

## Irradiation Initiated Grafting of Poly(butyl acrylate) onto Nano-sized Calcium Carbonate Particles

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**Abstract:** The present work reports the irradiation induced grafting polymerization onto nano-sized CaCO<sub>3</sub> particles, mainly focusing on the effects of pretreatment with silane coupling agent. It is proved that poly(butyl acrylate) can be grafted onto the nanoparticles using the technical route suggested by the authors, and the silane treatment of the nanoparticles promotes the grafting polymerization.

**Keywords:** Nanoparticles, irradiation grafting polymerization, CaCO<sub>3</sub>, polybutylacrylate.

Interfacial interaction in nanocomposites plays a leading role. As nanoparticles have a strong tendency to agglomerate, surface modification of the particles becomes critical for improving nanocomposites' performance.

For micro-size particulate fillers, a great deal of knowledge has been acquired with respect of surface modification<sup>1</sup>. Similarly, the surface treatment of nanoparticles can be conducted by the same techniques based on physical interaction or chemical reaction. The former is often concerned with surfactant and polymer encapsulation, while the later is related to coupling agent and graft polymerization. In comparison with micro-particles, it is more difficult for the surface modifiers to penetrate into the tightly agglomerated nanoparticles, especially in the case of physical treatment such as surfactant treatment or encapsulation with a polymer. Instead, graft polymerization onto the nanoparticles would be an effective way as the low molecular weight monomers can migrate into the nanoparticle agglomerates and then form long chains from the particles surfaces simultaneously.

Grafting of polymers onto inorganic particles can be realized by  $\gamma$ -irradiation, but only a few papers deals with nanoparticles. Fukano *et al.* published a series of works on irradiation-induced grafting polymerization of styrene and methyl methacrylate absorbed on several kinds of nanoparticles<sup>2-4</sup>. They found that the amount of the grafting polymer varies with the type of the inorganic substrate, with the maximum of about 30%. To obtain a higher grafting yielding, they conducted the grafting process under high vacuum condition ( $<10^{-4}$  mmHg). Actually, this is inconvenient for

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industrial applications.

The authors of the current work proposed another method in which the aforesaid strict conditions, such as high vacuum and purification of monomers, are no longer necessary<sup>5</sup>. Various polymers were successfully grafted on the surface of nano-SiO<sub>2</sub> by simultaneous irradiation, and they were proved to be connected with SiO<sub>2</sub> through Si-C and Si-O-C bonds. Meanwhile, however, it is found that CaCO<sub>3</sub> nanoparticles are quite difficult to be grafted by irradiation. Therefore, this paper studies the effect of pretreatment of CaCO<sub>3</sub> with silane coupling agent on the irradiation induced grafting polymerization onto nano-CaCO<sub>3</sub>, in hopes of developing a feasible technique for modifying the particles.

### Experimental

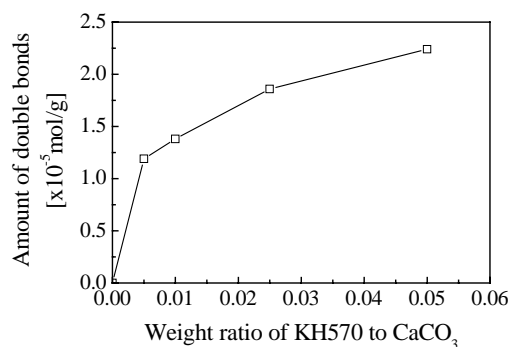
A KH570 silane coupling agent ( $\gamma$ -methacryloxypropyl trimethoxy silane) was used to introduce double bonds (*i.e.*, the reactive groups) onto CaCO<sub>3</sub> nanoparticles in a solution of 95% alcohol. The mixture of CaCO<sub>3</sub> and silane was refluxed at the boiling temperature of the solution for over 12 h of stirring. The reaction degree was tailored by the ratio of silane to the particles. The content of the double bonds adhered to the nanoparticles was detected according to the method stated in Ref.6. More details about the pretreatment are available elsewhere<sup>7</sup>. Then a mixture of nanoparticles/monomer (butyl acrylate) and a certain amount of *n*-hexane was irradiated by <sup>60</sup>Co  $\gamma$ -ray under atmosphere at room temperature. After exposure to a dose of 4Mrad, the solvent was recovered, and the dried residual powder was extracted by acetone in a Soxhlet apparatus for 48 h to separate the homopolymer. The residual poly(butyl acrylate) grafted CaCO<sub>3</sub> (CaCO<sub>3</sub>-g-PBA) was then dried in vacuum at 80°C until a constant weight was reached. By using a thermogravimetry (TGA)-Fourier transform infrared (FTIR) coupling spectroscope (TG-209/Victor-2, Netzsch Bruker), the percentage of grafting and the chemical structure of the modified nanoparticles were characterized.

### Results and Discussion

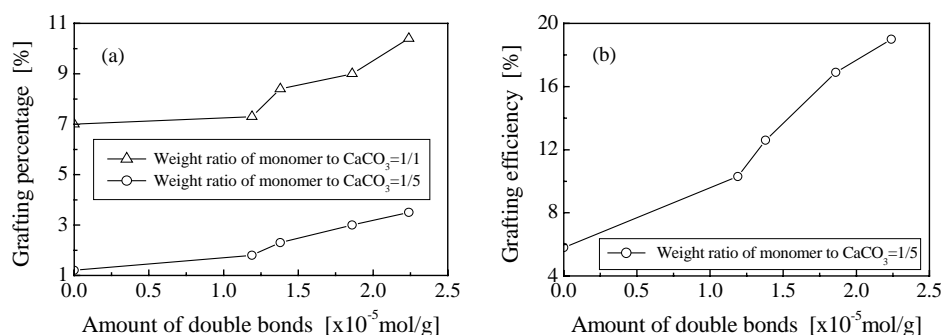
The introduction of reactive groups onto CaCO<sub>3</sub> is proved by **Figure 1**, in which the amount of the double bonds increases with a rise of the weight ratio of KH570 to the particles. It is also seen that the increase of double bonds levels off when the ratio of KH570 to the particles exceeds 0.03, implying that the content of hydroxyl groups on the particles has been nearly exhausted. As shown in **Figure 2**, the silane pretreatment evidently increases the percentage of grafting and grafting efficiency of PBA. This indicates that the double bonds are easier to be initiated by  $\gamma$ -irradiation than the hydroxyl groups on the particles, and furthermore, the polymerization is concentrated at the nanoparticles' surfaces. In fact, silane pretreatment has changed the particles surfaces from hydrophilic to hydrophobic, which must be beneficial to the approaching of the monomers. In addition, some silanol groups might remain after the silane pretreatment, which can also act as active points under irradiation circumstances. The details about the grafting reaction mechanism needs further study.

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**Figure 1** Amount of double bonds introduced onto CaCO<sub>3</sub> surfaces as a function of the weight ratio of KH570 to the nanoparticles.



**Figure 2** Percentage of grafting (a) and grafting efficiency (b) of CaCO<sub>3</sub>-g-PBA as a function of the amount of double bonds introduced onto CaCO<sub>3</sub> surface

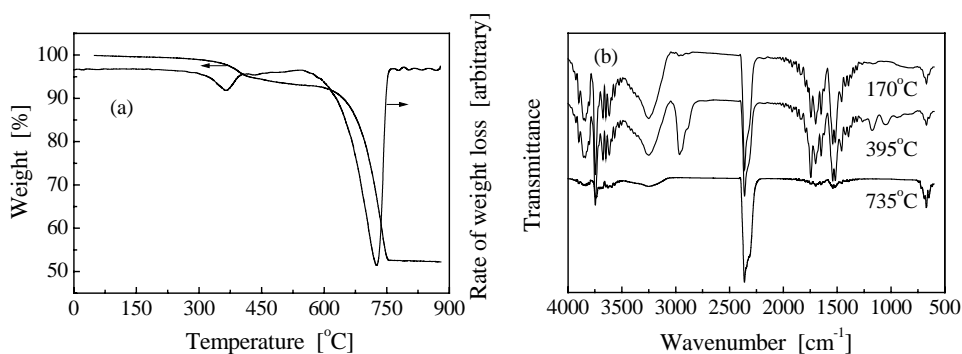


From **Figure 2**, it is also noted that the higher ratio of monomer to the nanoparticles, the higher percentage of grafting, while the dependence of percentage of grafting on the amount of double bonds keeps similar trend. It can be attributed to the fact that the polymerization rate increases with monomer concentration, which is consistent with the general law of solution polymerization. As a result, there is a greater possibility for the monomers to react with the double bonds on the nanoparticles' surfaces at the beginning of the reaction. Comparatively, in the case of lower ratio of monomer to the nanoparticles, the lower percentage of grafting can be explained by the blocking effect of the grafting polymers on the subsequent grafting reaction. That is, the surface double bonds cannot be initiated at the latter stage of polymerization as the growing polymer radicals and/or grafting polymer chains block the diffusion of the monomers to the particles' surfaces.

Pyrolytic manner of the grafted nano-CaCO<sub>3</sub> (**Figure 3(a)**) demonstrates that the grafting PBA remains on the particles after acetone extraction owing to the covalent bonding between the grafting polymer and the nanoparticles. It can be roughly estimated from the curves that the temperature corresponding to the maximum rate of weight loss of PBA lies in about 395°C, while CaCO<sub>3</sub> begins to decompose at around 600°C. The corresponding infrared spectra at different pyrolytic temperatures (**Figure**

**3(b)**) further prove the chemical structure of the grafted nano-CaCO<sub>3</sub>. As shown by the curve collected at 395°C in **Figure 3(b)**, the peaks at 2960cm<sup>-1</sup> and 1200~900 cm<sup>-1</sup> represent the stretching modes of C-H and C-O-C, respectively, confirming that the original materials should be PBA. In addition, the spectra recorded at 395 and 735°C mainly reflect the feature of CaCO<sub>3</sub> particles.

**Figure 3** TGA (a) and the corresponding FTIR (b) spectra of CaCO<sub>3</sub>-g-PBA (grafting percentage=6.15%).



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