Surface Modification of Magnesium Sulfate Whisker with Stearic Acid

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ABSTRACT: In order to enhance the interfacial adhesion between magnesium oxy sulfate whisker (MOSw) particles and polymers, the hydrophobicity of MOSw was improved by surface modification using stearic acid. The morphologies and structure of MOSw before and after surface modified (MOSw-SA) were characterized by field emission scanning electron microscope (FESEM) and X-ray powder diffraction (XRD). The interfacial interactions between MOSw and stearic acid were studied by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses. The results showed that the surface of MOSw was changed from being hydrophilic into being hydrophobic. And the stearic acid molecular binds strongly to the surface of MOSw. Chemical bond (COO-Mg<) was formed by the reaction between R–COOH and the hydroxyl group of MOSw. The reaction occurred only between the stearic acid and the surface of MOSw without altering MOSw’s morphology and crystal structure. Besides, the reaction mechanism of surface modification which was similar to the “acid-base neutralization” was proposed.

Keywords: magnesium sulfate whisker; surface modification; stearic acid

1 INTRODUCTION

Polymers have become more widely used in many fields, such as aerospace, electron and electricity, automobile manufacturing, architectural decoration, etc. However, most of polymers contain high carbon and hydrogen contents. Therefore, their poor flame retardancy restricts their practical applications in these fields. As a result, much attention has been paid to the flammability of polymer materials [1]. The most commonly-used method to control the flammability of materials is the addition of flame retardants, such as aluminum hydroxide (ATH), magnesium hydroxide (MH), magnesium oxy sulfate whisker (MOSw) and so on, to the polymer matrix, which are blended into polymer matrix to improve the flame retardancy [2].

MOSw is important inorganic flame-retarding filler which generally exists in the form of cocoon or sector aggregates. The individual magnesium oxy sulfate whisker shows a fibrous-like shape with the length of 10-100μm and diameter of 0.2-1μm. Initially, magnesium oxy sulfate (MOS) with amorphous form was prepared as a substitute for magnesium oxychloride cement since 1950s [3]. Temple C. prepared magnesium oxy sulfate cement and used it to reduce efflorescence in 1978. Furthermore, the crystal water of MOS creates water vapor at high temperatures, playing a role of fire retardant and smoke suppressant. Eills H. reported MOS as a composition of fire barrier coating on susceptible wood or plastic substrates, or other substances. The coating effectively prevents the ignition of and flame spread of fire on the coated substrate. By the 1990s, MOSw was first prepared by Ueno K. Outstanding mechanical properties are presented by MOSw, the same as other whiskers, for the inexistence of common defects in micron size [4]. In the last decades, MOSw has attracted much attention owning to easy preparation, low cost and advantages mentioned above. The application of MOSw is mainly
in polymer matrix composites. For example, Jiang Y. investigated the preparation and performances of MOSw/ABS and MOSw/PE composites [5, 6]. Nevertheless, as an inorganic filler, MOSw shows completely different compatibility with polymer matrix. On the other hand, the small dimensions of MOSw result in high surface free energy, leading to readily aggregation [7], which badly affects the performance of target composites. For brevity, the diametrically opposite polarity between hydrophilic MOSw and hydrophobic polymer seems to be the main barrier to the interfacial interaction [8]. Therefore, attempting to modify the surface properties of the MOSw is highly desirable for MOSw/polymer composites.

Surface modification is an effective pattern to ameliorate the interfacial compatibility [9, 10] between inorganic component and polymer matrix. Reports about surface modification of MOSw are mainly related to inorganic-organic, in-situ polymerization, emulsion polymerization technology and so on [11, 12]. For instance, the effect of nucleating agent (aromatic phosphoric acid) as a modifier on MOSw/polyolefin composites was investigated by Yamamoto S. The results showed the good compatibility of modified MOSw with polyolefin resin, which further improved the flexural modulus of elasticity and izod impact strength. Actually, fatty acids such as lauric acid and stearic acid are the most common modifiers of MOSw modification because of the low price and goodish effect. There are many papers about MOSw modified with fatty acids, for example, Han et al. discussed the effect of stearic acid, zinc stearate coating on the properties of synthetic hydromagnesite. The results showed that the surface of powders was changed from being hydrophilic to being lipophilic.

However, previous studies about surface modification of MOSw with fatty acids were mainly focused on the macro effect, seldom involved the reaction mechanism. Empirical procedures were taken without further exploration. Some papers published on the mechanism of fatty acid modified MOSw empirically as physical or chemical adsorption, esterification and so on [13, 14]. For example, Han Y. reported the modification of MOSw with sodium stearate. The results showed that the surface of whiskers was changed from being hydrophilic to being lipophilic, and both chemical and physical adsorptions were functioning sodium stearate and whiskers surface by FT-IR [15]. Cheng B. studied the surface modification of submicron spherical silica particles with butanedioic acid. FTIR and XPS results indicated that silica reacted with butanedioic acid by esterification [13]. In this paper, we prepared hydrophobic MOSw with stearic acid at first. A conventional coating/grafting surface might be formed after modification, which was considered to be monolayer and partial multilayer. The aim of this paper was to scrutinize the mechanism of this reaction, and several characterizations such as XPS, FT-IR were utilized. The results showed that chemical reaction rather than physical or chemical adsorption took place on the surface of MOSw since the emergence of COO-Mg< bonds, where Mg< denoted a surface magnesium site. For the sake of dynamic state approach, a pH meter was used to monitor the reaction process synchronously and the changes of pH and electrical potential values were used to analyze the intermediate process.

2 EXPERIMENTAL

2.1 Materials and synthesis

MOSw with a diameter of 0.5-1μm and a length of 10-50μm was obtained from a procedure described as follows: Magnesium sulfate and sodium hydroxide were mixed in aqueous solution by the molar ratio of 0.8/1, and then heated and vigorously stirred for several hours. Impurities were removed by the step of centrifuging and washing with plenty of water. The product was obtained after drying the solids that are left on the bottom. All other materials were commercially available and used as received unless otherwise noted.

2.2 Surface modification of MOSw

MOSw modified with several different stearic acid contents was prepared according to the two procedures described below.

2.2.1 Pretreatment of MOSw

The MOSw was dispersed in distilled water in the proportion of 1.00g to 50mL water, and then immersed in an ultrasonic bath at the power of 120W for 1h. Subsequently, the slurry of MOSw was obtained after 5h for magnetic stirring. All these operations were performed at room temperature.

2.2.2 Preparation of MOSw-SA

Stearic acid (1% to 9% weight fraction based on the MOSw) was dissolved in 95% ethanol solution (10mL). The stearic acid-ethanol solution was added into the slurry of MOSw which had been heated to 50-90°C with magnetic stirring for 0.5-2h. The product was cooled to room temperature, then filtered and washed with plenty of ethanol and distilled water to remove excessive fatty acid. The sample was collected and dried at 60°C in an oven for 12h.

2.3 Measurement

Water contact angle (WCA) instrument (DSA30, Kruss, Germany) was employed to determine the hydrophilicity of MOSw and MOSw-SA. Drops of deionized water (3μL) were deposited on six different spots of each surface. The values are averages of 6 measurements. Electrical potential and pH values were measured by a pH meter (PB-10, Sartorius, Germany).
About 30mL of reaction solution was respectively taken out hourly in the process of pretreatment of MOSw and once every 20 minutes in the process of preparation of MOSw-SA. The resulting supernatant was directly measured after centrifuged (9,000r/min for 2min). And the pH meter was calibrated before used.

2.4 Characterization

The morphology of MOSw and MOSw-SA was examined with a JSM-6701F field emission scanning electron microscope (FESEM) from JEOL using an acceleration voltage of 5.0kV. X-ray powder diffraction (XRD) pattern was determined by a Philips X’Pert X-ray spectrometer using Cu Ka radiation with a tube voltage of 40kV and a tube current of 35mA. X-ray photoelectron spectroscopy (XPS) measurement of MOSw and MOS-SA was carried out using PHI-5702 multifunction electron spectrometer (American Physical Electronics) equipped with an Al Kα X-ray source. The survey XPS spectra were taken at 100eV of constant analyzer energy mode with 0.4eV energy step size while high-resolution XPS spectra of Mg2p, C1s and O1s were taken at 29.35eV of constant analyzer energy and 0.125eV of energy step size. The samples were pressed into pellets with KBr and characterized on a Nicolet NEXUS2470 Fourier transform IR (FTIR) spectrometer (USA). Transition mode was used and the wave-number range was set from 4,000cm−1 to 400cm −1. A STA449F3 simultaneous thermal analyzer (German, Netzsch) was used under 5 ºC/min heating rate.

3 RESULTS AND DISCUSSION

3.1 Morphology of MOSw-SA

A fibrous morphology with a diameter of 100-200nm and a length of 10-20μm of MOSw is exhibited in Figure 1. The surface of MOSw is smooth and integrated (in the upper-right inset of Figure 1a). However, aggregation like cocoon-shape is obviously seen. MOSw-SA, by contrast, reveals much better dispersion. The upper-right inset of Figure 1b suggests the morphology of MOSw changes not obvious after modification. The straight edge of whiskers indicates that MOSw-SA maintains a high crystallinity level as that of MOSw. Their high-magnification SEM image showed that a thin layer was formed on the surface of MOSw-SA. Besides, the bottom-right inset of Figure 1a shows that contact angle of MOSw is 16°, which exhibits a hydrophilic character. While the contact angle of MOSw-SA (the bottom-right inset of Figure 1b) is 112°. The surface of MOSw was changed from being hydrophilic to being hydrophobic.

XRD patterns of MOSw and MOSw-SA also confirm this view (Figure 2). All these four patterns present uniform diffraction peaks at 2θ around 12°, 17°, 22°, 30° and 40°, assigned to (201), (202), (203), (111) and (114) crystal faces, respectively. Above all, we make sure that modification only occurs on the surface of MOSw without altering its crystal structure.

However, the intensity of these peaks decreases significantly with the increase of stearic acid content. This phenomenon can be well explained that a layer or layers of X-ray diffusing no-crystallizable stearic acid is covered on the surface of MOSw.

3.2 Surface chemical composition of MOSw-SA

Theoretically, modification of MOSw with stearic acid may be physical adsorption or chemical actions like chemical reaction and chemical adsorption. In light of the information provided by SEM and XRD, the varieties and states of different elements on the surface of MOSw-SA have been conducted in addition to XPS.

![Figure 1. SEM images of (a) MOSw and (b) 5wt% MOSw-SA.](image1)

![Figure 2. X-ray diffraction (XRD) patterns of (a) MOSw, (b) 1wt% MOSw-SA, (c) 5wt% MOSw-SA.](image2)
analysis. The full scan spectra and high-resolution C1s spectra of MOSw and 5wt% MOSw-SA are presented in Figure 3. Both MOSw and MOSw-SA show several main character peaks located at 984eV, 533eV, 285eV, 169eV and 50eV, which are assigned to O KLL, O1s, C1s, S2p and Mg2p signals, respectively. The appearance of C1s signal in Figure 3a is due to the surface contamination of organic chemicals during the transfer of MOSw to the vacuum chamber in a laboratory setting. The curve-fitting analysis of high-resolution C1s spectra of MOSw reveals the signal located at 284.8±0.1eV of C1 (C-C, C-H). However, there is a new signal appeared at 289.0±0.1eV for MOSw-SA after deconvolution. This signal is coded as C2 (O=C=O) and could be a powerful proof of modification.

Furthermore, the O/C and O/Mg ratios and the fraction of the decomposed C1s signal are summarized in Table 1. The O/C ratio of MOSw measured by XPS is 0.97 and 0.48 of MOSw-SA (see Table 1). The decrease in O/C ratio could be explained by the quite low O/C ratio of LA, only 0.13 theoretically. Yet O/Mg ratios increase from 1.58 to 1.80 after modification, since stearic acid (C18H36O2) contains O element without Mg element. It must be said, though, that the theoretical value of O/Mg ratio reaches to 2.67. The difference between theoretical and experimental values is probably due to the substitution of O atoms by the impurities. The fraction of C2 (O-C=O) peak increases from 0 to 6.10% after modification, but still is less than the theoretical value of stearic acid, which is due to the presence of alkyl groups of impurities. Otherwise, we could not consider the chemical actions from the XPS data, because the Mg-O bonds, even though different O atoms actually, always existed before and after modification. This technique can be only used to identify the composition of COO- group on the surface of MOSw-SA, but not distinguish between physisorbed stearic acid (COO-H) and products of chemical actions (COO-Mg or COO-Mg<).

Table 1. The O/C and O/Mg ratios and the fraction of the decomposed C1s signal for MOSw, MOSw-LA and lauric acid.

<table>
<thead>
<tr>
<th>Samples</th>
<th>O/C</th>
<th>O/Mg</th>
<th>Bending energy (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOSw</td>
<td>0.97</td>
<td>1.58</td>
<td>100</td>
</tr>
<tr>
<td>MOSw-SA</td>
<td>0.48</td>
<td>1.80</td>
<td>93.87 6.10</td>
</tr>
<tr>
<td>SA</td>
<td>0.13</td>
<td>-</td>
<td>94.44 5.56</td>
</tr>
</tbody>
</table>

Notes: 1 the surface contamination of organic chemicals during the transfer of MOSw to the vacuum chamber in a laboratory setting; 2 the theoretical values

3.3 Surface chemical composition of MOSw-SA

There are no conclusive evidences received from above whether the form of modification being physical absorption or chemical actions. The difference of these two kinds of actions should be told from the IR spectra. As seen in Figure 4, all the reaction products are thoroughly washed before analyzed. The mainly strong peaks in Figure 4a are respectively multiple peaks in 3,600cm⁻¹ region and single strong peak in 1,119cm⁻¹ region. The former is attributed to the stretching vibration of hydroxyl groups and the latter is assigned to the stretching vibration of SO₄²⁻. The weak peak in 1,638cm⁻¹ is assigned to the bending vibration of hydroxyl groups of crystal water. For MOSw-SA, there are four extra peaks appeared and respectively located at 3,170cm⁻¹, 2,923cm⁻¹, 2,852cm⁻¹ and 1,420cm⁻¹. Alkyl groups are confirmed by the absorption peaks at 2,923cm⁻¹ and 2,852cm⁻¹.

Figure 3. XPS spectra of (a) MOSw, (b) MOSw-LA and high-resolution spectra of C1s peak: (c) MOSw and (d) MOSw-SA.
corresponding due to CH$_2$ asymmetric and symmetric vibration. The broad moderate peak in 3,170 cm$^{-1}$ region is attributed to stretching vibration of intermolecular hydrogen bonding of O-H. Carboxyl groups are confirmed by the absorption peaks at 1,700 cm$^{-1}$ due to C=O stretching vibration (Figure 4c). Additionally, the weak peak at 931 cm$^{-1}$ is assigned to the out-of-plane bending vibration of O-H in carboxyl groups. For magnesium laureate, the strong peak in 1,700 cm$^{-1}$ is scarcely observed in Figure 4d, which indicates no free stearic acid on the surface after modification. Instead, several medium peaks located at 1,541 cm$^{-1}$, 1,472 cm$^{-1}$ and 1,427 cm$^{-1}$ (Figure 4d), which are respectively attributed to the asymmetric and symmetric stretching vibration of COO-group. The value of $\nu$(COO$^{-}$)-$\nu$(COO$^{-}$) is less than 164 cm$^{-1}$ that for the corresponding fatty acid salts as expected for the bidentate bridging mode of the carboxylate ligation.

As to MOSw-SA, there is a medium peak located at 1,421 cm$^{-1}$ and no peak in 1,700 cm$^{-1}$, which indicates the existence of COO-group on the surface of MOSw-SA. Hence, we confirm that chemical actions, including chemical reactions and chemical adsorption, rather than physical adsorption take place in the process of modification.

**Figure 4.** FT-IR spectra for: (a) MOSw, (b) 5wt% MOSw-SA, (c) stearic acid and (d) magnesium stearic.

With the hypothesis of chemical reactions, there are two different situations: Physisorbed SA-Mg, which is the product of the reaction of stearic acid and ionized Mg$^{2+}$, and stearic acid -Mg$^{2+}$ (SA-Mg$^{2+}$), where Mg$^{2+}$ denotes a surface magnesium site. In order to distinguish these two situations particularly, we employed thermogravimetric analyses as the most suitable characterization method. Set 5wt% magnesium stearic acid mechanically mixed with pure MOSw as the reference substance. As can be seen in Figure 5a, the significant endothermic peaks at 100-200°C are corresponded to the decomposition of stearic acid magnesium. With the increase of temperature, SA-Mg shows transitions from the crystalline to smectic (105°C), the smectic to nematic (175°C) and finally the nematic to liquid phase (195°C) in the DSC traces. However, the DSC curves of MOSw-SA and MOSw (Figures 5b and 5c) both show completely different traces with mechanically mixed MOSw/stearic acid magnesium (Figure 5a). It confirms that no physisorbed SA-Mg occurs on the surface of MOSw-SA. Hence, the chemical reaction should occur between stearic acid and Mg$^{2+}$ on the surface of MOSw.

**Figure 5.** DSC of (a) 5wt% stearic acid magnesium mechanically mixed with pure MOSw, (b) 5wt% MOSw-SA and (c) MOSw.

### 3.4 Proposed the reaction mechanism of surface modification of MOSw with stearic acid

The exact structure of MOSw is established based on literatures and XRD results (Figure 2). It is mainly built by Mg(OH)-6 in the infinite triple chains at b-axis (Scheme 1). In addition, water molecules and sulfate tetrahedrons are intercalated in the crystal packing. The occupancies of water molecules and sulfate tetrahedrons should be statistically as 1:2. The solid lines represent bonds to oxygen atoms above the plane of the magnesium atoms, the dotted lines represent bond to oxygen atoms below the plane.

In order to further investigate the dynamic state of this reaction, a pH meter is used to monitor the reaction process synchronously. Figure 6 shows the variation tendency of pH and electrical potential values. In the process of pretreatment, pH values of MOSw slurry almost invariably change, but remain alkalescence all the time. There should be some ionized OH- on the surface of MOSw after ultraphonic, stirring and heating procedure (Equation 1). While the stearic acid-ethanol solution is slightly acidic with the pH of 4.51 (Equation 2), the reaction between MOSw and stearic acid should occurs like “acid-base neutralization” (Equation 3). The formation of COO-Mg$^{2+}$ bonds is similar to SA-Mg, a single step with one water molecule being lost. After 1h modification, the pH of reaction solution reduces to minimum (10.11), and then increases slightly with reaction time prolonged. Scheme 1 shows the details of surface modification. Most of these weak interactions are disrupted
after being washed with plenty of ethanol and distilled water. The exterior alkyl groups lead to the hydrophobic changes of the surface of MOSw (Scheme S1).

**Scheme 1.** Representation of the connectivity of the magnesium octahedra in the infinite triple chains build by Mg(OH)-6 and proposed reaction between MOSw surface and stearic acid.

\[
\begin{align*}
\text{Mg(OH)}_2-0.2\text{MgSO}_4-0.4\text{H}_2\text{O}(s) + \text{H}_2\text{O} &\rightarrow [\text{Mg(OH)}_2-0.2\text{MgSO}_4-0.4\text{H}_2\text{O}(aq)] + m\text{C}_{11}\text{H}_{23}\text{C}-(aq) \\
&\text{heating} \\
&\text{stirring} \\
&\text{mC}_{11}\text{H}_{23}\text{C}^{-}\text{mC}^- &\text{Mg(OH)}_2-0.2\text{MgSO}_4-0.4\text{H}_2\text{O}(s)
\end{align*}
\]

4 CONCLUSIONS

MOSw-SA was prepared by a facile chemical method. The MOSw-SA shows great hydrophobic with the contact angle of 112° (maximum value) when the modification conditions are taken in 5wt% of stearic acid, 70°C and 60min. There are no obvious changes of the morphology and crystalline degree of MOSw after modification, and the only one to be certain is the presence of COO- group on the surface of MOSw-SA. We believe that the type of this modification is chemical reaction between stearic acid and Mg< based on the results of FT-IR and DSC. The dynamic state approach monitored by a pH meter reveals the change of c(H+) (or c(OH-)) in reaction process. To put it simply, MOSw forms several ionized OH- after ultraphonic, stirring and heating procedure. The stearic acid-ethanol solution is only slightly acidic (pH=4.51) since a small number of H+ ions from stearic acid. When the stearic acid-ethanol solution is added in the MOSw slurry, a reaction which is similar to the “acid-base neutralization” occurs on the surface of MOSw. It is worth noting that this reaction is different to the esterification, which is the conventional interpretation of surface modification. The proposed mechanism is not just for MOSw modified with stearic acid, surface modification of substrates containing OH- with fatty acids is also applied. This research provides a detailed explanation for a series of surface modification, which may be further used in the performance of whisker/polymer matrix composites.

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