



# Controlling and tuning the dispersion properties of calcined kaolinite particles in various organic solvents via stepwise modification method using 3-glycidoxypropyltrimethoxysilane and dodecylamine



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## ABSTRACT

The chemical modification of calcined kaolinite particle surface via stepwise method using 3-glycidoxypropyltrimethoxysilane (GPS) and dodecylamine was investigated. Silylation of kaolinite particles was controlled by varying the amount of GPS under almost anhydrous condition. FT-IR and thermal analysis indicated that silylation monolayer coverage on kaolinite particle surface increased with the increasing of the amount of additive GPS, reaching a maximum value of  $8.81 \mu\text{mol}/\text{m}^2$  when the mass ratio of kaolinite to GPS was up to 1:1. Further modification of the silylated kaolinite particle surfaces was accomplished using the modifier synthesized by the ring-open reaction of GPS and dodecylamine to form multilayer branches at the presence of  $\text{H}_2\text{O}$  ( $\text{pH} = 12$ ). The final modified kaolinite particle surfaces contained both hydrophobic long alkyl chains and hydrophilic groups, which were advantageous to homogeneous dispersion in low polar as well as polar solvents, respectively. Digital photographs and TEM images revealed that the final modified kaolinite particles were homogeneously dispersed in acetone, dioxane, ethanol, and THF, even better than raw kaolinite dispersed in ethanol. Meanwhile, the dispersion properties in low polar solvents such as xylene, cyclohexane and petroleum ether were also acceptable, and the aggregate particle size was near to primary particle size of raw kaolinite, or just a bit larger, increasing from 1.25 to 1.75–2.00  $\mu\text{m}$ .

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## 1. Introduction

It is well-known that the mechanical, physical and chemical properties of polymeric materials can be improved efficiently by incorporating adequate fillers in polymer matrix even at rather low loading [1–9]. The polymer composites have attached considerable attention because they combine the structure and chemical properties of both host polymer matrix and guest fillers and possess fascinating synergistic features [10,11]. Carbon black, silica and titania particles are the most traditional fillers to prepare polymer composites [7–9]. However, high costs, strong tendency to aggregate as well as pollution problems restrict the practical applications in industrial scale. Among fillers, many kinds of cheap, widespread, and environmental friendly clay minerals such as montmorillonite, attapulgite, mica, and hectorite have caused far-ranging appreciation of many scientists and enterprisers as credible alternative to dominant commercial reinforcing materials [2–6,12–15].

In general, clay minerals cannot be directly applied in preparing polymer composites for their hydrophilic surface. Therefore, it is necessary to treat clay particles in appropriate way. Over the past decades, many efforts have been devoted by numerous trailblazers to prepare organoclays and organoclay/polymer composites with excellent performances. According to previous literatures published in mainstream journals, several approaches were proposed to modify clays, e.g. adsorption, ion exchange with inorganic or organic cations, grafting of organic functional molecules or polymers, dehydroxylation and calcination [3,16], thereby making organoclays dispersible in organic solvents and rendering them more compatible with polymer matrix. Indeed, organoclays prepared by grafting exhibit excellent mechanical and thermal properties in comparison with other methods because the grafted molecules can be covalently anchored onto clay surface [17].

The majority of grafted clay minerals are 2:1 structure, mainly montmorillonite [2–5]. In contrast, relatively few works have been conducted on kaolinite for grafting reactions [17,18]. A main challenge is that the strong van der Waals and hydrogen bonds between adjacent layers of kaolinite make more difficult the access to Al–OH of interlayer space in most cases [19,20]. To overcome this problem,

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some small intercalation agents with high dipole such as dimethyl sulphoxide (DMSO) or N-methyl formamide (NMF) should be firstly intercalated into kaolin interlayer prior to the grafting reaction [1,17,19–21]. During the intercalation procedure, which might be lasted for as long as 20 days at room temperature [20], basal spacing between two consecutive layers can be enlarged accompanied by the broken of hydrogen bonds, which also facilitates the further introduction of the subsequent functional guest molecules. However, if calcined kaolinite were employed as raw material instead of layered kaolinite, the problem stated above might be left out of account. In addition, although hydroxyl groups are almost removed during calcination process, calcined kaolinite particles still possess a considerable number of chemical reaction sites, such as Al–OH groups, which may be attributed to the absorbed layers of hydroxyls formed on the surface of kaolinite when calcined kaolinite is exposed to the air [22]. Therefore, the chemical modification of calcined kaolinite with particular modifier is convenient compared with layered kaolinite under specific conditions and feasible in theory.

Ever since Plueddemann introduced the concept of silane coupling agents (SCAs) [23], which has 1–3 functional groups and 3–1 alkoxy groups, it has attracted great interest from theorists and experimentalists because the functional groups of organosilanes can provide versatile properties. In the last years, numerous kinds of SCAs have been synthesized and employed to modify particle surface to improve the compatibility of the hydrophilic particle surface with the hydrophobic polymer matrix [17,24–28]. The introduction of versatile functional groups by various SCAs onto particle surface not only influences the affinity between particle and polymer but also provides some reaction sites such as vinyls and amines, which enable further treatment with other compounds [26,29].

The design of novel modifiers and modification process has been focused on for a long time; however, another likewise important issue was often neglected in many researches. The traditional chemical modification of particle surface was utilized to convert the natural hydrophilicity to hydrophobicity [30–32], thereby increasing the affinity between modified particles and polymeric matrix. However, the hydrophobic surface of modified particles also brings trouble on themselves, which means particles capped with particular modifying agent can only be uniformly dispersed in a kind or series of solvents, thus the solvents used in the manufacturing process of composites will be restricted. For example, it might be difficult to obtain homogeneous dispersion of particles modified with hydrophobic groups in some polar solvents such as alcohols and ketones which are in common use in the preparation of composites yet [28,33]. Consequently, it is quite essential to develop techniques of controlling the dispersion properties of modified particles into various polarities organic solvents. Recently, there was a significant research on controlling of the hydrophobicity of TiO<sub>2</sub> surface using a novel anionic surfactant with a hydrophobic alkyl chain and a hydrophilic PEG chain [34]. The surface-modified TiO<sub>2</sub> particles can be successfully dispersed in various types of organic polar and apolar solvents such as DMSO, methanol, MEK, acetonitrile and toluene. Although the obtained suspension was stable for age, the study may be more reasonable if the researchers had paid closer attention to the complexity and costliness of synthesis procedure of this surfactant. Therefore, the main objective of this study is to seek for a facile and effective modification method to control and tune the surface properties of calcined kaolinite particles.

In the present work, we modified calcined kaolinite particles by stepwise method with 3-glycidoxypropyltrimethoxysilane (GPS) and dodecylamine. The raw kaolinite was firstly treated with GPS as an intermediate, and then the silylated kaolinite particles was modified using modifiers synthesized in the ring-open reaction of GPS and dodecylamine to form multilayer coverage at the

presence of H<sub>2</sub>O. The dispersion properties of modified kaolinite particles in organic solvents with various polarities were also investigated.

## 2. Experimental

### 2.1. Materials

The calcined kaolinite (Kt) was kindly supplied by Nanjing Profem chemical (Jiangsu) Co., Ltd., China. Its specific surface area (SSA) was found to be 12.5 m<sup>2</sup>/g (BET method). The chemical composition (mass%) analyzed by X-ray fluorescence (XRF) spectrometer was: SiO<sub>2</sub>, 49.88; Al<sub>2</sub>O<sub>3</sub>, 44.95; TiO<sub>2</sub>, 1.04; Fe<sub>2</sub>O<sub>3</sub>, 0.76; P<sub>2</sub>O<sub>5</sub>, 0.74; Na<sub>2</sub>O, 0.46; CaO, 0.27; K<sub>2</sub>O, 0.26; MgO, 0.22; ignition loss, 1.18. The sample was ground and sieved, and 200 mesh powder was selected. Dodecylamine (98%) and GPS (97%) were obtained from Aladdin Reagents Co., Ltd., Shanghai, China. Acetone, dioxane, ethanol, ethyl acetate, THF, xylene, cyclohexane, petroleum ether, N,N-dimethylformamide (DMF), and sodium hydroxide were of analytical grade purity and purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

### 2.2. Preparation of silylated kaolinite particles using GPS as an intermediate

In this step, raw Kt particles were modified with GPS. All equipment was rigorously dried before use. Into a 250 mL four-necked flask, equipped with a mechanical stirrer, a thermometer and a reflux condenser, Kt and xylene were injected to form 10 wt.% slurry and then the desired amount of GPS (mass ratio of Kt to GPS varied from 10:1 to 1:1) was added into the suspension, followed by vigorously stirring for 8 h at 125 °C. After that the modified kaolinite particles were collected by centrifugation and washed with xylene for 4 times to eliminate the excess reagents thoroughly. Finally, the particles were dried in a vacuum oven at 80 °C overnight and ground to powder. The modified kaolinite was denoted as Kt<sub>X</sub>-GPS, where X represented the mass ratio of Kt to GPS.

### 2.3. Preparation of modifier using GPS and dodecylamine

All equipment was rigorously dried before use. Typically, 4.85 g dodecylamine was dissolved into 25.00 g DMF (molecular sieve-dried) in a 250 mL four-necked flask and then 2.50 g GPS were charged, followed by stirring for 48 h at 50 °C [35]. In this reaction, the total mole of dodecylamine was approximately 1.5-fold excess over that of epoxy groups to ensure that GPS could react completely with dodecylamine.

### 2.4. Further modification of Kt-GPS particles

5.00 g as-prepared Kt-GPS particles, 50.00 g DMF (molecular sieve-dried) and 0.57 g pH-controlled water, were added to the reaction solution of Section 2.3, and then the mixture was maintained at 30 °C for 48 h under stirring. The additive water was equimolar to the methoxy groups of GPS used in Section 2.3. The pH of the additive water was kept at 12 using NaOH. The reaction products were separated by centrifugation and aged in an oven at 100 °C overnight. After aging, enough time had elapsed for complete hydrolysis and condensation of the residual methoxy groups. Finally, the aged product was separated by centrifugation and washed 4 times with ethanol and acetone, then dried in a vacuum oven at 80 °C overnight. The final product was denoted as Kt<sub>X</sub>-GPS-DDA, where X represented the mass ratio of Kt to GPS.

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