

## Effects of silica on the morphology, structure, and properties of thermoplastic cassava starch/poly(vinyl alcohol) blends

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**ABSTRACT:** Thermoplastic cassava starch (TPS)/poly(vinyl alcohol) (PVA)/silica (SiO<sub>2</sub>) composites were prepared by a melt-mixing method. The effects of the content and surface properties of SiO<sub>2</sub> on the processing, mechanical properties, thermal stability, morphology, and structure of the TPS/PVA/SiO<sub>2</sub> composites were investigated. With increasing SiO<sub>2</sub> content, the plasticizing times of the TPS/PVA/SiO<sub>2</sub> composites were shortened. After the SiO<sub>2</sub> surface was treated with a silane coupling agent (KH550), the plasticizing times of the TPS/PVA/SiO<sub>2</sub> composites decreased significantly. The tensile strength, elongation at break, and Young's modulus of the TPS/PVA/SiO<sub>2</sub> composites increased. The mechanical properties of the TPS/PVA/SiO<sub>2</sub> composites containing treated SiO<sub>2</sub> were higher than those with untreated SiO<sub>2</sub>. The thermal decomposition temperatures of the TPS/PVA/SiO<sub>2</sub> composites were improved with the addition of SiO<sub>2</sub>. The presence of inorganic fillers was beneficial to the improvement of the thermal stability of the polymers. The reaction between the treated SiO<sub>2</sub> and the starch molecules was beneficial to the formation of more stable structures. The treated SiO<sub>2</sub> indicated good interfacial adhesion and uniform dispersion in the matrix. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44020.

**KEYWORDS:** composites; nanoparticles; nanowires and nanocrystals; plasticizer

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### INTRODUCTION

In recent decades, with the exhaustion of oil resources and the environmental problems caused by petroleum-based plastics, the search for substitutes for petroleum resources has been a hot research topic in the field of plastic production. Therefore, the development of renewable and environmentally friendly polymers has become a great subject and has triggered interest. Starch as an important natural polymer material has renewable, biodegradable, and environmentally friendly properties, and this has garnered the interest of many researchers.<sup>1–3</sup> Starch has been widely applied in the fields of packaging, papermaking, spinning, food, and medicine because of its advantages; these advantages include a good hydrophilicity, biocompatibility, and biodegradability.<sup>4</sup> However, starch cannot undergo thermoplastic processing because of the many intermolecular and intramolecular hydrogen bonds in its macromolecules; these restrain the movement of molecular chains by the strong interaction forces. Therefore, plasticizers, such as glycerol, water, formamide, and urea, have usually been used to weaken the hydrogen bonds of starch molecules and improve the processing properties of starch.<sup>5</sup>

In addition to the processing properties of starch, the enhancement of the mechanical properties and water resistance of starch have attracted a large amount of attention. Poly(vinyl alcohol) (PVA) is

also a kind of biodegradable material, and it has excellent membranous and emulsification properties.<sup>6,7</sup> Moreover, PVA has a good compatibility with starch; thus, PVA has been applied to improve the mechanical properties and water resistance of starch through changes in the ratios of starch/PVA blends and the molecular weight and alcoholysis degree of PVA.<sup>8–10</sup> It has been reported<sup>11,12</sup> that when the ratio of starch and PVA was 60/40, thermoplastic cassava starch (TPS)/PVA blends had good mechanical and waterproof properties. The reason was that interpenetration, entanglement, and crosslinking structures likely formed between the starch and PVA molecules. Sreekumar *et al.*<sup>13</sup> used glycerol as a plasticizer, and the optimal content of glycerol was determined in the plasticization of starch/PVA blends. The incorporation of inorganic fillers, such as nanosilica (nano-SiO<sub>2</sub>), nanoclays, titanium dioxide (TiO<sub>2</sub>), and carbon nanotubes could play important roles in improving the properties of polymers.<sup>14–19</sup> Tang *et al.*<sup>14</sup> reported that there were increases in the tensile strength and water resistance of starch/PVA composites with the addition of nano-SiO<sub>2</sub>. Xiong *et al.*<sup>19</sup> found that silica (SiO<sub>2</sub>) not only improved the mechanical properties but also reduced the water absorption of starch/PVA blends. Lou *et al.*<sup>20</sup> investigated the effect of nano-TiO<sub>2</sub> on the mechanical properties of PVA, and the mechanical properties of the composites were enhanced. Sreekumar *et al.*<sup>18</sup> studied the tensile properties and

**Table I.** Formulations of the TPS/PVA/SiO<sub>2</sub> Composites

Sample code	TPS (phr)	PVA (phr)	SiO <sub>2</sub> (phr)	Glycerol (phr)
TPVS-0	60	40	0	40
TPVS-2	60	40	2	40
TPVS-5	60	40	5	40
TPVS-7	60	40	7	40

thermal stability of starch/PVA/nano-TiO<sub>2</sub> composites and found that the compatibility of starch and PVA could be controlled by nano-TiO<sub>2</sub>. Jose *et al.*<sup>21</sup> reported that the mechanical properties and compatibility of starch/PVA blends were enhanced by the addition of carbon nanotubes.

Although there have been some studies on starch/PVA/SiO<sub>2</sub> composites,<sup>5,19,22</sup> the effect of nano-SiO<sub>2</sub> surface characteristics on the structure and properties of starch/PVA blends needs further investigation. The surface characteristics of SiO<sub>2</sub> play an important role in the dispersion of SiO<sub>2</sub> and the interaction between SiO<sub>2</sub> and the matrix; this affects the properties and structures of starch/PVA/SiO<sub>2</sub> composites. Therefore, in this study, the effects of the surface characteristics and content of SiO<sub>2</sub> on the plasticizing process, structure, mechanical properties, and thermal stability of TPS/PVA blends were investigated. The dispersion of SiO<sub>2</sub> and the reaction between SiO<sub>2</sub> and the starch molecules were analyzed to explore the relationship between the surface characteristics of SiO<sub>2</sub> and the properties and structures of the TPS/PVA/SiO<sub>2</sub> composites.

## EXPERIMENTAL

### Materials

Cassava starch (amylose content = 17.2%, moisture content = 13.0%) was provided by Guangxi State Farms Mingyang Biochemical Co., Ltd. PVA (1799) was bought from Guizhou Crystal Organic Co., Ltd. SiO<sub>2</sub>, with a particle size of 200 nm, was procured from Shengzhen Jingcai Chemical Co., Ltd. Glycerol (analytical reagent) and alcohol (analytical reagent) were purchased from Chinasun Specialty Products Co., Ltd. The silane coupling agent (KH550) was obtained from Shanghai Yaohua Brand Chemical Co.

### Sample Preparation

In the treatment of the SiO<sub>2</sub> surface, the silane coupling agent (2 wt % SiO<sub>2</sub>) was prepared in a 10% concentration of ethanol solution. The distilled water was gradually dropped into the solution, and we let the silane hydrolyze for 30 min.<sup>23,24</sup> Then, SiO<sub>2</sub> was added to the solution, and it was mixed at 25 °C at a speed of 1000 rpm for 3 min in a high-speed mixer (Tianjin Test Instrument Co., Ltd.). After that, SiO<sub>2</sub> was repeatedly washed by absolute ethanol and filtered to remove the unreacted coupling agent. The treated SiO<sub>2</sub> was dried in a vacuum oven at a temperature of 35 °C for 2 h.

The TPS/PVA/SiO<sub>2</sub> composites were prepared with the melt-mixing method, and glycerol was used as a plasticizer. The cassava starch, PVA, SiO<sub>2</sub>, and glycerol were weighed according to Table I and then preliminarily mixed in a high-speed mixer (Tianjin Test Instrument Co., Ltd.) at 25 °C at a speed of 1000 rpm for 5 min. The mixtures were stored in a sealed plastic bag

at room temperature for 24 h to allow the starch to be fully swelled by glycerol. After that, the mixtures were melt-mixed in a rheometer (RM-200A, Harbin Hapro Electric Technology Co., Ltd.) at 140 °C at a speed of 45 rpm for 6 min. The composites were compressed into 2 mm thick plates with a compression-molding instrument (XLB-D-400\*400) at 160 °C at a pressure of 14 MPa for 15 min.

### Processing Properties

The processing properties of the TPS/PVA/SiO<sub>2</sub> composites were determined by a torque rheometer (RM-200A, Harbin Hapro Electric Technology Co., Ltd.); the experimental conditions were described previously. During this period, the mixing time and torque values of the composites were recorded.

### Fourier Transform Infrared (FTIR) Spectroscopic Analysis

FTIR spectra were obtained with an FTIR spectrometer (IS10, Thermo Scientific) with the averaging of 32 scans ranging from 500 to 4500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

### Mechanical Properties

The mechanical properties were determined with a universal testing machine (XWW-20, Chengde Jinjian Testing Instrument Co., Ltd.) according to GB/T1040-2006. The samples were cut into dumbbell-shaped specimens with dimensions of 115 × 6 × 2 mm<sup>3</sup>. The tensile speed was 50 mm/min, and the test temperature was 25 °C. Each composition was tested with at least five specimens, and the average values were calculated.

### Thermal Analysis

The thermal decomposition was tested with a thermogravimetric (TG) analyzer (Discovery, TA Instruments). A sample weighing approximately 7 mg was heated from 40 to 700 °C at a 20 °C/min heating rate in an ultrapure nitrogen atmosphere with a flow rate of 25 mL/min.

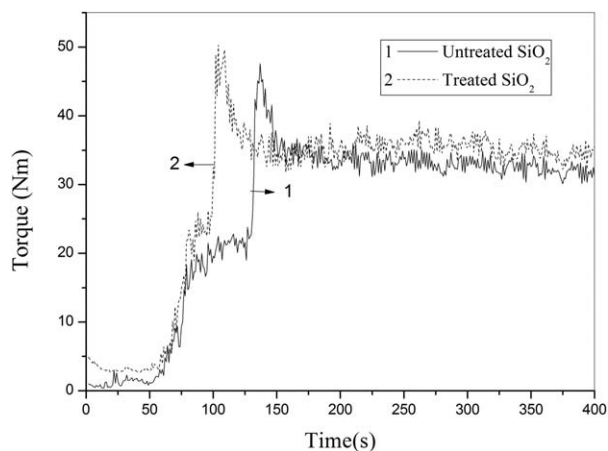
### Scanning Electron Microscopy (SEM) Analysis

The fractured surfaces of the composites were characterized by SEM in an EVO18 microscope (Carl Zeiss) with a tungsten filament operating at 10 kV. The samples were fractured with liquid nitrogen, and the cross sections were coated with gold to make the fractured surfaces conductive for better observation.

## RESULTS AND DISCUSSION

### Processing Properties

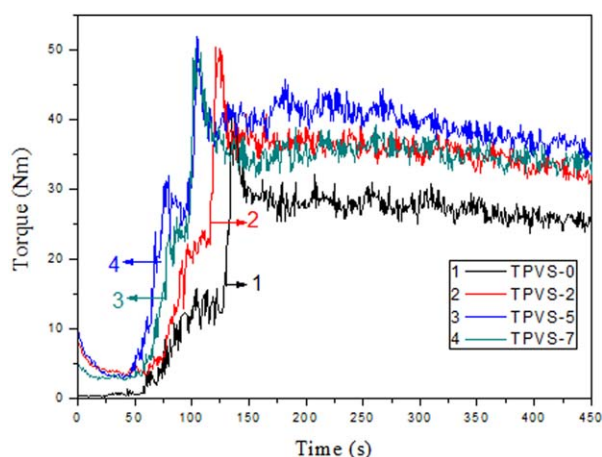
The effects of the untreated and treated SiO<sub>2</sub> on the processing curves of the TPS/PVA/SiO<sub>2</sub> composites are shown in Figure 1. The plasticizing time and torque were obtained from the processing curves. The plasticization of starch was related to the movement of starch molecules, which was affected by the hydrogen bonds and free volume of the starch molecules. The *plasticizing time* refers to the time that the starch molecules began the plastic flow after the hydrogen bonds of the starch molecular chains were interrupted. Therefore, the plasticizing time reflected the rate of the plasticizing process of the materials. The *plasticizing torque* refers to the state of the materials after the completion of the plasticization; it reflects the viscosity and structure of the materials. As shown in Figure 1, the plasticizing time of TPS/PVA containing the treated SiO<sub>2</sub> was shorter than that of the untreated SiO<sub>2</sub>. The plasticization of starch was



**Figure 1.** Effects of the untreated and treated  $\text{SiO}_2$  on the processing curves of the 60/40/7 TPS/PVA/ $\text{SiO}_2$  composite.

related to the free volume of the starch molecules, which was greatly influenced by the addition of  $\text{SiO}_2$ . The effects of inorganic fillers on the free volumes of polymers have been investigated by many researchers. Zhang *et al.*<sup>25</sup> investigated the effects of rectorite platelets on the distribution of the free-volume hole size in epoxy/rectorite nanocomposites and found that the organic rectorite plays the role of the skeleton, and the free volume of the composite material was larger than that of the epoxy resin.

After the  $\text{SiO}_2$  surface was treated by the silane coupling agent,  $\text{SiO}_2$  disrupted the hydrogen bonds of the starch molecules and created a larger free volume of starch; this increased the mobility of the starch molecules and was beneficial to the enhancement of the plasticizing process.<sup>26–28</sup> In addition, the plasticizing torque of TPS/PVA containing the treated  $\text{SiO}_2$  was higher than that of TPS/PVA containing untreated  $\text{SiO}_2$ . This was attributed to the formation of more stable structures between the treated  $\text{SiO}_2$  and starch molecules and is discussed in a later section.



**Figure 2.** Effect of the treated  $\text{SiO}_2$  content on the processing curves of the TPS/PVA/ $\text{SiO}_2$  composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

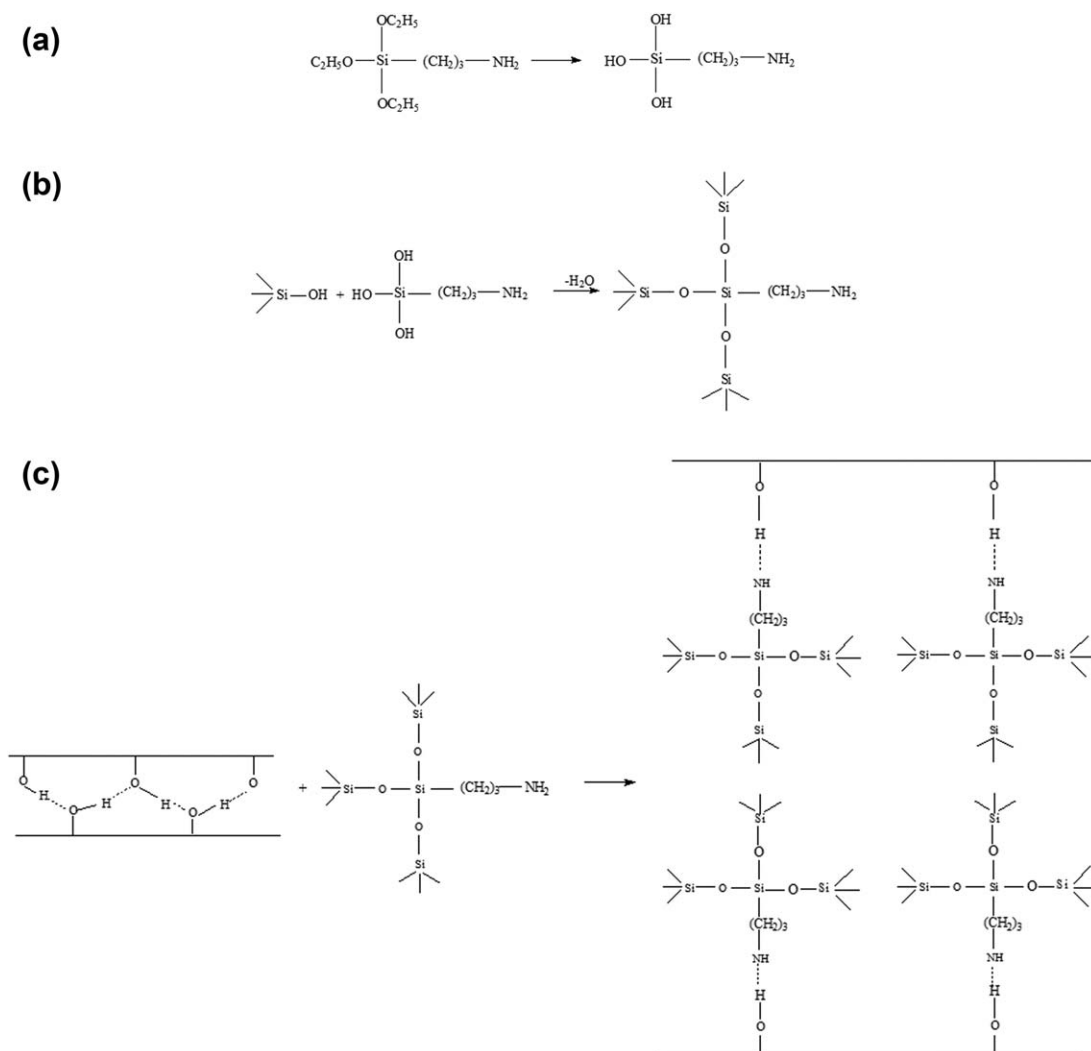
**Table II.** Plasticizing Time, Plasticizing Torque, and Balance Torque Values of the TPS/PVA-Treated  $\text{SiO}_2$  Composites in Mixing Processing

Sample code	Plasticizing time (s)	Plasticizing torque (N m)	Balance torque (N m)
TPVS-0	135	41.1	26.6
TPVS-2	125	50.4	35.7
TPVS-5	105	52.0	40.3
TPVS-7	103	50.3	36.1

The effects of the  $\text{SiO}_2$  content on the processing of the TPS/PVA blends are shown in Figure 2. The plasticizing peaks of all of the composites were noticeable; this indicated that the TPS/PVA/ $\text{SiO}_2$  composites were plasticized. The plasticizing time and torque of the TPS/PVA/ $\text{SiO}_2$  composites are listed in Table II. With increasing  $\text{SiO}_2$  content, the plasticizing time of the TPS/PVA/ $\text{SiO}_2$  composites was shortened. The plasticization of starch was greatly affected by the content of  $\text{SiO}_2$ . It was reported that an increase in filler content could increase physical crosslinking and this would lead to a decrease in the free volume of polymers.<sup>29,30</sup>

As for the starch materials, because of the large number of hydroxyl groups existing in the starch molecules, the intermolecular and intramolecular hydrogen bonds were easily formed, and this restrained the movement of starch molecular chains. After the addition of  $\text{SiO}_2$ , the hydrogen bonds of the starch molecules were disrupted by  $\text{SiO}_2$  particles, and this resulted in increases in the free volume and the movement ability of the starch molecules. This promoted plasticization of the TPS/PVA blends. However, the excess  $\text{SiO}_2$  content likely caused the aggregation of  $\text{SiO}_2$  particles and caused a decrease in the free volume. Therefore, it was indicated that there was no further decrease in the plasticizing time with increases in  $\text{SiO}_2$  above 5 phr. Furthermore, we found that the plasticizing and balance torque of the TPS/PVA/ $\text{SiO}_2$  composites were enhanced with the increase of  $\text{SiO}_2$  content. The reason was that the viscosity of the TPS/PVA/ $\text{SiO}_2$  composites increased with the increasing content of  $\text{SiO}_2$ .<sup>31</sup> In addition, the formation of the new structure between the starch molecules and  $\text{SiO}_2$  resulted in an increase in the torque, and the structure of the TPS/PVA/ $\text{SiO}_2$  composites is discussed in the following section.

The reactions between the starch molecules and  $\text{SiO}_2$  are shown in Figure 3. A hydrolysis reaction of KH550 occurred, and this formed the active multihydroxyl silanol [Figure 3(a)]. Then, the hydrolyzed KH550 reacted with the hydroxyl of the  $\text{SiO}_2$  surface [Figure 3(b)]. The treated  $\text{SiO}_2$  could easily react with starch molecules, and this led to breaking of the intramolecular and intermolecular hydrogen bonds [Figure 3(c)]. The purpose of the plasticizing process of starch was to destroy the intermolecular and intramolecular hydrogen bonds in the starch macromolecules. If the starch was not well plasticized, the starch molecules aggregated under the action of hydrogen bonds; thus,  $\text{SiO}_2$  could not easily react with the starch molecules. After the treatment of the  $\text{SiO}_2$  surface, the addition of treated  $\text{SiO}_2$  promoted the plasticization of starch because of the reaction between treated  $\text{SiO}_2$  and starch molecules. In addition,



**Figure 3.** Reaction process of the starch molecules with  $\text{SiO}_2$ : (a) the hydrolysis reaction of the silane coupling agent (KH550) is shown, (b) the surface of the  $\text{SiO}_2$  was treated through the reaction of  $\text{SiO}_2$  with the hydrolyzed KH550, and (c) the starch molecules was reacted with the treated  $\text{SiO}_2$ .

the treated  $\text{SiO}_2$  had better interfacial adhesion with the polymer matrix.

#### FTIR Analysis

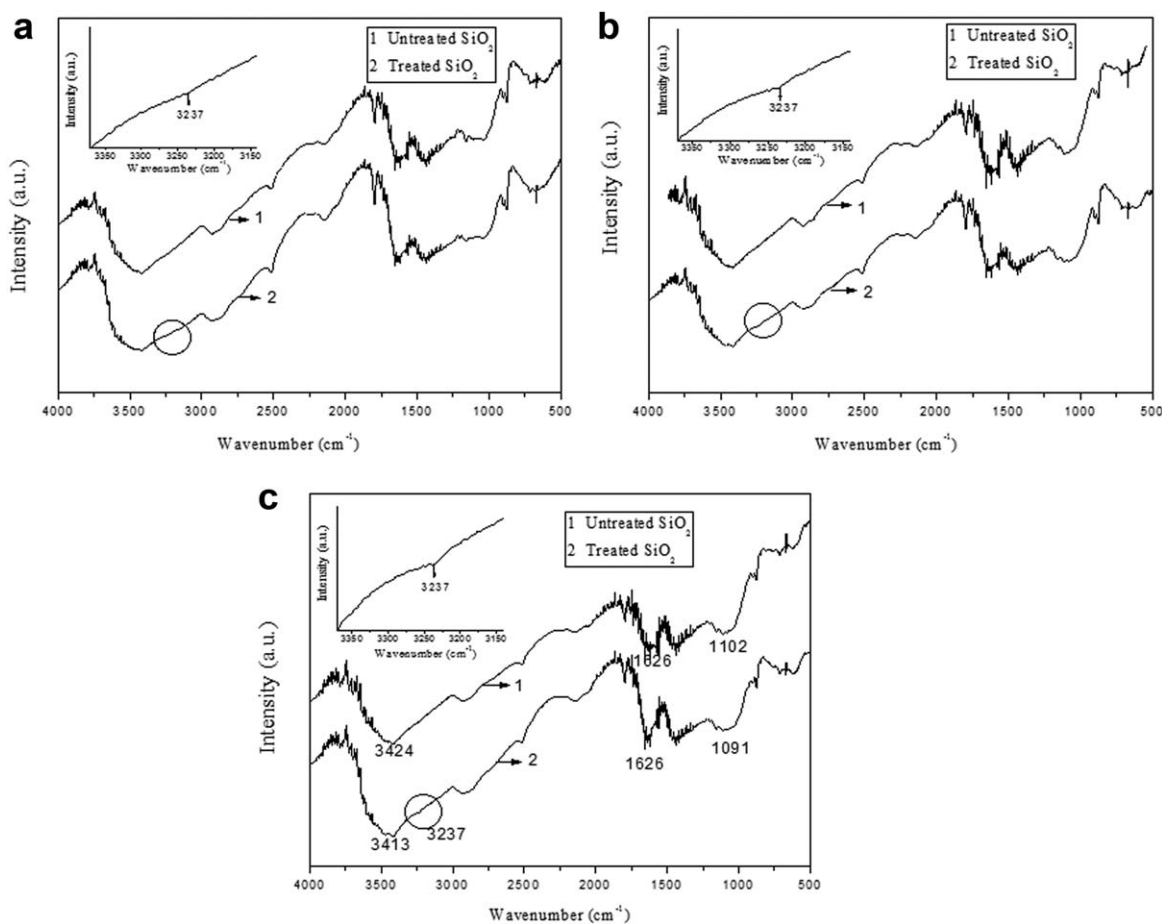
The effects of the untreated and treated  $\text{SiO}_2$  on the FTIR spectra of the TPS/PVA blends are shown in Figure 4. The band at  $3400\text{ cm}^{-1}$  was attributed to the stretching vibrations of the hydroxyl ( $-\text{OH}$ ) groups. We observed that the wave numbers of the  $-\text{OH}$  groups in the TPS/PVA containing untreated and treated  $\text{SiO}_2$  were  $3424$  and  $3413\text{ cm}^{-1}$ , respectively.<sup>4</sup> The  $\text{SiO}_2$  surface treated by KH550 enhanced the hydrogen-bond interactions between the  $\text{SiO}_2$  particles and the matrix. The treated  $\text{SiO}_2$  disrupted the hydrogen bonds of the starch molecules and created free volume in the starch; this increased the mobility of the starch molecules and was beneficial to the enhancement of the process of plasticization. Therefore, the treated  $\text{SiO}_2$  had a promoting effect on the plasticization of the TPS/PVA blends; this was consistent with the results of the processing experiment. The absorption peak of  $3237\text{ cm}^{-1}$  corresponded to the stretching vibrations of the  $-\text{NH}$  group (the amplification of

the FTIR spectra in Figure 4). Liu and Liu<sup>32</sup> investigated the surface of  $\text{SiO}_2$  treated by a silane coupling agent (KH550), and the absorption peak at  $3200\text{--}3450\text{ cm}^{-1}$  became wide and strong because of the absorption peak of the treated  $\text{SiO}_2$  containing amino groups. With the increase in the  $\text{SiO}_2$  content, the absorption peak at  $3237\text{ cm}^{-1}$  became clearer, and the intensity became stronger. The appearance of the  $-\text{NH}$  group indicated that the surfaces of  $\text{SiO}_2$  were already modified by KH550 through a chemical reaction.<sup>33,34</sup> In addition, the increase in the intensity of the peak at  $1626\text{ cm}^{-1}$  was attributed to the bending stretching of  $-\text{OH}$ ; this indicated an increase in the hydrogen-bond interactions.<sup>35</sup> The absorption peak at  $1102\text{ cm}^{-1}$  was assigned to the stretching vibrations of  $\text{Si}-\text{O}-\text{Si}$ . The decrease in the wave number and the increase in the intensity indicated the enhancement of the  $\text{Si}-\text{O}-\text{Si}$  group.

#### Thermal Properties

The thermal properties of the TPS/PVA/ $\text{SiO}_2$  composites were characterized by TG analysis. The TG and the differential thermogravimetry (DTG) curves are indicated in Figure 5(a,b),



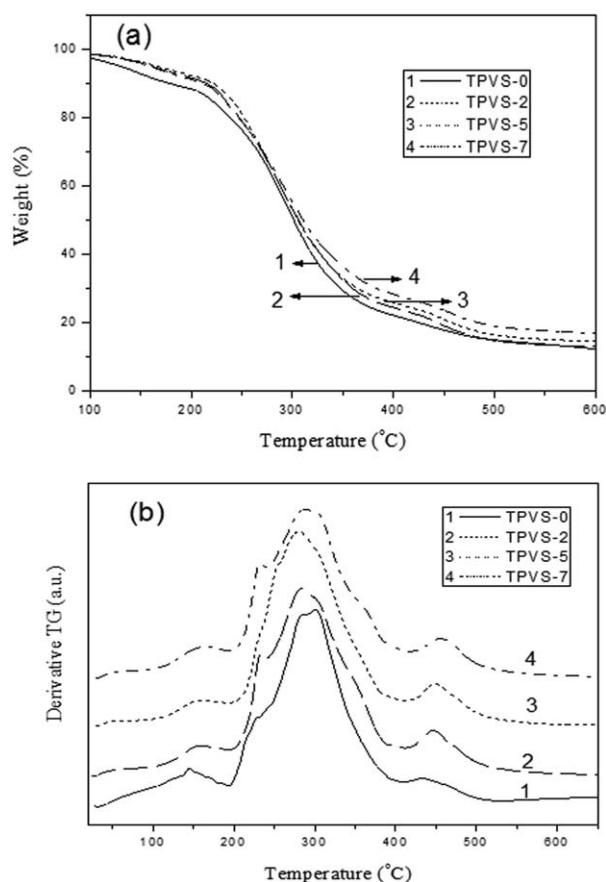


**Figure 4.** Effects of the untreated and treated  $\text{SiO}_2$  on the FTIR spectra of the TPS/PVA blends: (a) TPVS-2, (b) TPVS-5, and (c) TPVS-7.

respectively, and the data are summarized in Table III. The mass loss of the composites occurred in four temperature stages. The mass loss in the first stage ( $<160^\circ\text{C}$ ) was the evaporation of water. As shown in Table III, there was an increase in the first-stage decomposition temperature ( $T_d$ ) after the addition of  $\text{SiO}_2$ , and there was a small increase with increasing  $\text{SiO}_2$  content. The second stage ( $160\text{--}250^\circ\text{C}$ ) was the volatilization of glycerol. The second-stage  $T_d$  value changed from  $225.8$  to  $230.3^\circ\text{C}$  when the  $\text{SiO}_2$  content was varied from 0 to 7 phr. A significant stage was the third stage ( $250\text{--}400^\circ\text{C}$ ), which showed the highest thermal decomposition peak.<sup>36</sup> This was attributed to the decomposition of the starch and PVA. A gradual increase in the third-stage  $T_d$  value was observed. The fourth stage ( $400\text{--}500^\circ\text{C}$ ) was the further decomposition of the starch and PVA because of the combustion of the pyrolysis residue.<sup>37</sup> We observed a significant improvement in the fourth-stage  $T_d$  value from  $436.5$  to  $457.8^\circ\text{C}$  with the increase in the  $\text{SiO}_2$  content. Furthermore, we also found that other  $T_d$  values, such as the denotative initial decomposition temperature ( $T_{id}$ ), the temperature at 50% loss, and the denotative terminated decomposition temperature ( $T_{td}$ ) of the TPS/PVA/ $\text{SiO}_2$  composites, also shifted to higher temperatures. The addition of  $\text{SiO}_2$  had a great increasing effect on the  $T_d$  values of the TPS/PVA blends. The presence of inorganic fillers are beneficial to the improvement of the thermal stability of polymers. The  $T_d$  values of inorganic

fillers are higher than those of polymers; thus, inorganic fillers are usually applied to enhance the thermal properties of polymers.<sup>38–40</sup> The  $T_d$  values are mainly related to the content of inorganic particles and the structure of polymer composites. An appropriate increase in content of inorganic particles was beneficial to the enhancement of the thermal stability of the polymers. In addition, the compatibility of the TPS/PVA blends was improved after the addition of  $\text{SiO}_2$ . At a content of 5 phr  $\text{SiO}_2$ , the chemical reaction between  $\text{SiO}_2$  and the starch molecules formed more stable structures, which played an important role in improving  $T_d$ . The more stable the structure was, the more energy was needed to destroy the structure. The stable structures of the TPS/PVA/ $\text{SiO}_2$  composites included the hydrogen-bond reaction between  $\text{SiO}_2$  and TPS molecules, the good interfacial adhesion between  $\text{SiO}_2$  and the matrix, and the uniform dispersion of  $\text{SiO}_2$ , which improved the thermal stability of the TPS/PVA blends.

It was reported by Sreekumar *et al.*<sup>13,41</sup> that the width of the highest decomposition peak at 0.2 in the DTG curve ( $\Delta T$ ) at the maximum degradation provided evidence for the homogeneity of their blends. The decrease in  $\Delta T$  indicated an increase in the homogeneity of the polymer blends. As shown in Table III, the  $\Delta T$  values of the TPS/PVA/ $\text{SiO}_2$  composites decreased with the addition of  $\text{SiO}_2$ , particularly in the TPVS-5 sample.



**Figure 5.** Thermal decomposition curves of the TPS/PVA-treated SiO<sub>2</sub> composites: (a) TG and (b) DTG curves.

At a content of 5 phr SiO<sub>2</sub>, the noticeable reduction of  $\Delta T$  was ascribed to the increase in the homogeneity of TPS/PVA blends. The compatibility of the TPS/PVA blends was improved after the addition of SiO<sub>2</sub>. An increase in the compatibility of polymer blends by inorganic fillers with high surface areas has been reported by Jose *et al.*<sup>21</sup> and Mallick *et al.*<sup>42</sup> Furthermore, an increase in the compatibility would be beneficial to the enhancement of the thermal stability of the blends.

The effects of the untreated and treated SiO<sub>2</sub> on the TG and DTG curves of the TPS/PVA/SiO<sub>2</sub> composites are shown in Figure 6(a,b), and the results are summarized in Table IV. The treated SiO<sub>2</sub> greatly improved  $T_d$  of the TPS/PVA/SiO<sub>2</sub> composites. As shown in Table IV,  $T_{id}$  and the temperature at 5% loss increased from 225.0 to 229.2 °C and 141.3 to 166.5 °C, respectively. In addition, we also found that  $\Delta T$  of the TPS/PVA

blends containing the treated SiO<sub>2</sub> was lower than that of the untreated SiO<sub>2</sub>. The decrease in  $\Delta T$  was attributed to the increase in the homogeneity of the TPS/PVA blends; this indicated that the compatibility of the starch/PVA blends was improved by the treated SiO<sub>2</sub>. The SiO<sub>2</sub> surface treatment by KH550 promoted better dispersion of SiO<sub>2</sub> in the TPS/PVA blends. Furthermore, the chemical reaction between SiO<sub>2</sub> and the starch molecules form more stable structures and played an important role in improving  $T_d$ . We noted that the disappearance of the second decomposition stage indicated a decrease in the volatilization of glycerol. The majority of glycerol plasticized with the starch and PVA molecules, as was also evident from the results of FTIR analyses and the plasticizing data discussed previously.

### Mechanical Properties

The tensile strength, elongation at break, and Young's modulus values of the TPS/PVA/SiO<sub>2</sub> composites are indicated in Figure 7(a–c). With the increase in SiO<sub>2</sub> content, the tensile strength, elongation at break, and Young's modulus of the TPS/PVA/SiO<sub>2</sub> composites increased and reached maximum values when the concentration of SiO<sub>2</sub> was 2 phr. Furthermore, we also found that the mechanical properties of the TPS/PVA/SiO<sub>2</sub> composites containing treated SiO<sub>2</sub> were higher than that of the untreated SiO<sub>2</sub>. The reaction between the treated SiO<sub>2</sub> and the starch molecules formed more stable structures; this were beneficial to the improvement of the mechanical properties of the TPS/PVA/SiO<sub>2</sub> composites. The mechanical properties of the TPS/PVA/SiO<sub>2</sub> composites were confirmed from the analyses of the plasticizing curves and the FTIR results.

Effects of filler contents on the mechanical properties of the polymer composites have been obtained by a lot of researchers in previous studies. Teixeira *et al.*<sup>43</sup> used cellulose cassava bagasse nanofibrils (CBNs) as reinforcing nanoparticles to prepare thermoplastic cassava composites. The mechanical properties of the starch/CBN nanocomposites showed an increase and then a significant decrease with the CBN content. Kampeerappun *et al.*<sup>17</sup> found that a starch/montmorillonite composite film showed an improvement in the tensile properties at low montmorillonite contents. Jia *et al.*<sup>44</sup> investigated the starch and PVA composite film containing nano-SiO<sub>2</sub> through orthogonal testing, and the results indicate that the optimum tensile strength of the composite was obtained at a concentration of 2.0% nano-SiO<sub>2</sub>. Similar results from the previous studies indicated that the nanoparticle content showed an optimal value in improving the mechanical properties of the polymers. This was because the dispersion of nanoparticles in the matrix played an

**Table III.** Thermal Decomposition Data of the TPS/PVA-Treated SiO<sub>2</sub> Composites

Sample code	$T_d$ (°C)				$T_{id}$ (°C)	Temperature at 50% loss (°C)	$\Delta T$ (°C)	$T_{td}$ (°C)
	First stage	Second stage	Third stage	Fourth stage				
TPVS-0	145.4	225.8	282.5	436.5	221.2	301.5	145.6	349.9
TPVS-2	155.4	231.2	284.5	447.2	225.8	306.2	145.1	371.1
TPVS-5	154.1	—	284.9	448.9	229.2	307.8	136.5	371.5
TPVS-7	155.8	230.3	285.4	457.8	222.5	310.8	145.5	373.5

**Table IV.** Thermal Decomposition Data of the 60/40/5 TPS/PVA/SiO<sub>2</sub> Composites

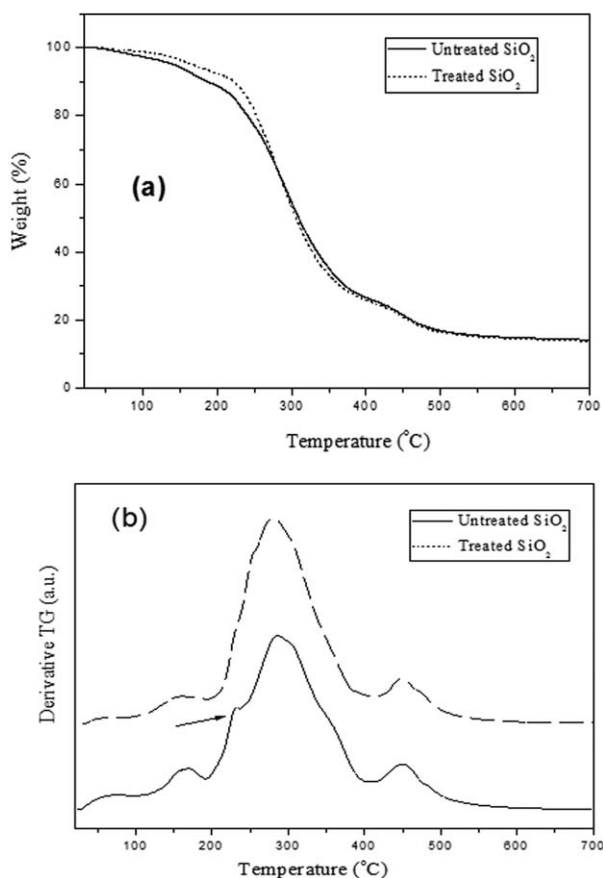
Sample code	$T_d$ (°C)				$T_{id}$ (°C)	Temperature at 5% loss (°C)	Temperature at 50% loss (°C)	$\Delta T$ (°C)	$T_{td}$ (°C)
	First stage	Second stage	Third stage	Fourth stage					
TPVS-5 (untreated SiO <sub>2</sub> )	154.9	229.6	285.2	449.1	225.0	141.3	307.1	150.2	371.4
TPVS-5 (treated SiO <sub>2</sub> )	154.1	—	284.9	448.9	229.2	166.5	307.8	136.5	371.5

important role in the mechanical properties of composites, which were closely related to the content of nanoparticles. At low contents of nanoparticle, the nanoparticles were uniformly dispersed in matrix, and this was beneficial to the improvement of the tensile properties. Excess filler content likely caused the poor particle distribution and led to a decrease of the mechanical properties.<sup>17</sup> Liu *et al.*<sup>45</sup> investigated the mechanical properties of starch-carbon nanotube (multiwalled nanotube) composites and observed that small fractions of filler in improving the mechanical properties could be attributed to the good dispersion of the fillers in the starch matrix and strong interfacial adhesion. However, the high content of SiO<sub>2</sub> did not uniformly disperse in the TPS/PVA blends, and the aggregation of SiO<sub>2</sub> likely occurred; this resulted in a decrease of the mechanical properties.<sup>35</sup> When the content of treated SiO<sub>2</sub> was 2 phr,

SiO<sub>2</sub> was uniformly dispersed in the TPS/PVA blends, and this is discussed in the following SEM analysis.

### SEM Analysis

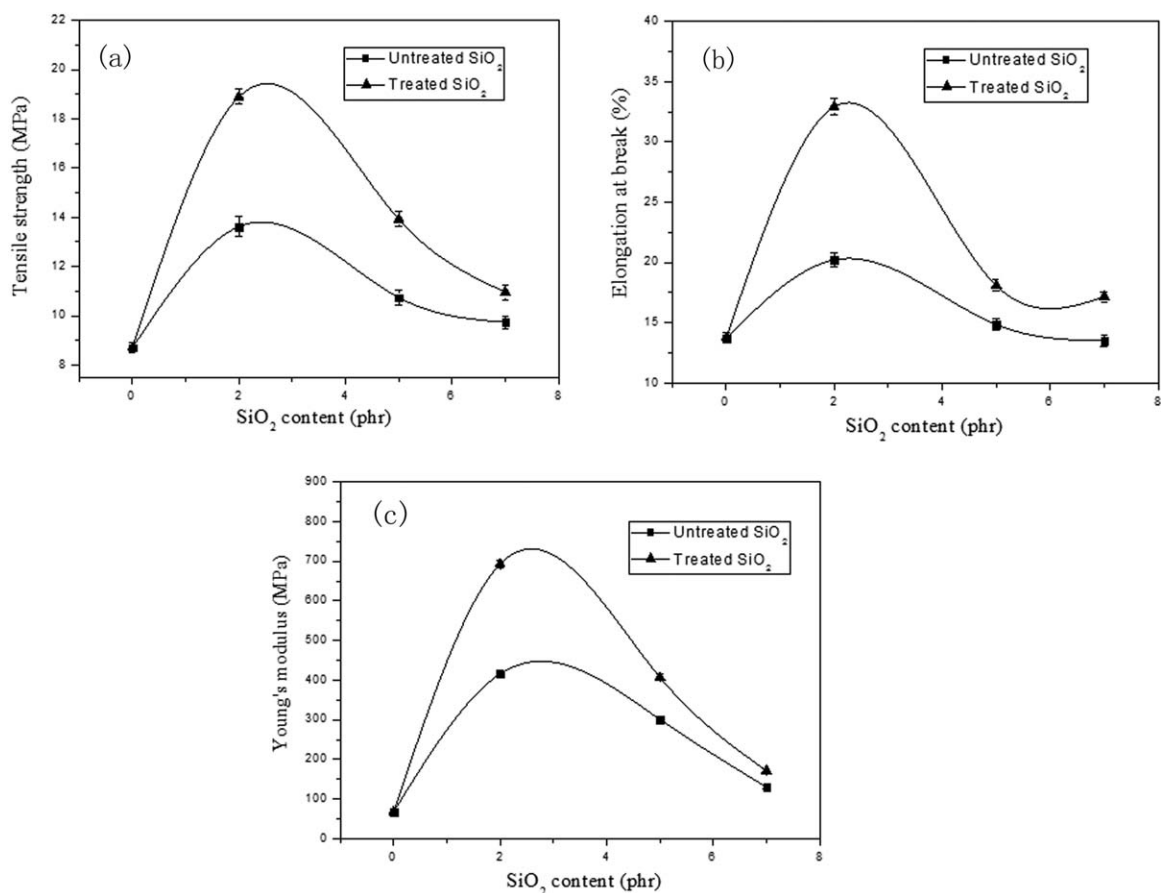
SEM images of the TPS/PVA/SiO<sub>2</sub> composites are shown in Figure 8. We observed, as shown in Figure 8(a,b), that the interface between the untreated SiO<sub>2</sub> particles and the matrix was not good. This easily exposed the SiO<sub>2</sub> particles in the sample's fractured section. It was more noticeable in the larger magnification in Figure 8(b') that there were a lot of untreated SiO<sub>2</sub> particles greatly aggregated in the TPS/PVA blends. SEM images of the TPS/PVA blends containing treated SiO<sub>2</sub> are shown in Figure 8(c,d,d'). We found, as shown in Figure 8(c,d), that the granules of starch were not noticeably visible; this indicated that the starch was well plasticized. It is also shown that the interface between the treated SiO<sub>2</sub> particles and the matrix became blurred; this indicated good interfacial adhesion. In addition, the SiO<sub>2</sub> particles were uniformly and finely dispersed in the matrix with the lower SiO<sub>2</sub> content. With increasing SiO<sub>2</sub> content, the agglomeration of SiO<sub>2</sub> easily occurred, and this led to a decrease in the mechanical properties of the composites. The reaction of amine on the surface of SiO<sub>2</sub> with the starch hydroxyls was conducive to increases in the compatibility and stability of the blends.<sup>35</sup> It is more clearly demonstrated in the larger magnification in Figure 8(d') that the treated SiO<sub>2</sub> was uniformly dispersed in the polymer matrix. The reason was that the SiO<sub>2</sub> treated by the silane coupling agent made the SiO<sub>2</sub> surface change from hydrophilic to hydrophobic; this favored the dispersion, rather than aggregation, of SiO<sub>2</sub>. The uniform dispersion of the treated SiO<sub>2</sub> in the starch/PVA blends caused an increase in the mechanical properties of the composites compared with the untreated SiO<sub>2</sub>; this was in conformity with the processing properties, mechanical properties, and FTIR results, as discussed earlier.



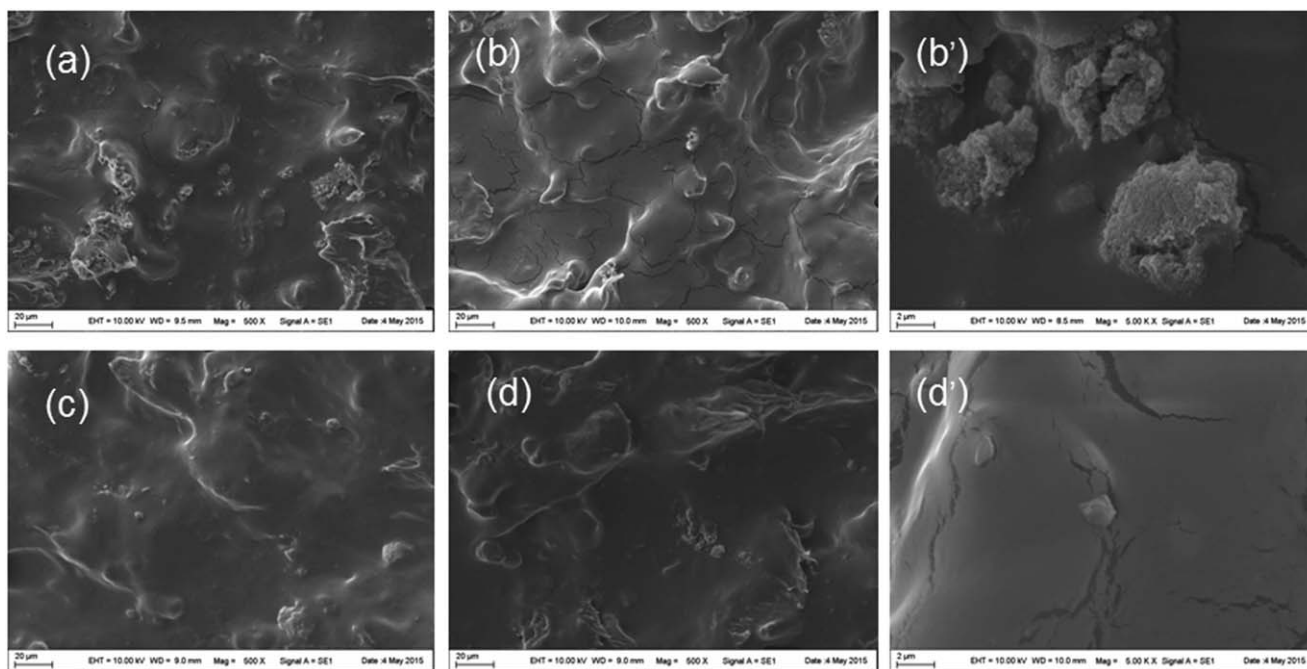
**Figure 6.** Thermal decomposition curves of the 60/40/5 TPS/PVA/SiO<sub>2</sub> composites: (a) TG and (b) DTG curves.

### CONCLUSIONS

TPS/PVA blends containing different contents and surface characteristics of SiO<sub>2</sub> were prepared by a melt-mixing method. After the SiO<sub>2</sub> surface was treated by KH550, the plasticizing time of the TPS/PVA/SiO<sub>2</sub> composite was shorter than that of the untreated SiO<sub>2</sub>. The treated SiO<sub>2</sub> disrupted the hydrogen bonds of the starch molecules and created free volume in the starch; this increased the mobility of the starch molecules and was beneficial to the enhancement of the process of plasticization. With increasing SiO<sub>2</sub> content, the plasticizing time of the TPS/PVA/SiO<sub>2</sub> composites decreased, and the torque of the TPS/PVA/SiO<sub>2</sub> composites was enhanced. After the surface of SiO<sub>2</sub> was treated by the silane coupling agent, hydrogen bonds between the starch molecules and treated SiO<sub>2</sub> were formed.



**Figure 7.** Effects of SiO<sub>2</sub> on the mechanical properties of the TPS/PVA blends: (a) tensile strength, (b) elongation at break, and (c) Young's modulus.



**Figure 8.** SEM images of the TPS/PVA/SiO<sub>2</sub> composites: (a) TPVS-2 containing untreated SiO<sub>2</sub> (500 $\times$ ), (b) TPVS-5 containing untreated SiO<sub>2</sub> (500 $\times$ ), (b') TPVS-5 containing untreated SiO<sub>2</sub> at a larger magnification (5000 $\times$ ), (c) TPVS-2 containing treated SiO<sub>2</sub> (500 $\times$ ), (d) TPVS-5 containing treated SiO<sub>2</sub> (500 $\times$ ), and (d') TPVS-5 containing treated SiO<sub>2</sub> at a larger magnification (5000 $\times$ ).



The  $T_d$  values of the TPS/PVA/SiO<sub>2</sub> composites were improved with the addition of SiO<sub>2</sub>. The presence of inorganic fillers was beneficial to the improvement of the thermal stability of the polymers. There was an increase in the compatibility of the TPS/PVA blends in the presence of SiO<sub>2</sub> particles. The good interfacial adhesion between SiO<sub>2</sub> and the matrix and more stable structures were beneficial to the improvement of the thermal stability of the TPS/PVA blends.

With increasing SiO<sub>2</sub> content, the tensile strength, elongation at break, and Young's modulus values of the TPS/PVA/SiO<sub>2</sub> composites increased and reached their maximum values when the concentration of SiO<sub>2</sub> was 2 phr. At low SiO<sub>2</sub> contents, the SiO<sub>2</sub> was uniformly and finely dispersed in the matrix. With a further increase in the SiO<sub>2</sub> content, SiO<sub>2</sub> displayed an aggregation phenomenon in the matrix. In addition, the treated SiO<sub>2</sub> was more uniformly dispersed in the TPS/PVA blends and had better interfacial adhesion with the matrix compared with the untreated SiO<sub>2</sub>.

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