

SURFACE MODIFICATION OF CaCO_3 WITH DENDRITIC CARBOXYLIC ACIDS*

Zhao-xia Guo and Jian Yu**

*Institute of Polymer Science and Engineering, Department of Chemical Engineering,
Tsinghua University, Beijing 100084, China*

Abstract Nanometer calcium carbonate was modified with Frechet type polyether dendrons bearing a COOH group at the focal point by a wet-coating technique in dichloromethane at room temperature. The interaction between CaCO_3 and the dendritic modifier was proven by IR and mass spectroscopy of the modified CaCO_3 after thorough extraction with dichloromethane. The amount of tightly bonded organic modifier was estimated by TGA. It was shown that the amount of bonded molecules decreased with increasing generation number due to the larger number of branches. Compared to unmodified CaCO_3 , the modified CaCO_3 possess different dispersibility in water and in organic solvents.

Keywords Calcium carbonate, Surface modification, Polyether dendrimer, Dendritic carboxylic acid

INTRODUCTION

Calcium carbonate has been extensively used as a particulate filler in the manufacture of paint, paper, rubber, plastics, and so on. It is often treated with a surface modifier to aid its incorporation and dispersion in the matrix and to prevent loss of mechanical properties^[1]. Fatty acids (especially stearic acid) are the most widely used surface modifiers, and are usually precoated onto CaCO_3 by a wet-coating (in which a solvent is used) or a dry-blending (in this technique, CaCO_3 and fatty acid are mixed without use of a solvent) technique. The mechanism of the interaction between CaCO_3 and fatty acid has been studied by various authors^[2–4]. Other organic acids^[1, 5], such as unsaturated fatty acids and unsaturated polymeric acids have also been used as interesting surface modifiers, however, dendritic acids (*i.e.* dendrimers) have not been utilized for such purposes.

Dendrimers are a relatively new class of molecules. They have a well controlled three-dimensional structure with a high degree of branching and a large number of functional groups on the surface which can be easily designed according to need. These unique topological features make dendrimers interesting candidates as surface modifiers of CaCO_3 . Surface modification of particulate fillers, especially nanometer-sized particles, is an efficient way to improve the properties of the filled materials.

Here we report the surface modification of nanometer CaCO_3 with dendritic carboxylic acids using a wet-coating method. Frechet type polyether dendrons^[6, 7] bearing COOH groups at the focal points were used to demonstrate the possible interaction between CaCO_3 and the dendritic modifier. A comparative study was carried out using the well-known surface modifier, stearic acid, under the same treatment conditions.

EXPERIMENTAL

Materials and Characterization

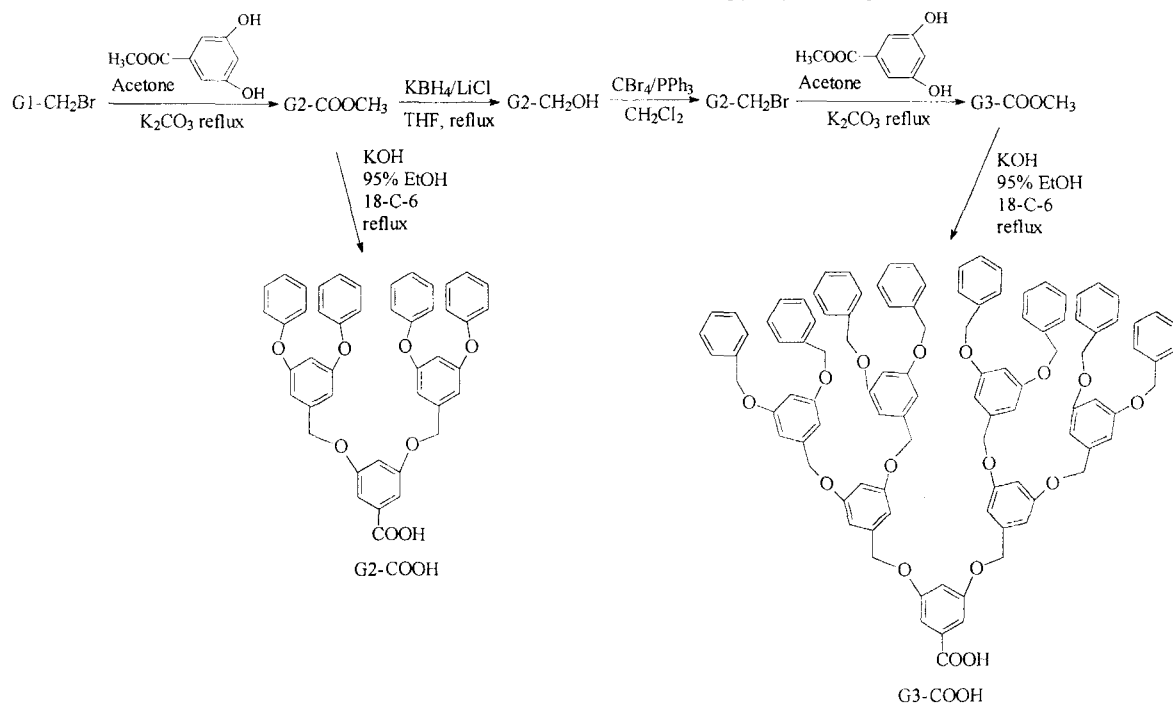
CaCO_3 was obtained from Beijing University of Chemical Technology with diameters ranging from 30 to 100 nm

* This work was supported by Tsinghua-Zhongda Postdoctoral Science Foundation and China Postdoctoral Science Foundation.

** Corresponding author: Jian Yu (于建), E-mail: yujian@chemeng.tsinghua.edu.cn

Received July 10, 2001; Revised September 7, 2001; Accepted September 11, 2001

and a specific surface area of 23 m²/g. Polyether dendrons bearing COOH groups at the focal points (G2-COOH and G3-COOH) were synthesized according to slightly modified literature procedures^[8–10] using easily available methyl 3,5-dihydroxybenzoate as the sole repeating unit, as shown in Scheme 1. The modified CaCO₃ powders were characterized by FTIR on a Nicolet Magna-IR 750 spectrometer using the diffuse reflectance technique (DRIFT). One part of modified CaCO₃ was diluted with four parts of KBr. DRIFT difference spectra were obtained by subtracting the spectrum of unmodified CaCO₃. The transmittance spectra (FTIR-TS) in KBr pellets were recorded on a Nicolet 560 FTIR spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA 2050 instrument with a heating rate of 10 K/min in N₂ atmosphere, and a sample of 10 mg. A mass spectroscopic study was carried out on a VG TRIO 2000 GC/MS spectrometer at a pyrolysis temperature of 600 °C.



Scheme 1 The synthetic scheme of polyether dendrons

Treatment of CaCO₃ with Polyether Dendrons

CaCO₃ (1 g) was added to a stirred solution of polyether dendron (G2-COOH or G3-COOH, 30–100 mg) in CH₂Cl₂ (10 mL). The mixture was stirred for 30 min, and was then ultrasonically agitated for 30 min, and further stirred for 23 h at room temperature. The solvent was evaporated *in vacuo*, the residue was extracted with CH₂Cl₂ using a Soxhlet apparatus for 28 h until no acid was detected in the extract, then dried *in vacuo* at 100 °C for 8 h. The bonded amount of acid was determined by TGA.

RESULTS AND DISCUSSION

Coating of CaCO₃ with Stearic Acid

As stearic acid is the most widely used and the best studied surface modifier of CaCO₃, we took it as a reference compound. Thus, CaCO₃ was treated with stearic acid using the same procedure as for polyether dendrons. The adsorption isotherm was shown in Fig. 1. It was observable that a plateau was reached when the amount of stearic acid used for treatment was beyond 4% (wt% to CaCO₃) with a maximum amount of adsorption around 4% (wt% to CaCO₃) (*i.e.* 0.14 mmol of stearic acid/gram of CaCO₃) which was slightly lower than the monolayer coverage (5%) calculated from the specific surface area (23 m²/g) of CaCO₃ and the cross sectional area of stearic acid (0.20 nm²^[11]). Papirer *et al.*^[2] studied the coating of CaCO₃ from toluene solution using a tracer method and obtained a similar adsorption isotherm after Soxhlet extraction with toluene. The maximum adsorption amount,

according to the authors, indicated monolayer coverage where the stearic acid molecules are fixed perpendicularly to the solid surface. Fekete *et al.*^[3, 12] investigated the surface coating of CaCO_3 in the dry-coating system using a dissolution technique and also obtained a similar adsorption isotherm for all the tested organic solvents with the same maximum adsorption amount, which indicated multilayer coverage according to the authors.

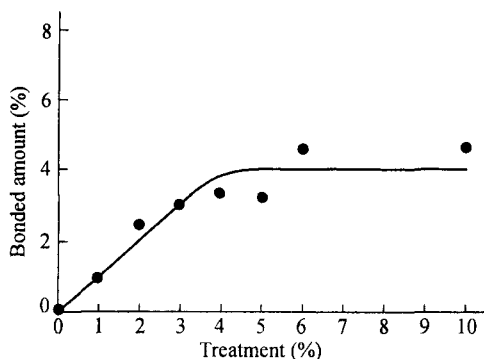


Fig. 1 Adsorption isotherm of stearic acid on CaCO_3

Modification of CaCO_3 with Polyether Dendrons

It has been shown that the success in coating CaCO_3 with stearic acid could probably be attributed to the ionic character of CaCO_3 ^[3]. The mechanism could include the reaction shown in Scheme 2. Dendritic carboxylic acids would be expected to undergo the same type of reaction with CaCO_3 .



Scheme 2

Figure 3 shows the DRIFT spectra of CaCO_3 (upper line) and CaCO_3 treated with polyether dendron G2-COOH (middle line) and DRIFT difference spectrum of CaCO_3 treated with polyether dendron G2-COOH (lower line). Aromatic bands at 3068 and 3035 cm^{-1} and ether bands at 1165 and 1051 cm^{-1} derived from polyether dendron G2-COOH appear in the spectrum of treated CaCO_3 , indicating the existence of polyether coating, *i.e.* possible interaction between CaCO_3 and the dendritic carboxylic acid. The characteristic peak of aromatics at 1597 cm^{-1} is not observed in the spectrum of treated CaCO_3 due to the overlapping of the intense and broad huge peak of CaCO_3 at 1458 cm^{-1} , but it is detectable in the DRIFT difference spectrum, showing further evidence for the existence of aromatic coating. The absence of a characteristic carboxyl group at 1700 cm^{-1} (compared with Fig. 2) and the presence of a carboxylate bond at 1571 cm^{-1} in the DRIFT difference spectrum provide verification in support of the mechanism of interaction which is through the formation of carboxylate salt (Scheme 2). Mass spectroscopy gives supplementary evidence supporting the presence of aromatic coating. After pyrolysis at 600°C, benzyl group (mass 91) which is the surface group of polyether dendron was detected as basic fragment (relative intensity 100%), two other fragments at mass 165 (4%) and 180 (6%) derived from the part including the focal point of the polyether dendron were also observed, indicating the presence of carboxylate group.

The maximum amount of coating of polyether dendrons on CaCO_3 was evaluated using treatment amounts of 3%–10% (wt% to CaCO_3), basing on the adsorption isotherm obtained with stearic acid treatment. As seen from Table 1, the bonded amount was constant with an average value around 3% for both generation 2 & 3, corresponding to 0.040 mmol/g (of CaCO_3) for G2-COOH and 0.019 mmol/g for G3-COOH. Comparing with linear stearic acid treatment, the maximum coating amounts (by weight) with polyether dendrons was only slightly lower, but the numbers of adsorbed molecules were only a quarter (with G2-COOH) and one seventh (with G3-COOH). This seems reasonable, as polyether dendrons are highly branched with 4 (for G2-COOH) and 8 (for G3-COOH) benzyl groups at the surface, having a much bigger cross sectional area. The maximum coating

amount with G3-COOH was similar to that with G2-COOH, but the number of adsorbed molecules with G3-COOH was much less (only a half) than with G2-COOH because of the increased number of branches.

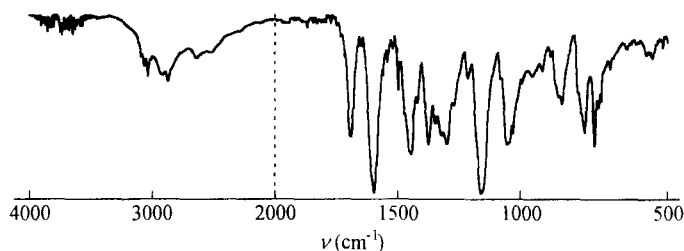


Fig. 2 FTIR-TS spectrum of G2-COOH

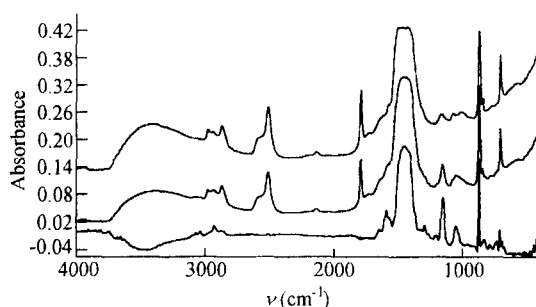


Fig. 3 DRIFT spectra of CaCO_3 (top) and CaCO_3 treated with polyether dendron G2-COOH (middle); DRIFT difference spectrum of CaCO_3 treated with polyether dendron G2-COOH (bottom)

Table 1. Coating of dendritic carboxylic acids on CaCO_3

Treatment (%)	3	4	5	6	10
Bonded amount (%), G2-COOH	2.9	3.1	3.7	–	3.1
Bonded amount (%), G3-COOH	2.9	3.1	3.8	2.7	–

– Have not measured

The surface property of CaCO_3 has been changed from hydrophilic to hydrophobic by coating with polyether dendrons. The original CaCO_3 was easily dispersed in water and formed big agglomerates in cyclohexane under ultrasonic irradiation. On the contrary, the coated CaCO_3 quickly settled down in water and could be dispersed in cyclohexane under ultrasonic irradiation. This is similar to CaCO_3 coated with stearic acid^[13].

In conclusion, it has been shown that dendritic carboxylic acids have some affinity for CaCO_3 surface with relatively strong interaction (not extractable by dichloromethane), although they have large steric hindrance. Thus, dendritic carboxylic acids can be used as surface modifiers of CaCO_3 , the molar amount of adsorbed molecules decreased with increasing generation number due to larger number of branches.

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