

Synthesis of Silicon Ester Dispersants and Its Application in CaCO₃/Polyethylene Composites

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Received 3 September 2009; accepted 20 April 2010

DOI 10.1002/app.32701

Published online 11 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Silicon ester dispersants were prepared using transesterification between ethyl petroleum silicate and the alkyl alcohols by different molecular masses. The dispersants were used to modify calcium carbonate (CaCO₃), and their effect on the mechanical properties of CaCO₃/polyethylene (PE) composites was investigated. The transesterification was confirmed by gas chromatography (GC). The optimal conditions for the preparation of silicon ester dispersants were 110°C for 3 h with 2% catalyst by weight and fixed molar ratio of isooctyl alcohol to

ethyl petroleum silicate of 3 : 1. Fourier transmission infrared spectroscopy (FTIR) results indicated that the dispersants were coating to the CaCO₃ particles. Dispersant with octadecanol as its solvable chain enabled the best modification effect. CaCO₃/PE composites modified by dispersants demonstrated improved mechanical properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2244–2249, 2010

Key words: polymer composites; silicon ester dispersants; calcium carbonate; polyethylene

INTRODUCTION

It is well-known that surfactants coupling agents and hyper dispersants have been developed to modify surface polarity of inorganic powders to improve their dispersion in organic resins.^{1–4} The molecular structure of traditional dispersants or surfactants, contains both a hydrophobic group and a hydrophilic group, which is made of a long nonpolar alkyl group and a short polar group, respectively. The two groups are opposite in solubility and polarity.^{5,6} Because of the molecular characteristics of traditional dispersant, they can reduce the interfacial tension and improve the dispersion in a water-based biphasic resin system. However, such molecular structure limits its steric stabilization in a nonaqueous dispersive system.^{7,8} To overcome the limitations of traditional dispersants in the nonaqueous dispersion system, a new type of polymer dispersant so called hyper-dispersant, which has the unique dispersion effect on the nonaqueous dispersion system, has recently gained increasing attention.^{9,10} It actually has two different functional groups, one is the anchoring group which attracts to the surface of the fillers and the other is the solvable chain which is

compatible with the resin.¹¹ Zhang et al. synthesized a hyper-dispersant agent with polyethylene (PE) glycol (PEG) and polyacrylic acid as the solvable chain, and studied its influence on dispersion and stabilization of SiO₂ fillers.¹² Sun et al. prepared the PE polyamine-poly (12-hydroxylauric acid) ester hyper-dispersant agent of 12-hydroxylauric acid as the solvable chain and PE polyamine as the anchoring group, respectively.¹³ Yan et al.¹⁴ used hyper-dispersant agents to modify nano-CaCO₃ to improve the strength and toughness of PVC/nano-CaCO₃ composites. For example, the tensile strength of 37.7 MPa and the impact strength of 39.7 kJ/m² were achieved. Feng et al.¹⁵ also investigated the effect of polyester-type hyper-dispersant agent on mechanical properties of PP/inorganic particle composites, finding that the tensile strength and impact strength of the composites enhance 29% and 22.8 %, respectively.

In this article, low molecular weight silicon ester dispersants of the similar structure to the aforementioned hyper-dispersants, were prepared by transesterification with the objective to solve the shortcoming from the short polar structure in traditional dispersants and to leverage the advantages of long polymeric chains in hyper-dispersants providing the steric stabilization around the nanoparticles as fillers. The as-prepared dispersants possess the anchoring group of silane and solvable alkyl alcohol chain of different chain length. Such rarely-explored dispersants were used to successfully modify CaCO₃ micro-particles and their effect on the mechanical properties of CaCO₃/PE composites was investigated.

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Contract grant sponsor: Department of Public Education of Anhui Province; contract grant number: KJ2008A001.

EXPERIMENTAL

Materials

Ethyl petroleum silicate and industrial coupling agent F2 ($[Al(OCH_3)_3]_n$) were supplied by Wuxi Prospect Chemical Reagent. Isooctyl alcohol was supplied by Shanghai Chemical Reagent Factory. Stannous octoate, dodecanol, octadecanol and liquid paraffin were supplied by Sinopharm Chemical Reagent. Polyethylene (PE TR-490) was supplied by Chevron Phillips and polyethylene (PE-6070) was supplied by Xinjiang Dushanzi. The density and melt flow index of PE TR-490 is 0.957 g/cm^3 and 0.2600 g/10 min , respectively. The density and melt flow index of PE-6070 is 0.964 g/cm^3 and 7.5386 g/10 min , respectively. The $CaCO_3$, which was prepared by grinding, was provided by Anhui Hengtai non-metal material technology. The average diameter of particles was $10 \mu\text{m}$. Other materials were of chemical purity (CP) grade. All materials were used as received.

GC and optimal condition analysis

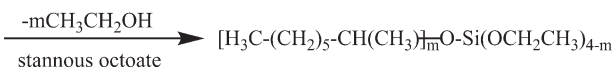
A desired amount of ethyl petroleum silicate and catalyst were put into a 250 mL three-neck flask under the protection of nitrogen at 40°C for 10 min. A desired amount of isooctyl alcohol was also added to the flask and held for 2 h. The reaction solution was then treated under vacuum for 1 h to obtain main products and by-products. The optimal reaction temperature, amount of catalyst, reaction time and the reaction ratio of ethyl petroleum silicate to alcohol were evaluated. Apart from isooctyl alcohol (8C), dodecanol (12C), and octadecanol (18C) were also used as reactive monomers alternatively; the reaction scheme for the synthesis of silicon ester dispersant agent is presented in Scheme 1.

Modification of $CaCO_3$

$CaCO_3$ particles were dried at 110°C in a vacuum oven for 2 h, to which quantitative F2 and dispersants (8C, 12C, and 18C) were added, respectively. All of them were kept in the oven at 110°C for 1 h. After that, the mixtures were transferred into a high-speed medicinal mixer quickly, first stirring at the speed of 700 rpm for 2 min and then increasing the speed to 1440 rpm for 5 min. The treated $CaCO_3$ were not washed and used in preparing $CaCO_3/PE$ composites directly.

Preparation of $CaCO_3/pe$ composites

Two types of PEs, PE-6070, and PE TR-490 were used. Because the melt flow index of PE TR-490 was very low, so it is not recommended for masterbatch



Scheme 1 The reaction scheme for the synthesis of silicon ester dispersant agent.

preparation; while the melt flow index of PE-6070 was high and it can carry out homogeneous melt mixing with $CaCO_3$. Based on melt flow properties and wettability to $CaCO_3$, PE-6070 was chosen for master batch preparation while PE TR-490 was used for mechanical test specimen preparation.

Blends of $CaCO_3$ and PE-6070 were prepared by mechanical mixing in an internal mixer Torque Rheometer (XSS-300, Shanghai Kechuang Rubber Plastic Mechanical Equipment in China) equipped with a mixing chamber of 60 mL with roller blades in the following conditions: temperature of mixing of 200°C , mixing time of 6 min, the rotational speed of 60 rpm. The composites were prepared in a Plastic Injection Molding Machine (HTI 90-F5B, Haitai Plastic Machinery, China). The specimens were prepared by injection molding process by adding the PE TR-490 and the masterbatch. The temperature of the cylinder and the mold were $180\text{--}200^\circ\text{C}$ and 25°C , respectively. The hold time was 5 s when the injection pressure was 90–100 Mpa. The concentration of $CaCO_3$ filler used in the master batch was 80 wt % and the precise amount of filler present in each one of the different formulations of PE composites, as determined from ash-content tests, was indicated in Table V. A total of five samples were studied for the ash content test for each PE composite formulation. The oven used for these tests was Thermo-gravimetric Analyzer (Netzsch TG-209-F3).

Characterization

Gas chromatography and FTIR analysis

Gas chromatographic separation and determination of by-product and ethanol (99%) was performed on a GC-1024 (Shimadzu, Japan). The presence of the silicon ester dispersant on the surface of $CaCO_3$ particles was characterized by Fourier transform infrared (FTIR) (Nicolet-IR). The samples for infrared analysis were prepared using potassium bromide (KBr) pellets.

Viscosity and sedimentation measurement

The modified $CaCO_3$ (3.0 g) with silicon ester coating was dispersed in 25 mL measuring cylinder filled with 20 mL liquid paraffin with oscillating up and down and dispersing with ultrasonic at 20°C for 15 min. Put it aside for 24 h and record the volume

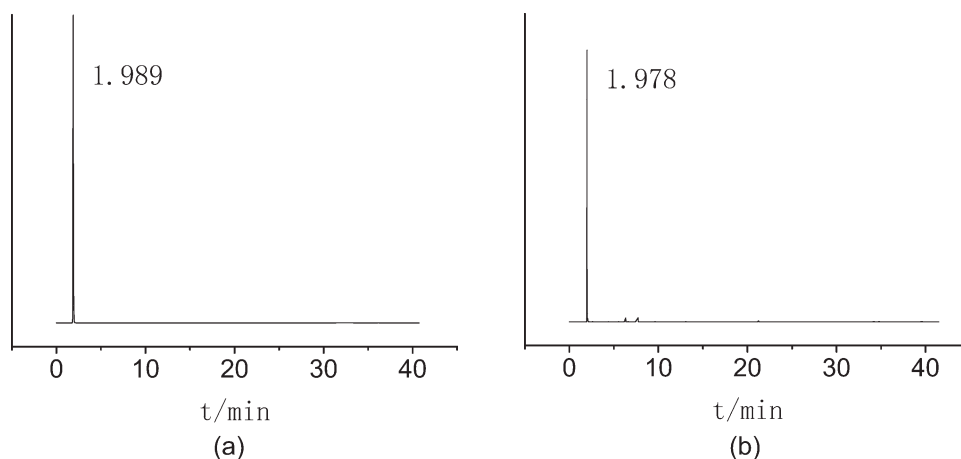


Figure 1 Gas chromatogram of ethanol (a) and by-product (b).

of settled powder as V_p (mL), then calculated the settlement volume by $V_p/3.0$ (mL g^{-1}). The viscosity is measured by rotational viscometer (NDJ-7).

Mechanical properties

The specified test method for tensile test is ASTM D638–2003. The specified test method used for the flexural test is ASTM D790–2003. The tensile strength, flexural strength and flexural modulus were examined by an Electronic Universal Testing Machine (CMT-4304, Shenzhen Sans Testing Machine, China). The span for the measuring of flexural strength and flexural modulus was 64 mm. At least five specimens were used for each test to get the average value.

The notched impact strength was measured with a Reger Impact Tester according to ASTM D-256. The samples have the size of 4 mm \times 10 mm \times 80 mm. The notched depth of the sample is 0.2 times of its width. Impact testing at room temperature was performed after the sample placed at 25°C over 24 h.

RESULT AND DISCUSSION

GC and optimal condition analysis

Figure 1 show the gas chromatogram of ethanol and by-products, which were obtained from the transesterification of ethyl petroleum silicate and isoocetyl alcohol. The retention time of ethanol and by-product was almost the same [Fig. 1(a,b)]. Moreover, colorless and transparent by-product has a thick alcohol-like odor proving that the transesterification of ethyl petroleum silicate and isoocetyl alcohol took place in the way shown in Scheme 1. The Gas Chromatogram also confirmed that the transesterification took place when isoocetyl alcohol was replaced by dodecanol and octadecanol.

The dispersants for CaCO_3 powder were obtained using 2% catalyst and the molar ratio (2 : 1) of isoocetyl alcohol to ethyl petroleum silicate at varied reaction temperature for 3 h. The viscosity and the sedimentation volume of modified CaCO_3 in liquid paraffin were listed in Table I.

As shown in Table I, the sedimentation volume of modified CaCO_3 in liquid paraffin is lower than that of unmodified CaCO_3 , except for the reaction temperature at 150°C. Furthermore, the viscosity of modified CaCO_3 is also lower than that of unmodified CaCO_3 . When transesterification temperature was 110°C, the modified CaCO_3 had the smallest sedimentation volume and viscosity. Sedimentation volume reflects the dispersion property of inorganic particles in the liquid. If the inorganic particles are well dispersed in the liquid, the liquid have better wettability on the particles, and the aggregation and adhesion between the particles become difficult. When these particles deposited, they will have the smaller sedimentation volume. The addition of dispersants decreases the surface polarity of inorganic powder, and increases the dispersion and compatibility between inorganic powder and liquid paraffin.¹⁶ Therefore, the temperature was set at 110°C in following experiments.

The influence of different amounts of catalyst on the sedimentation volume and viscosity of CaCO_3

TABLE I
The Effect of Reaction Temperature on Sedimentation Volume and Viscosity of CaCO_3 Modified by Dispersants in Liquid Paraffin

Temperature (°C)	Sedimentation volume after 24 h (mL g^{-1})	η (mPa s)
unmodified	4.8	44.0
90	4.3	35.5
110	3.7	34.1
130	4.4	37.6
150	5.0	42.5

TABLE II
The Effect of the Amount of Catalyst on the Sedimentation Volume and Viscosity of CaCO₃ Modified by Dispersants in Liquid Paraffin

Catalyst content (wt %)	Sedimentation volume after 24 h (mL g ⁻¹)	η (mPa s)
Unmodified	5.2	44.5
1%	4.6	34.3
2%	4.0	33.0
3%	5.0	37.5
4%	5.4	41.8
5%	5.6	39.8

modified by dispersants in liquid paraffin is shown in Table II.

As shown in Table II, when the amount of catalyst was 2%, the modified CaCO₃ had the smallest sedimentation volume and rotational viscosity in liquid paraffin. Therefore, the optimal catalyst content was approximately 2%.

The effect of the reaction time on the sedimentation volume and viscosity of CaCO₃ modified by dispersants in liquid paraffin was shown in Table III. As indicated in Table III, comparing with unmodified CaCO₃, the modified one has lower sedimentation volume in liquid paraffin, except when the reaction time was 5 h. Moreover, a viscosity reduction was observed of the modified CaCO₃ in liquid paraffin. When the transesterification time was 3 h, the modified CaCO₃ had the smallest sedimentation volume and rotational viscosity in liquid paraffin. Therefore, the optimal value of reaction time was about 3 h.

The effect of the molar ratio of isooctyl alcohol to ethyl petroleum silicate on the sedimentation volume and viscosity of CaCO₃ modified by dispersants in liquid paraffin was shown in Table IV. The sedimentation volume of modified CaCO₃ after 24 h in liquid paraffin had a trend to decrease with the increasing molar ratio of isooctyl alcohol to ethyl petroleum silicate. When the molar ratio of isooctyl alcohol to ethyl petroleum silicate was 3 : 1, the modified CaCO₃ had the smallest sedimentation volume and rotation viscosity in liquid paraffin. There-

TABLE III
The Effect of the Reaction Time on the Sedimentation Volume and Viscosity of CaCO₃ Modified by Dispersants in Liquid Paraffin

Time (h)	Sedimentation volume after 24 h (mL g ⁻¹)	η (mPa s)
Unmodified	5.2	45.3
3	3.5	32.0
5	5.7	39.1
7	4.2	36.0
9	4.0	35.5

TABLE IV
The Effect of the Molar Ratio of Isooctyl Alcohol to Ethyl Petroleum Silicate on the Sedimentation Volume and Viscosity of CaCO₃ Modified by Dispersants in Liquid Paraffin

Molar ratio	Sedimentation volume after 24 h (mL g ⁻¹)	η (mPa s)
Unmodified	5.2	45.5
1 : 1	4.9	37.0
2 : 1	4.8	36.5
3 : 1	4.6	35.8

fore, the optimal molar ratio of isooctyl alcohol to ethyl petroleum silicate was 3 : 1.

To sum up the optimal conditions of the preparation of low molecular-weight silicon ester dispersants are as follows: reaction temperature is 110°C, the amount of catalyst is 2%, reaction time is 3 h, and the molar ratio of isooctyl alcohol to ethyl petroleum silicate is 3 : 1. The same optimal conditions were adopted when isooctyl alcohol is replaced by dodecanol and octadecanol, respectively.

CaCO₃ modified by silicon ester dispersants

The FTIR spectra of silicon ester dispersant (8C), unmodified CaCO₃ and CaCO₃ modified by silicon ester dispersant were shown in Figure 2. The absorbance of Si—O—C at 1090 cm⁻¹ exists in silicon ester dispersant [Fig. 2(a)] and modified CaCO₃ without extraction [Fig. 2(d)], while there are no absorbance of Si—O—C at 1090 cm⁻¹ in modified CaCO₃ extracted by ethanol [Fig. 2(c)]. The similar phenomenon is also observed in the absorbance of C—H at 2880 cm⁻¹ and 2930 cm⁻¹ in Figure 2(a,c,d). These results indicate that the dispersants were coating to the CaCO₃ particles.

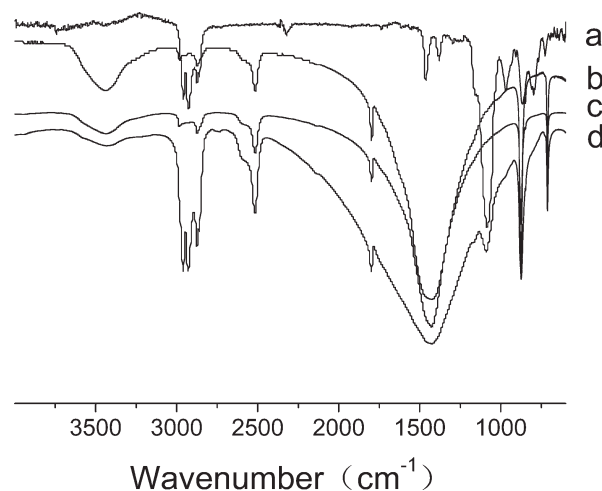


Figure 2 FTIR spectra of: (a) silicon ester dispersant (8C), (b) CaCO₃, and CaCO₃ modified by silicon ester dispersant ((c) extracted by ethanol, (d) without extraction).

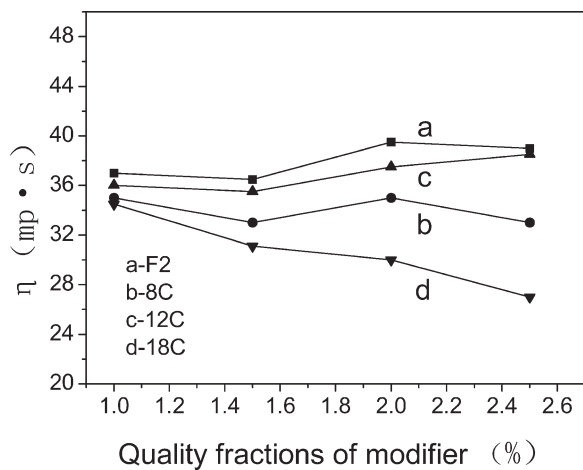


Figure 3 The viscosity of CaCO_3 modified by different modifier in liquid paraffin. (a) F2, (b) 8C, (c) 12C, (d) 18C.

Figures 3 and 4 show the viscosity and sedimentation volume of CaCO_3 modified by different modifier in liquid paraffin. The viscosity and the sedimentation volume were lowest when it was modified by 18C. Especially, when the modifier was 2.5%, comparing with industrial coupling agent F2, the inorganic powder modified by dispersants have lower viscosity and sedimentation volume in liquid paraffin. So the modification effect of the dispersant 18C was considered to be the best.

Mechanical properties of CaCO_3/PE composites

Table V shows the effect of different dispersants on the mechanical performance of CaCO_3/PE composites when the amount of the dispersant was 2.5%. Comparing with unmodified CaCO_3/PE composite, the mechanical properties of modified CaCO_3/PE composite was improved. The impact strength of CaCO_3/PE composites increased obviously, especially when it was modified by dispersants 12C and 18C with the increasing ratio of more than 50%. The impact strength of CaCO_3/PE composites modified by dispersants is higher than the composites modified by F2.

At the same time, it can be seen that the flexural strength and flexural modulus of CaCO_3/PE composites increases obviously with the addition of disper-

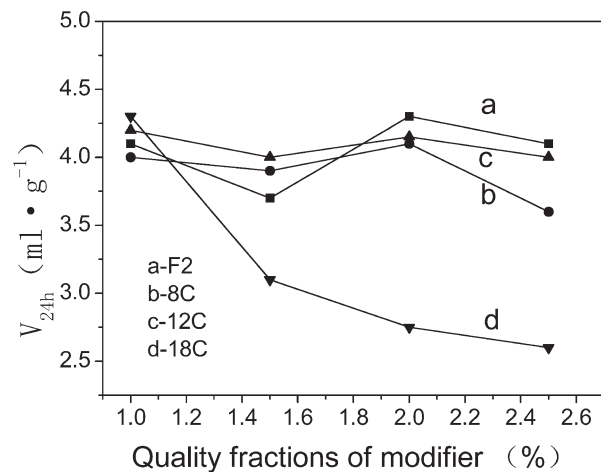


Figure 4 The sedimentation volume of CaCO_3 modified by different modifier in liquid paraffin. (a) F2, (b) 8C, (c) 12C, (d) 18C.

sants 8C, 12C, and 18C, especially with 8C and 18C. The tensile strength of the composites with dispersants is almost unchanged.

Comparing with the unmodified composite, the addition of dispersants improved the surface polarity of inorganic powder and increased the compatibility between inorganic powder and organic resin. All the dispersants could improve the compatibility between the PE matrix and the CaCO_3 particles, increasing the degree of dispersion of the CaCO_3 particles and thus improving the mechanical properties of composites, especially for impact strength as shown in Table V.

The length of nonpolar structure of the surface of dispersants didn't change much, just be 6C. Judging from the mechanical properties test, CaCO_3/PE composites modified by 12C possess a comparative advantage in improving the toughness of composites. Relatively speaking, the mechanical property of composite material modified by dispersant with 18C is best. The 18C dispersant can improve the toughness of the composites without reducing its rigidity.

CONCLUSION

Silicon ester dispersants with different alkyl alcohol as solvable solvents were prepared by transesterification.

TABLE V
Effect of Different Dispersants on Mechanical Properties of CaCO_3/PE Composites

Sample	Impact strength (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	The amount of filler (CaCO_3) (%)
Unmodified	$31.7^{+5.5}_{-2.6}$	$18.1^{+1.2}_{-0.3}$	$822^{+11.5}_{-13.3}$	$20.0^{+1.0}_{-0.8}$	$30.1^{+1.1}_{-0.7}$
F2	$41.4^{+3.4}_{-5.0}$	$18.6^{+0.6}_{-1.1}$	$846^{+10.3}_{-14.8}$	$20.3^{+1.2}_{-0.6}$	$29.5^{+1.0}_{-0.4}$
8C	$44.9^{+5.8}_{-2.7}$	$20.4^{+0.9}_{-0.3}$	$978^{+13.7}_{-9.8}$	$20.6^{+0.8}_{-1.1}$	$30.3^{+0.6}_{-1.1}$
12C	$55.2^{+4.5}_{-3.5}$	$18.7^{+0.4}_{-0.9}$	$891^{+13.5}_{-11.2}$	$20.7^{+0.7}_{-1.2}$	$29.8^{+0.4}_{-0.9}$
18C	$51.5^{+3.9}_{-4.3}$	$19.8^{+0.6}_{-1.1}$	$941^{+10.3}_{-13.8}$	$20.1^{+1.1}_{-0.9}$	$30.0^{+0.8}_{-0.5}$

Gas chromatography was used to confirm the transesterification. The optimum conditions of the preparation of silicon ester dispersants were obtained. FTIR results suggested that the dispersants were coating to the CaCO_3 particles. CaCO_3/PE composites modified by silicon ester dispersants possess better mechanical properties, with dispersant 18C presenting the best modification effect. CaCO_3/PE composites modified by silicon ester dispersants possess better mechanical properties.

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