Study on Interaction between Aluminum Hydroxide and Vinyltriethoxy Silane by Gas Chromatography-Mass Spectrometry

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Abstract. The main aim of this work is to investigate the volatile products and their concentrations from reaction of aluminum hydroxide (ATH) and vinyltriethoxy silane (VTES) decane. The upper solution of the reactants was abstracted and charred by gas chromatography-mass spectrometry (GC-MS), and the interactions between ATH and VTES can be proved by the GC-MS product. In this result, the possible mechanism of VTES and ATH was proposed. Surface water on aluminum hydroxide (ATH) was proved to contribute to the hydrolysis of VTES.

1. Introduction
Aluminum hydroxide (ATH) is widely used in the cable industry as a flame retardant additive. Owing to its strong polarity, ATH aggregates easily and has poor dispersion in polymer matrix, which lead to decreased performance.

Improved interfacial interactions of hydrophilic ATH with hydrophobic polymers and an effective coupling are key parameters for better compound properties. So coupling agents silanes are widely used to modify the particle surface and improve the interaction between filler and polymer matrix. Many studied have shown that silanes not only gained positive effects for enhancing dispersion of inorganic fillers but also improved the mechanical and flame retardant of the polymer significantly [1]. Methods for surface modification of inorganic fillers with silane are usually divided into three classes: on-line modification, dry and wet process [2]. The ultrafine fillers can be obtained fast by on-line modification [3-4]. In the case of wet process, extensive research and related modification mechanism have been reported [5]. Luo et al [6]. Modified magnesium hydroxide (MH) through silanization reaction with γ-aminopropyltriethoxysilane (γ-APS) as coupling agent in aqueous solution and found that γ-APS hydrolysis and condensation are activated in alkaline solution, facilitating multilayer adsorption of γ-APS molecules on the surface of MH. Ren et al [7]. Modified aluminum hydroxide (ATH) with KH-792 as silane in ethanol solution and investigated by x-ray photoelectron spectroscopy (XPS) and found that the siloxane group of KH-792 coupling agents can be bonded chemically on ATH surface.
Dry process attracted more attention due to its simplicity and easily industrialized advantages. However, the details of the interaction between filler and silane in the case of dry process remain still unclear. Lan et al [1]. Modified MH with vinyltriethoxysilane (VTES) by dry process and studied the interfacial interaction between MH and VTES. The results showed that VTES molecule bound to the surface of MH.

In this study, the interaction of ATH and VTEO silane was studied with the help of GC-MS, possible reaction mechanisms of VTES silane and ATH is also proposed.

2. Experimental

2.1. Materials
EVM (Ethylene vinyl acetate copolymers) was supplied by ARLANXEO with the trade name Levapren 700 PXL with Mooney viscosity 60 at 100°C, Germany. Aflux 18 (primary fatty amine) used as anti-stick agent was obtained from Rhein Chemie. Paraffinic wax as grade LSB 20 was purchased from Pinsheng Chemicals Co. (Shanghai). Antioxidant Vulcanox HS/LG (2, 2, 4-trimethyl-1, 2-dihydroquinoline) was from Lanxess. Perkadox 14- 40B-pd (Di (ter-butylperoxyisopropyl) benzene) was from AkzoNobel, and the coagent Rhenofit TRIM (70% trimethylolpropane trimethacrylate, 30%silica) was obtained from Rhein Chemie. Flame Retardant ATH (Aluminum hydroxide) was obtained from Nabaltec as grades Apyral 200SM (untreated), with an average particle size (D50) of 0.4 μm and a BET surface of 15 m2/g. Silane-coupling agent VTES (vinyltriethoxysilane, boiling point is 160 to 161°C) was supplied by Degussa, n-Decane (99%, boiling point is 173.8 to 174.4°C) was obtained from Alfa Aesar. Ethanol was purchased from Sigma-Aldrich Chemie GmbH (boiling point is 78.3°C).

2.2. Preparation of ATH / VTES samples
VTES silane was added into ATH at a ratio of 0.03g to 0.135g : 5g by wt (equivalent to 1 to 4.5 phr in a compound with 160 phr ATH), then dispersed in 15g decane in a sealed container, without stirring or shaking. The decane served as a low viscosity matrix instead of a polymer to facilitate the subsequent analysis. The dispersion kept for 1 hour at room temperature or at 120°C which would be a typical mixing temperature in internal mixer. The trials were carried out in a closed glass vessel with pressure valve. Once the pressure is out of range, the valve will open. After that, the sample was rest for 30mins. The upper clear solution was then taken into the closed vessel for GC with the fixed during heating program and detected by MS. In this work, the effects of various ratios of VTES silane to ATH were studied.

2.3. Compounding
The formulation for EVM/ATH composites is shown in Table 3. VTES was added into ATH before mixing. After that, EVM was mixed with silane-treated ATH on a two-roll mill. Then Aflux 18, paraffinic wax, TMQ was successively added within 2 min, peroxide Luperox F40 and coagent TRIM was added for an additional 2 min. Fianlly, and the mixture was compounded for additional 4 min.

2.4. Analysis
A TGA from TA Instrument, Q500, was used for thermogravimetric analysis. All thermal degradation experiments were done under nitrogen purge. A heating rate of 10K/min from 30°C to 600°C was used for all experiments. A Thermo Quest Trace GC 200 Gas Chromatograph coupled with the Thermo Finnigan Trace DSQ. Separation of the products in the evolved gases was obtained by using ZB Wax. The injection port of the GC was set at 250°C. The GC column was programmed from 60 °C (3 min) with a heating rate of 5°C/min to 120 °C and then a heating rate of 15 °C/min to 280 C. The energy of 70 eV was used for electron ionization. Helium was used as a carrier gas for all the GC–MS experiments. The maximum molecular weight that can be detected by this GC–MS instrument is approximately 550 Da.
3. Results and discussion

3.1. Thermal analysis of ATH

The TGA thermograms from ATH in nitrogen is shown in Fig. 1. ATH began to lose weight at 123°C, before 180°C, weight loss is 0.8% which is considered as the loss of ATH surface water. This is consistent with the moisture content of this ATH grade [8]. The derivative of weight loss reached its maximum 262°C. The weight loss between 180°C to 300°C is 28.6%. The char left at 600°C is 65.9%. ATH thermolysis was studied by Z.S.Gu [9] and summarized as reactions below, In the first stage of dehydration, a small amount of gibbsite is converted to boehmite (AlO (OH)), in the second stage of dehydration, residual gibbsite (Al (OH)3) decompose into an amorphous phase Al2O3. In the third stage of dehydration, all boehmite decompose into γ- Al2O3.

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} & \xrightarrow{198-280^\circ\text{C}} (\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})_3 \cdot (\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})_3 + 0.5\text{H}_2\text{O} \\
(\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})_3 & \xrightarrow{280-420^\circ\text{C}} (\text{Al}_2\text{O}_3)_3 \cdot (\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})_3 + 2\text{H}_2\text{O} \\
(\text{Al}_2\text{O}_3)_3 & \xrightarrow{420-570^\circ\text{C}} 3\text{Al}_2\text{O}_3 + 0.5\text{H}_2\text{O}
\end{align*}
\]

Therefore, it is considered that ATH did not start to dehydrate when the sample was kept at 120°C in this study.

![Figure 1. TGA thermogram from the decomposition of ATH in nitrogen.](image)

3.2. Qualitative analysis of hydrolysis of silane in the presence of ATH

Gas chromatography-mass spectrometry is the technique to detect simultaneously the presence of decomposition products qualitatively and quantitatively [10]. The number of peaks shown in the total ion chromatogram (TIC) represents the number of compounds detected by GC–MS. The relative intensity of each peak corresponds to the relative concentration of each compound [11]. In addition to library matching, representative species were provided according to the retention time. As a control experiment a total ion chromatogram from the upper solution of liquid mixture of VTES and decane (stored at 120°C-125°C, mass ratio of VTES to decane is 0.03g: 15g) is shown in Fig.2. The products are a direct result of the decomposition and recombination of decane during heating. All the products were identified by MS and categorized as follows: C9H20, decane isomers C10H22 (traces), n-decane C10H22, C10H20 (traces), Methyl-propyl-cyclohexan, Butyl-cyclohexan, Undecane, Ethylenyl-triethoxy silane, C12H24 respectively. As expected, neither hydrolysis products ethanol nor VTES dimer were found in VTES / Decane (mass ratio is 0.03g: 15g) when samples stores at 120°C-125°C for 1 hour or at room temperature.
Next, the experiments were conducted in the presence of ATH. The results showed all the products detected from the upper solution in VTES / ATH / Decane mixture (mass ratio is: 0.03g/5g/15g, prepared at room temperature) are the same with the ones in VTES / Decane samples except ethanol. The abundance of Ethyenyl-triethoxy-silane decreased obviously comparing to the one in VTES / Decane sample.

It is observed that ethanol was detected at 3.3min in the presence of ATH, which is the only difference between VTES / ATH / Decane and VTES / Decane samples.

Modification mechanism of silane coupling agent on inorganic filler surface by wet process is depicted in Fig.2 [5, 12]. First, the silane monomer are hydrol yzed in the presence of water and yield silanol groups, then self-condensation of silanol groups takes place. The remaining silanol groups are physically adsorbed to the hydroxyl groups of inorganic fillers through hydrogen bonds. Under heating, the hydrogen bonds can be converted to covalent bonds and free water was formed [5].

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\begin{align*}
\text{Si} & \quad \text{X} \quad \text{X} \\
\text{R} & + 3\text{H}_2\text{O} \quad \text{Hydrolysis} \quad \Rightarrow \quad \text{Si} & \quad \text{OH} \quad \text{OH} \\
& \quad \text{R} & \quad \text{OH} \quad + 3\text{HX} \\
\text{3} & \quad \text{Si} & \quad \text{R} & \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
& \quad \text{Condensation} \quad \Rightarrow \quad \text{Si} & \quad \text{R} & \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
& \quad \quad \quad + 2\text{H}_2\text{O} \\
\end{align*}
\]

**Figure 2.** Reaction mechanism of silane coupling agent on inorganic filler surface by wet process

In the present of 0.8% surface water on ATH (5g) powder, it is considered that VTES will hydrolysis and liberate ethanol. However, the amount of surface water is 0.04g (0.8% × 5g) in the ATH / VTES / Decane sample, it is uncertain whether ethanol is produced from VTES hydrolysis or from the reaction between Si-OC\textsubscript{2}H\textsubscript{5} groups of VTES with hydroxyl groups of ATH. In order to figure out this clearly, the ways of ethanol produced will be discussed in the next.

3.3. Effect of ATH surface water

In order to figure out the effect of ATH surface water on the ethanol produced, ATH was dried at 100°C for 3.5h in a vacuum oven. ATH / VTES / Decane mixture (mass ratio is: 5g/0.03g/15g) was prepared at 120°C. Ethanol concentration comparison was shown in Tab. 1. It is showed that the amount of ethanol decreased slightly from 0.15mg/ml to 0.12mg/ml after ATH drying.

| Table 1. Ethanol concentration tested by GCMS in ATH / VTES / Decane |
|-------------------------|------------------------|
| Ethanol, mg/ml          | ATH without drying     | ATH after drying  |
|                         | 0.15                   | 0.12              |
Although absorbed water on the surface of ATH had been removed by drying, the hydrolysis reaction still had been observed. And 120℃ is far below the decomposition temperature of ATH. Thus, it is proved that Si-OC₂H₅ group of VTES reacted with hydroxyl groups of ATH.

The reaction mechanism of VTES with the Magnesium hydroxide (MH) in dry process was proposed in Fig.3 [5], in which it is considered that Si-OC₂H₅ of VTES reacted with hydroxyl groups of MH and liberate ethanol. Covalent chemical bonds (Si-O-Mg) were formed [13,14]. It is much easier for Si-OC₂H₅ of VTES to react directly with hydroxyl groups of MH than hydrolyzing to yield Si-OH first before reacted with hydroxyl groups of MH in the thermodynamics.

![Figure 3. Action mechanism of VTES on MH surface by dry process](image)

### 3.4. Reaction mechanism of VTES silane and ATH

ATH was dried at 100℃ for 3.5h in a vacuum oven, all reactions were carried out at 120℃ for 1 hour. The VTES concentration was varied from 0.62 to 2.8% per ATH (equivalent to 1 to 4.5 phr in a compound with 160 phr ATH).

Fig.4 showed that ethanol concentration increased from 0.15 mg/ml to 0.62 mg/ml with the increasing of VTES/ATH wt% from 0.62% to 0.94%. When the VTES/ATH wt% changes from 0.94% to 2.5%, we can see that ethanol concentration increased slightly and centred around 0.6-0.7 mg/ml. This indicate that VTES amount has slight influence on the ethanol generation. Which may indicate the reaction of VTES with ATH is almost complete. While VTES/ATH wt% increases to 2.8%, it is found that the ethanol amount is up to 1mg/ml.

Fig.5 shows the relationship between consumed VTES and the actual ethanol produced in terms of mmol/ml of ATH and VTES reaction. The line in circle is the assumption that each VTES silane molecule produce one ethanol molecule. The line in square is the experimental relationship between reacted VTES and ethanol generated with hydroxyl group of ATH sample. The result indicated that approximately one VTES silane molecule has reacted one hydroxyl of ATH.

In this study, ethanol is produced mainly from the reaction of VTES and ATH, only a small part is from VTES hydrolysis.
4. Conclusion
Using GCMS, the production of ethanol is obtained. It showed that VTES has reacted with ATH. Quantitative analysis shows that one silane molecular react with one hydroxyl group from ATH. These finding shows that VTES is forming covalent bonds with ATH particles.

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