

# Surface modification of silica nanoparticles by hexamethyldisilazane and n-butanol



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## ABSTRACT

In this article, surface modification of silica nanoparticles were carried out with different reagents such as - epoxy resin, hexamethyldisilazane (HMDS) and *n*-butanol. The aim of this study is to generate a hydrophilic type of silica which is well dispersed in polar solvent as rubber, resin, paint, oil, grease, etc. With that purpose, we have modified the silica with the reagents chosen above. After modification, the silica nanoparticles have had the hydrophobic surface. As the first step, we have applied this material as the dispersed phase to synthesize lubricants, preventing metal corrosion of equipment and machine operating in extreme environment. The nanoparticles were prepared from rice husk using precipitation method, these particles have the particle size in the range from 20 nm to 30 nm and the surface area of 49.046 m<sup>2</sup>/g. Several analytical methods including Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET), Dynamic Contact Angle (DCA), Thermogravimetric/Differential Thermal Analyzer (TG/DTA) have proven the interaction between the organic groups and the silica surface. In which, DCA has indicated the surface modification of material when it changes from hydrophilic form to hydrophobic form.

## 1. Introduction

Silica material is valuable in different fields, for instance, to improve surface and mechanical properties of material. It can be used as fillers or additives in material such as paint, synthetic rubber, resin, adhesives, sealants, grease and insulation (Kang et al. 2001). In 1956, Gerhard Kolbe observed the formation of spherical silica particles from tetrathoxysilane in ethanol using ammonia as a base catalyst. After that, Werner Stober improved the precipitation procedure to synthesize silica having the particle size from 50 nm to 500 nm (Sugimoto 2000). Since then, the synthesis of silica has made a huge progress.

Several studies indicated that newly formed silica is inappropriate to be used as additives for some types of material because of its hydrophilicity and moisture instability. The reason is the presence of –OH groups, which are polar

and hydrophilic on silica surface (Fig. 1). These –OH groups exist in various different forms, for example, isolated silanol ( $\equiv\text{Si-OH}$ ), geminal silanol ( $=\text{Si}(\text{OH})_2$ ) or vicinal silanol in which –OH groups link together by hydrogen bond. There are also the siloxane groups ( $\equiv\text{Si-O-Si}\equiv$ ) on the surface of silica and a certain amount of water is adsorbed which can be desorbed by physical methods (Zhuravlev 2000; Nam et al. 2015; Jal et al. 2004).

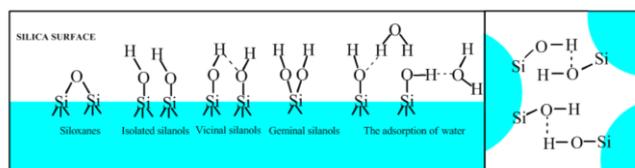


Fig. 1 Surface structure of silica particles

Therefore, in order to increase the compatibility between silica and materials as: paint, synthetic rubber, resin, adhesives, sealants, grease, insulation, etc., the surface of silica particles needs to be modified from hydrophilic form to hydrophobic form. Currently, several studies have been carried out for surface treatment of silica particles, especially the studies to select the optimum reagent and modification procedure. Different reagents afford different surface properties of silica which can be applied in diverse fields (Fuji et al. 2007; Fuji et al. 2000; Hunter et al. 2009). In this article, we introduce some silica nanoparticles modification methods with different typical organic compounds including alcohol, epoxy resin and organosilanes.

In reality, there are many different reagents for the modification of nano-silica. However, through research, we have chosen epoxy, hexamethyldisilazane (HMDS) and *n*-butanol as the modifying reagents. After modification, the silica particles have been applied as dispersed phase for lubricants, preventing metal corrosion; dispersing silica in natural rubber as the reinforcing material.

Results also show that nano-silica after modification is highly compatible with the dispersing environments such as rubbers and lubricants, forming a dispersed system relatively homogeneous and stable. Dispersed-modified-nano-silica lubricants prevent metal corrosion better and can work in high temperature and pressure. Dispersed-modified-nano-silica rubbers have lower abrasion, higher strength, and lower rolling resistance among many other improved properties.

## 2. Materials and methods

### 2.1. Materials

Imidazole 99%, hexamethyldisilazane (HMDS)  $\geq 99\%$  (Sigma), epoxy resin (E44), acetone 99.5%, toluene 99.5%, ethanol, sodium hydroxide, hydrochloric acid, carbon tetrachloride  $\geq 99.5\%$  (China), *n*-butanol  $\geq 99.5\%$ ; the specific surface area of silica nanoparticles used to modify must be larger than  $25 \text{ m}^2/\text{g}$ . In this study, silica nanoparticles was prepared from rice husk (Vietnam) by precipitation method (Rafiee et al. 2012; Nam et al. 2015).

### 2.2. Preparation

#### 2.2.1. Preparation of Silica Nanoparticles

The silica particles were synthesized from rice husk by the following process:

In the first step, the purified rice husk was heated at  $500^\circ\text{C}$  for 5 hours in furnace to obtain the husk ash, followed by the addition of 2M NaOH solution into the ash and the mixture was heated for 4 hours at  $100^\circ\text{C}$ . Then, the solution obtained was filtered and stirred while a 2M HCl solution was added until the white precipitate was formed. After centrifugation, the precipitate was separated, washed and dried to release the silica nanoparticles.

#### 2.2.2. Preparation of silica/epoxy resin

Two grams of silica was mixed with 1 g of epoxy resin in a round-bottomed flasks, followed by the dispersion of the

mixture in toluene in the presence of 0.2 g imidazole. Then, the mixture was well stirred and refluxed at  $100^\circ\text{C}$  for 2 hours. After the reaction, the residual imidazole was removed by adding acetone then washing the precipitate and centrifuging to separate the precipitate. The resulting precipitate was further dispersed in acetone and well stirred at room temperature for 2 hours. The final precipitate was separated and dried in vacuum at  $100^\circ\text{C}$  for 10 hours.

#### 2.2.3. Preparation of silica/HMDS

In the first step, the silica nanoparticles were dried for 4 hours at  $100^\circ\text{C}$ . Then the following steps were carried out: Two grams of silica was dispersed in toluene in the first beaker, stirred well on a magnetic stirrer. 0.5 ml HMDS and toluene were added into the second beaker, stirred well on a magnetic stirrer. The materials in two beakers were then mixed together and added into a round-bottom flask and refluxed at  $110^\circ\text{C}$  for 24 hours. After the reaction, the precipitate was separated and washed with toluene to remove the residual HMDS. The next step involved further wash of precipitate by ethanol to obtain the final precipitate. Finally, the product was washed several times and dried at  $110^\circ\text{C}$  for 4 hours.

#### 2.2.4. Preparation of silica/*n*-butanol

The silica nanoparticles were dried in vacuum for 4 hours at  $100^\circ\text{C}$ , this step is aimed to remove a certain amount of physical adsorbed water on the particle surface. The next step was the chlorination of the silica surface by  $\text{CCl}_4$  gas at  $150^\circ\text{C}$  for 20 minutes. The products obtained were then added into a round-bottom flask, stirred and refluxed with *n*-butanol at  $118^\circ\text{C}$  for 4 hours. Finally, the silica particles were separated and dried in vacuum at  $110^\circ\text{C}$  for 16 hours.

### 2.3. Equipment and Experimental methods

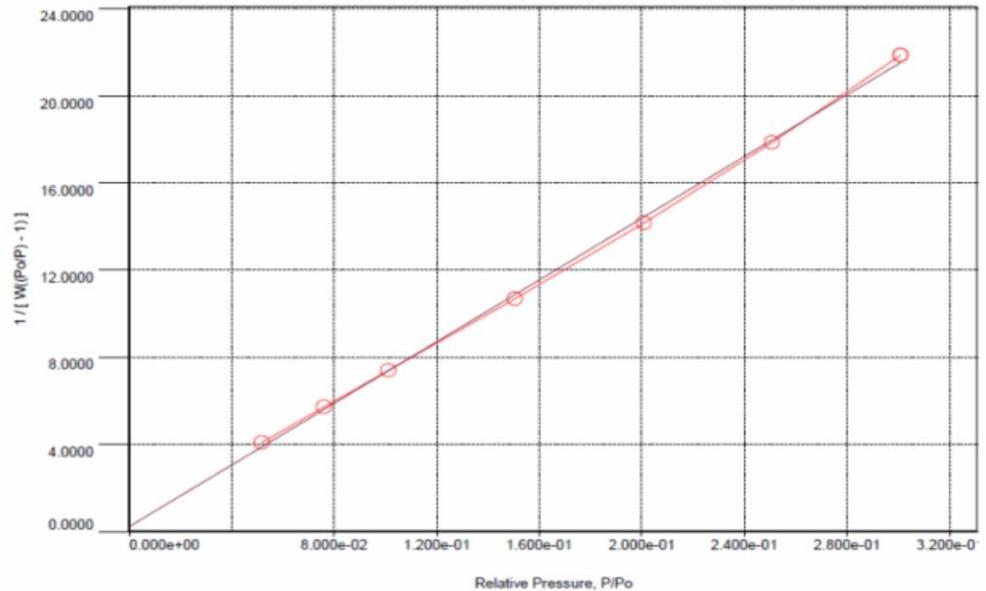
In this study, the surface characteristic of silica before and after the modification were confirmed by the following methods and equipment: IR spectra of the samples in the form of thin film were recorded on Fourier GX - PerkinElmer – USA; Thermogravimetric analysis was taken on TG/DSC – Setaram-France; specific total surface area (BET) was determined on Micromeritics ASAP 2010, Dynamic Contact Angle (DCA) was determined using Wilhelmy methods on DCA300-Thermo Cahn; SEM images was obtained on S4800-NIHE- Hitachi.

## 3. Results and discussion

### 3.1. Structural characteristic of particles

Silica nanoparticles were synthesized from rice husk using precipitation method, the product obtained was then dried before measuring the specific total surface area (BET). The BET nitrogen adsorption results in Fig. 2 indicate that the silica synthesized has the specific total surface area of  $49,046 \text{ m}^2 \text{ g}^{-1}$  which can be used for the modification.

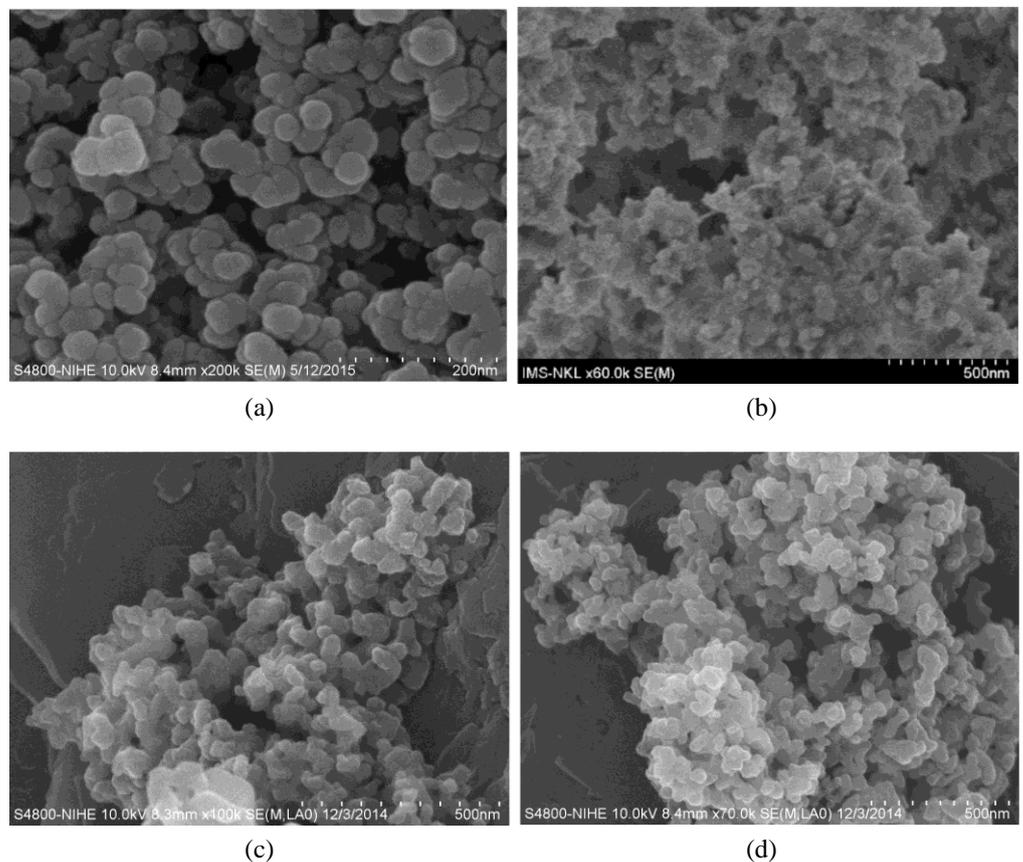
**Fig. 2** BET nitrogen adsorption

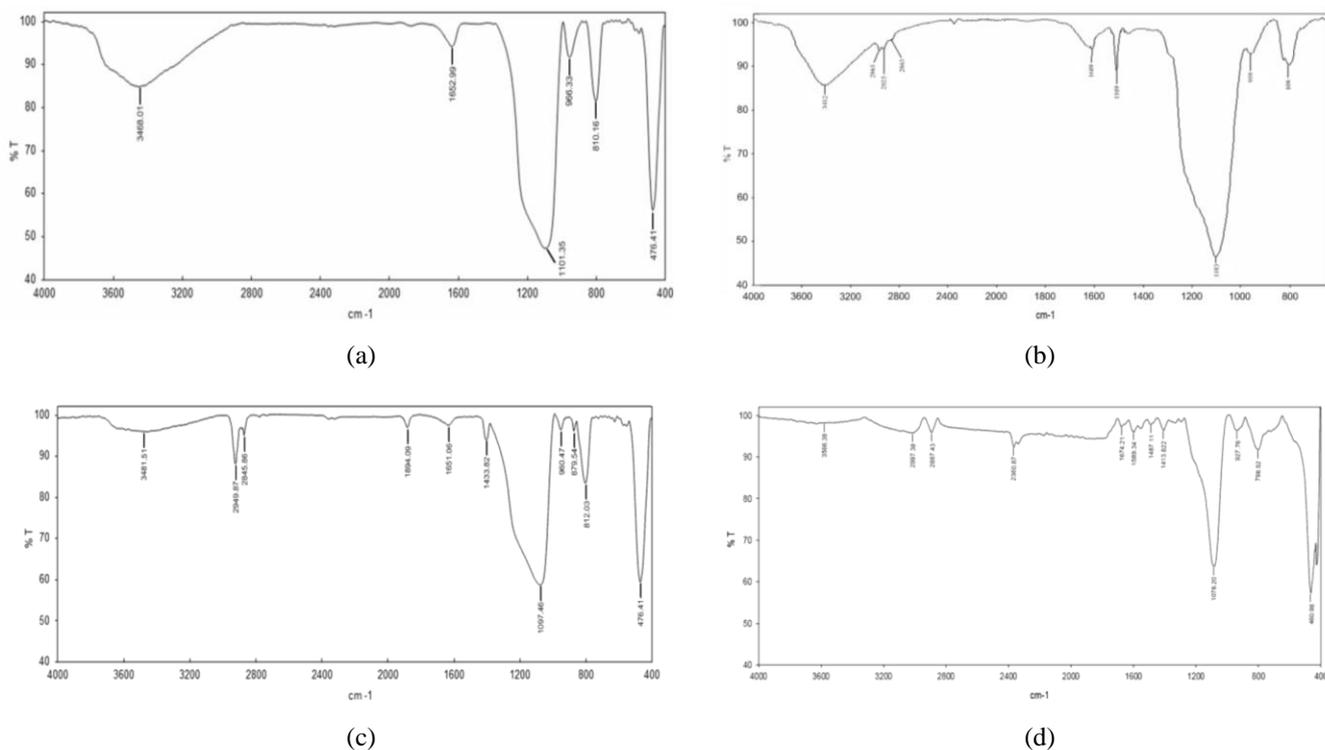


Scanning electron microscope (SEM) images of silica powder were taken to study the structure of particles. The results show that the as-synthesized silica particles have the particle size in the range of 20 nm to 30 nm and are relatively uniform (Fig. 3a). The silica particles tend to gather together to form a large aggregation, this phenomenon can be explained by the hydrogen bonds between  $-OH$  groups on silica surface (Fig. 1). After modifying with different reagents including epoxy resin, HMDS and *n*-butanol, the silica particles had changed but only slightly in size, the results taken show that the new particle size is in the range of 40 nm to 50 nm (Fig. 3b, 3c, 3d). However, the agglomeration of the

modified silica particle, especially in the silica particles modified with epoxy resin, increase significantly to form a large aggregation of particles. The reason is that the surface interacted with organic groups and was dispersed to form a large aggregation of particles. Fig. 3b indicates that the silica/epoxy resin particles show the best agglomeration because the epoxy resin molecules are large in size, which makes these particles easier to combine. There was also the agglomeration among the silica/HMDS and silica/*n*-butanol particles, however; it was not as much as among the silica/epoxy resin particles.

**Fig. 3** SEM images of (a) silica as-synthesized, (b) silica/epoxy, (c) silica/HMDS and (d) silica/*n*-butanol





**Fig. 4** FTIR spectrum of (a) silica as-synthesized, (b) silica/epoxy, (c) silica/HMDS and (d) silica/*n*-butanol

### 3.2. Infrared spectroscopy of silica modified materials (FTIR)

Based on the Fourier-transformed Infrared spectroscopy (the nano-silica sample used in IR was made as thin films of 50  $\mu\text{m}$  thickness; spectral band:  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ ; resolution:  $4\text{ cm}^{-1}$ ; nano-silica sample: powder form compressed with KBr) of as-synthesized silica particles (Fig. 4a) and silica/epoxy modified particles (Fig. 4b), it can be seen that the as-synthesized silica particles show a band at  $3468\text{ cm}^{-1}$  which represents the stretching of the free  $-\text{OH}$  groups, these groups uphold water to adsorb physically on silica surface; there is also an asymmetry stretch band of  $\text{Si-O-Si}$  at  $1101\text{ cm}^{-1}$ ; the  $\text{Si-O}$  stretching in silanol group shows a band around  $966\text{ cm}^{-1}$ ; the symmetry stretching of  $\text{Si-O-Si}$  in silica network is characterized by  $810\text{ cm}^{-1}$  band; and the band at  $1652\text{ cm}^{-1}$  is characteristic of the stretching of the water molecules surrounding the silica particles which can be removed after drying the silica modified in vacuum.

After the modification with epoxy resin, new bands of modified silica which are different to the band of as-synthesized silica appeared. Fig. 4b indicates two new bands at  $2863\text{ cm}^{-1}$  and  $2965\text{ cm}^{-1}$  which are characteristic of the stretching of  $\text{CH}_2$  group on the carbon chain of epoxy; the band of  $-\text{OH}$  groups is also located at  $3412\text{ cm}^{-1}$  which indicates that  $-\text{OH}$  groups still presented on silica surface; however, the intensity of these bands of modified silica is smaller than that of as-synthesized silica; the absorption band at  $1103\text{ cm}^{-1}$  of modified epoxy is identified for the asymmetry stretching of  $\text{Si-O-Si}$ ; the absorption bands associated with  $\text{C=C}$  bond stretching come from the aromatic ring located at  $1509\text{ cm}^{-1}$  and  $806\text{ cm}^{-1}$ .

It indicates that the reaction between  $-\text{OH}$  groups and oxirane groups of epoxy has occurred which made the silica

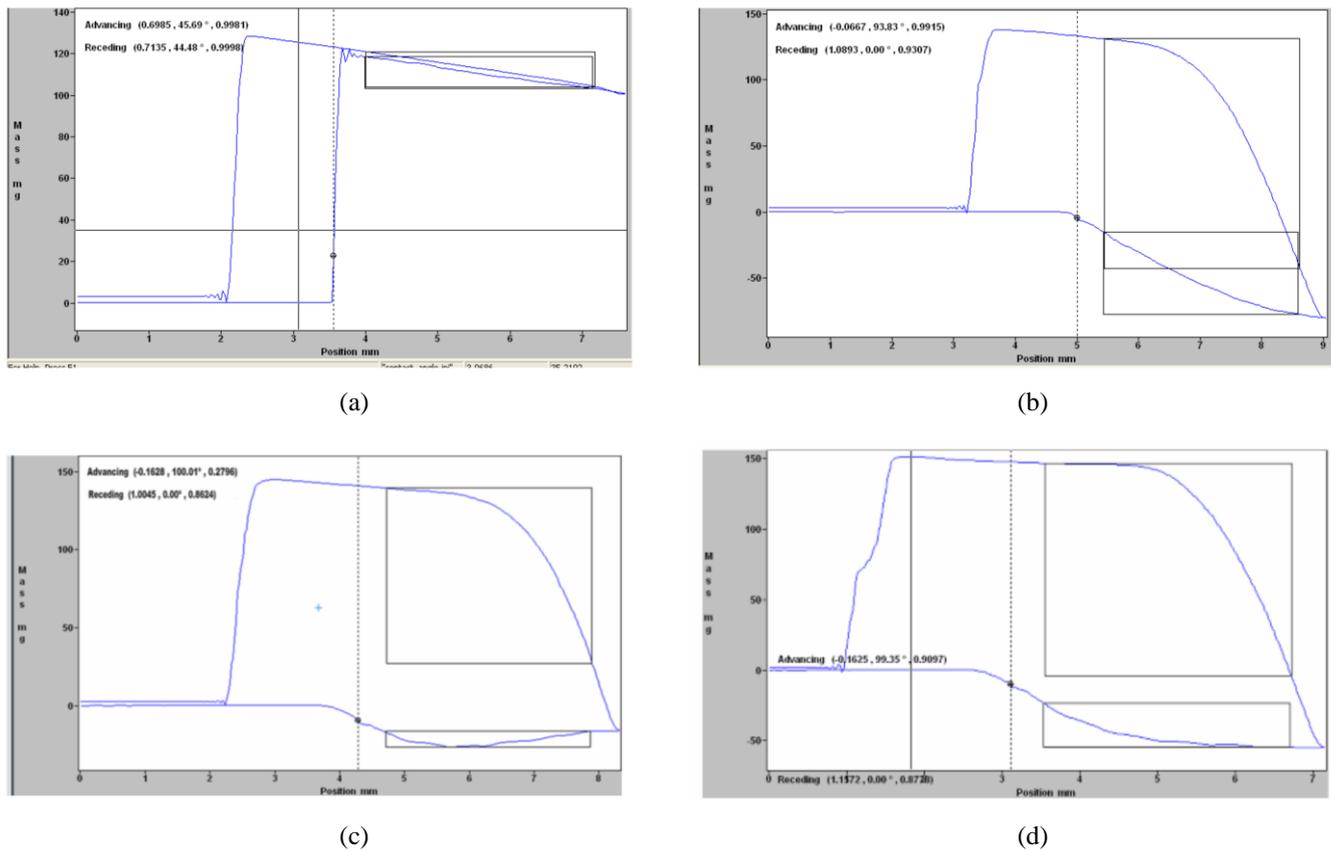
surface attached to organic groups; and hence, the silica particles change from hydrophilic form to hydrophobic form.

On the FTIR spectrum of silica modified with HMDS (Fig. 4c), there are two bands at  $2845\text{ cm}^{-1}$  and  $2949\text{ cm}^{-1}$  representing the stretching of  $-\text{CH}_3$  groups. The silica modified with HMDS also gives a band at  $3481\text{ cm}^{-1}$ , however the intensity of this peak is much lower compared to that of as-synthesized silica. The reason is that after the modification, the  $-\text{OH}$  groups were replaced by  $-\text{CH}_3$  groups, which reduces the intensity of  $-\text{OH}$  groups stretching. In addition, there is a certain amount of water adsorbed on silica surface. The reduction in the amount of  $-\text{OH}$  groups after modification is also related to the decrease in intensity of the bands at  $1651\text{ cm}^{-1}$  and  $966\text{ cm}^{-1}$ . The band at  $879\text{ cm}^{-1}$  of silica modified with HMDS associates with the stretching of  $\text{Si-C}$ . The adsorption band at  $1433\text{ cm}^{-1}$  is assigned to the asymmetry stretching of  $-\text{CH}_3$  groups.

The FTIR results show that the polar  $-\text{OH}$  groups were replaced by the nonpolar groups of HMDS.

The FTIR results of silica modified with *n*-butanol (Fig. 4d) show simultaneous presence of silica and modifying reagents. After the modification, the intensity of  $-\text{OH}$  group at  $3468\text{ cm}^{-1}$  decreases remarkably because of the replacement by the butoxyl groups. The decrease in the amount of  $-\text{OH}$  groups after modification is also related to the decrease in intensity of the peak at  $966\text{ cm}^{-1}$ . The butoxyl groups are characterized by the adsorption bands of  $2997\text{ cm}^{-1}$  and  $2887\text{ cm}^{-1}$  which represent the symmetry and asymmetry stretching of  $\text{C-H}$  in methylene groups and methyl groups. Furthermore, the adsorption bands at  $1413\text{ cm}^{-1}$ ,  $1487\text{ cm}^{-1}$  are the stretching of methyl groups.

The FTIR results indicate the presence of butoxyl groups on the surface of silica modified with *n*-butanol.



**Fig. 5** DCA of (a) silica as-synthesized, (b) silica/epoxy, (c) silica/HMDS and (d) silica/n-butanol

### 3.3. Dynamic Contact Angle (DCA)

The hydrophobicity of silica before and after modification is assessed using Wilhelmy method dynamic contact angle measurement. The nano-silica sample was spread all across the 10 x 12 x 0.5 mm rectangular glass. Sample soaking and dragging speed: 150  $\mu\text{m/s}$ , depth: 4 mm. Fig. 5 shows the dynamic contact angle measurement results of as-synthesized silica and silica modified with epoxy, HMDS and *n*-butanol, respectively.

The wetting dynamic contact angle of as-synthesized silica (Fig. 5a) was  $45.69^\circ$  and increased significantly to  $93.83^\circ$  after modification with epoxy resin. This angle is determined from the graph showing the relationship between the mass and the depth of the sample dipped into the liquid. The increase in wetting dynamic contact angle of silica indicates the change from hydrophilic property into hydrophobic.

Silica particles are hydrophilic because of polar nature of  $-\text{OH}$  groups on the surface of silica. After modifying with epoxy resin, the rings in epoxy groups were opened followed by the attack of the  $-\text{OH}$  groups of silica. This reaction caused the appearance of nonpolar hydrocarbon groups on the surface, which then strongly decrease the hydrophilicity of silica.

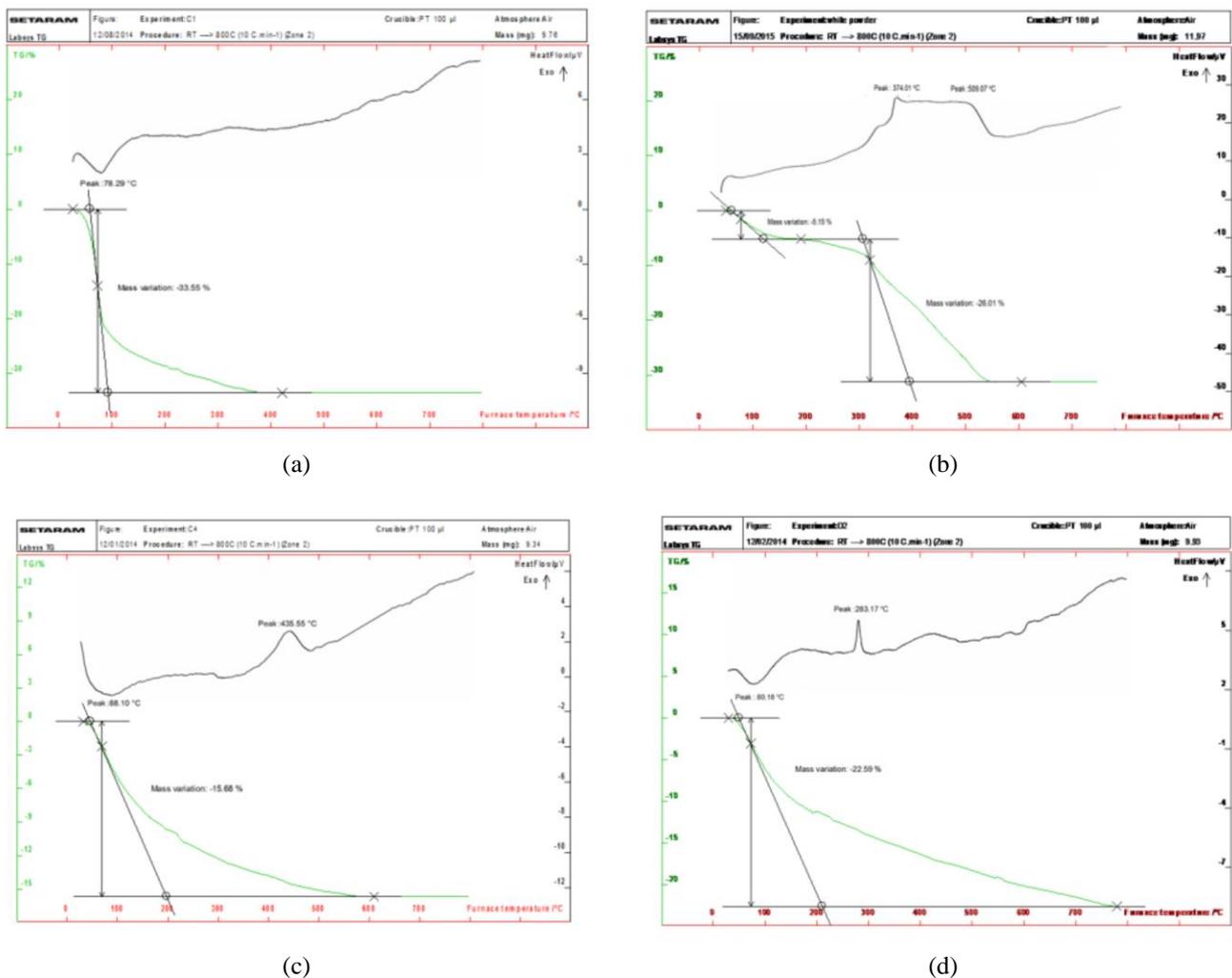
According to Fig. 5a, for as-synthesized silica, right after the ring touching water surface, the mass of silica increased sharply then decreased slowly. It shows a high affinity of as-synthesized silica to water. Conversely, on Fig. 5b, for silica modified with epoxy, after touching water surface, the mass

of silica increased insignificantly then reduced dramatically below zero. It reveals a weak interaction between the modified silica and water. Therefore, the modification changed the characteristic of material surface, reduced hydrophilicity of material. On the basis of this property, silica particles can be well dispersed in nonpolar environment.

Similarly, the measurement of wetting dynamic contact angle of silica modified with HMDS (Fig. 5c) was conducted, the result taken was  $100.01^\circ$ . Based on the increase in the dynamic contact angle from  $45.69^\circ$  to  $100.01^\circ$ , it can be concluded that the surface of silica changed from hydrophilic form to hydrophobic form.

The results can be explained by looking at the structure of silica surface and HMDS. During the modification procedure with HMDS, the hydrogen in  $-\text{OH}$  groups were replaced by  $-\text{Si}(\text{CH}_3)_3$  groups making the silica surface be covered by nonpolar and hydrophobic  $-\text{Si}(\text{CH}_3)_3$ .

Likewise, the dynamic contact angle of silica modified with *n*-butanol is  $99.35^\circ$  (Fig. 5d), much larger than the angle of as-synthesized silica. It once again indicates that the silica surface changed from hydrophilic form to hydrophobic form. According to the previous researches (Zhuravlev 2000; Jal et al. 2004; Takei et al. 1999), the results in dynamic contact angle can be explained as following: during the modification process, a part of  $-\text{OH}$  groups were replaced by the butoxyl groups. And these nonpolar hydrocarbon groups on the surface raises the dynamic contact angle.



**Fig. 6** TG/DTA curves of (a) silica as-synthesized, (b) silica/epoxy, (c) silica /HMDS and (d) silica/n-butanol

The DCA method results show that the different modification reagents give different dynamic contact angles. The modification with HMDS made the largest change in the characterization of silica surface (highest hydrophilicity) followed by *n*-butanol and epoxy resin reagents. The change from hydrophilicity to hydrophobicity is an important property which increases the interoperability of silica in nonpolar solvent.

The DCA results of silica modified with epoxy resin, HMDS and *n*-butanol are in consistency with the FTIR results, respectively.

### 3.4. Thermogravimetric analysis

Thermogravimetric analysis conditions: in the atmosphere, 100  $\mu$ L platinum cup, rate of increasing temperature: 10°C  $\text{min}^{-1}$  from room temperature to 800°C.

Fig. 6 shows the TG and DTA curves of as-synthesized silica and silica modified with epoxy resin, HMDS and *n*-butanol.

According to the diagram of as-synthesized silica (Fig. 6a), there is a strong decline in the mass of silica in the temperature range between 70°C and 150°C together with

endothermic process. Further increase in temperature resulted in a slight decrease in mass of silica. It can be explained by the high water adsorptivity of silica surface. From 70°C to 150°C, water was desorbed. The desorption of water is characterized by a peak at 78°C on the DTA curve. Further increase of temperature caused the dehydration of -OH groups on silica surface which is represented as following:

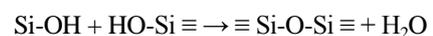


Fig. 6b shows the results for silica modified with epoxy; there was a slow reduction in silica mass which occurred in two steps. In the first step from 80°C to 120°C, the desorption of water from silica surface resulted in the decline of 5.1% in mass. In the second step, from 200°C to 550°C, the drop of 26.1% in mass was caused by the decomposition of organic compounds on silica surface. There is a wide exothermic peak in the range between 374°C and 509°C induced by the decomposition of the epoxy ring. These results confirm the presence of epoxy ring on silica surface. The epoxy groups are readily interacted with silica surface and are decomposed at 300°C. The results are in consistency with the previous studies of silica modified with epoxy (Sipaut et al. 2007;

Vansant et al. 1995; Vejayakumaran et al. 2008).

For silica modified with HMDS (Fig. 6c), the mass also decreased gradually by 15.6% as the temperature increased to 600°C due to the desorption of residual water on silica surface. Furthermore, another reason for the decrease in the mass of silica is the decomposition of the organic group on silica surface. According to the plot, there is a stable interaction between  $-\text{Si}(\text{CH}_3)_3$  groups of HMDS and silica surface; however, when the temperature was raised up to 200°C, this interaction can be broken. The wide exothermic peak at 435°C is supposedly caused by the combustion of HMDS.

For silica modified with *n*-butanol (Fig. 6d), there is also a decline in mass at the temperature below 100°C together with endothermic process caused by the evaporation of water adsorbed on silica surface. When the temperature further increased, the mass after modification dropped by 22.59%. In addition, the plot of silica/*n*-butanol shows an exothermic peak at 283°C which are not presented on the plot of as-synthesized silica. Therefore, it can be concluded that the exothermic process is caused by the decomposition of butoxyl groups on silica surface. The results once again indicate the presence of butoxyl groups on silica surface.

#### 4. Conclusions

Having synthesized silica with particles size ranging from 20 nm to 30 nm from rice husk using precipitation method. Having modified silica surface by different reagent: epoxy resin, hexamethyldisilazane and *n*-butanol. Having studied the structural characterization of silica particles before and after modification. The results of FTIR, SEM, DCA, TG/DTA confirmed the combination between silica surface and organic groups. The DCA method completely indicated the change of material surface from hydrophilic to hydrophobic. Having already evaluated the hydrophobicity of silica surface using dynamic contact angle measurement. The results show the largest change when using HMDS for modification, followed by *n*-butanol and epoxy resin as reagents. Having begun to study the application of dispersing nano-silica into lubricants, for lubricating and prevent metal corrosion.

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