-g- CaCO_3) complex on the surface of CaCO_3 particles. Consequently, no matter what reaction occurred, the coupling agents are initially grafted or anchored on the surface of the particles at one or several spots, which fulfills steric hindrance between inorganic particles^{12,17}. Above factors give rise to the homogeneous dispersion of particles in ethyl acetate and maintain a stable colloidal dispersion for a long time. We can more intuitionistic see from Fig. 3. Furthermore, it is shown modified efficiency of KH-570 and NDZ-311 is better than KH-550 and SG-Si171.

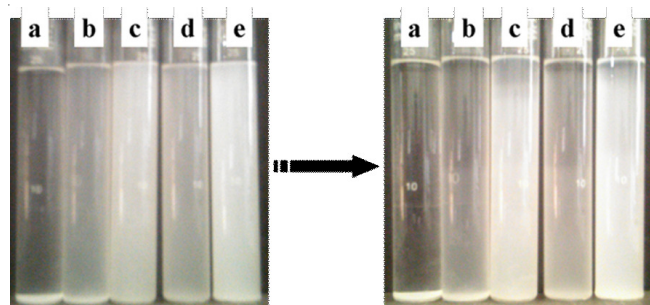


Fig. 3. Photographs of dispersion stabilized of ultra-fine CaCO_3 particles in ethyl acetate solution by time: (a) neat CaCO_3 ; (b) modified CaCO_3 with KH-550; (c) modified CaCO_3 with KH-570; (d) modified CaCO_3 with SG-Si171 and (e) modified CaCO_3 with NDZ-311; and left is ultrasonic dispersion samples after 10 min, the right is ultrasonic dispersion samples after 3 days

Conclusion

Ultra-fine CaCO_3 particles were modified by coupling agent (KH-550, SG-Si171, KH-570 and NDZ-311). Study results show that coupling agents have been anchored on the surface of CaCO_3 particles, the modified CaCO_3 particles presented a more stable colloidal dispersion in ethyl acetate than that of untreated CaCO_3 and the modified efficiency of KH-570 and NDZ-311 is better than KH-550 and SG-Si171.

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