



## Effect of silanization time on the surface modification of anhydrous borax

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### ABSTRACT

The silanization process to alter the surface properties of anhydrous borax powders was investigated using an organosilane of 3-(Trimethoxysilyl) propyl methacrylate. Silanization treatments were carried out in anhydrous toluene at constant reaction temperature and silane loading. For optimizing the surface coating in the silanization processes, different processing periods (1, 6, 12, and 24 hours) were attempted. The surface-treated powders were characterized by solubility and wettability tests.

### 1. Introduction

The search for alternative raw materials or the functionalization of existing raw materials for different purposes in the ceramic sector becomes a major necessity in parallel with the increase in energy demands along with the developing industry. The properties of ceramic materials reflect the nature of the powder used in the manufacturing process. The preferred powders may not have tailored properties, which will allow it to be immediately introduced into a process, or they may not be a naturally occurring material. In these instances, the functionalization of powders may be required [1].

There is an upsurge of interest in recent years to the surface modification since it is difficult to acquire the desired properties in one material. Surface modification of powders is a method that focuses on improving or modifying some specific properties that are not inherent. Some examples of surface properties that can be improved or modified are flowability, dispersibility, solubility, wettability (hydrophilic/hydrophobic properties), electrostatic, electric, magnetic, optical, colour, flavour, taste, particle shape/sphericity, sinterability and solid-phase reactivity [2].

The coating process includes the covering of particulate materials such as powders with a surrounding layer of a modifier agent. The uniform coatings in the range of a few nanometers to a few microns in thickness can be applied to a variety of substrates ranging

from submicron particles to millimeters. The modifier agent can be introduced to the system in solid, liquid, or suspension forms. Generally, from this point of view, coating processes can be classified as wet coating, dry coating, and melt coating [3].

There are many ways to create a hydrophobic surface by changing the surface properties with a reactive chemical that reduces surface energy. According to the principles of interface coupling, the hydrophilic entities can be changed to hydrophobic one by reducing the amount of hydroxyl groups on the particle surface, which is expected to chemically react, with various organic surface-modifying substances such as fatty acids and their derivatives, surfactants, resins, various organometallic compounds, titanate, and silane coupling agents [4].

To endow the powder surface with hydrophobicity, the coexistence of the low surface energy resulting from the coating of hydrophobic materials are the necessary conditions [5]. Among various modifiers, the silane coupling agent has attracted much attention due to its amphiphilicity [6] and low surface energy; thus, they are widely used due to the improvement of surface-related properties of powders. Fluorine-containing chemicals like fluoroalkyl silanes have been used as low surface energy materials for the fabrication of many superhydrophobic surfaces. These chemicals are not only expensive but also environmentally hazardous. Reducing the cost, increasing the durability of the final products, simplifying the fabrication process,

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and using nontoxic materials are a few concerns that need to be solved for large-scale manufacturing of superhydrophobic surfaces [7]. However, even being environmental friendly and non-toxic, some of the modifiers do not show hydrophobic properties. Therefore, for surface modification, the selection of modifier types is becoming more crucial, because it might be difficult to find a modifier that can work well with host particles.

Although silane treatment is an effective and popular method for the surface coupling of materials, researchers have reported several problems that can be faced during the process. The most important one is the control of the hydrolysis and condensation reactions, which are the key processes that directly affect the success of the treatment. The rate and duration of these reactions depend on many factors, such as the properties of the surface, the type of organosilane to be used, the type of solvent to be used, the water content, solution pH, and the silane concentration [8]. However, there is uncertainty with regard to whether silane molecules are sufficiently attached to oxide surfaces during silanization time. Unfortunately, there are not many studies in the literature that examine the relationship between silanization time and coating/grafting yield.

Borates are indispensable constituents of most industrial ceramic and glass products, offering both excellent glass-forming and fluxing properties [9,10]. Anhydrous borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) produced via fusion of hydrated forms of borax at approximately 1000 °C [11] is preferred to other hydrous forms in high-temperature applications since it does not cause any foaming problems arising from dehydration of the water [10]. However, anhydrite form of borax is water-soluble due to its inherent properties like the hydrated forms. The solubility values of anhydrous-, penta- and decahydrate borax are given in the product datasheet to be 3.15, 4.63, and 6.15 wt.% at 25 °C, respectively [12].

The various dissolved salt ions within the water can move to the material in the manufacturing process (e.g., during glazing by immersion) due to diffusive and convective transport. The dissolved salts can crystallise at the surface or inside the material when environmental conditions change, such as temperature [13]. Soluble salts may cause severe and repetitive damage to porous materials, due to crystallisation and hydration pressure, and also thermal expansion. Individual or the combined effects of these factors generate interior stresses within the material, eventually leading to microscopic defects [14-17]. Additionally, the mass loss and moisture absorption due to the solubility and hygroscopic nature of borates, respectively, causes problems in mass balance in multicomponent systems [18]. Moreover, solubility and ion release of some borates in aqueous suspensions negatively affect dispersion stability [19].

The industrial applications of some borates are limited due to their solubility behaviour in aqueous systems

and cause some application failures unless the preventive precautions against interaction with water are taken. The high-cost fritting process is the only industrial method currently applied to make water-soluble borates insoluble. Despite its commercial importance, an industrially alternative method to the fritting process to prevent solubility of borates has not yet been found. However, a few studies on the production of lower-cost calcined borate, as an alternative approach, are available in the literature [19]. This study aims to identify the conditions for the preparation of surface-modified anhydrous borax powders that possess water-insoluble or poorly soluble properties for their utilisation in aqueous systems without the need for a fritting process. It is also aimed to pave the way for developing new boron powders, having low solubility, and high hydration resistance by a facile and cost-effective route.

## 2. Materials and methods

### 2.1. Materials

Anhydrous borax powders (ANB) of purity 99% and size less than 0.5 mm was supplied by Eti Mine Enterprises (Turkey). ANB powders have angular-shaped, discrete, and non-agglomerated particles. Before the surface modification, anhydrous borax powders were grinded for 2 h in a planetary ball mill to obtain particles smaller than 100  $\mu\text{m}$ . Their measured  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  values were 6.5  $\mu\text{m}$ , 40.6  $\mu\text{m}$ , and 100.6  $\mu\text{m}$ , respectively, and the BET surface area was 1.0022  $\text{m}^2/\text{g}$ . The resulting anhydrous borax powders are denoted as ANBp.

The organosilane coating material 3-(Trimethoxysilyl) propyl methacrylate (TMSPM, CAS No: 2530-85-0) was purchased from Sigma-Aldrich and was directly used without further purification. Table 1 shows some properties of the organosilane coupling agent.

Table 1. Some properties of silane coupling agent.

Property	Value
Formula	$\text{C}_{10}\text{H}_{20}\text{O}_5\text{Si}$
Molecular Weight (g/mol)	248.35
Density ( $\text{g}/\text{cm}^3$ )	1.045
Boiling Temperature ( $^{\circ}\text{C}$ )	190
Ignition Temperature ( $^{\circ}\text{C}$ )	265

### 2.2. Silanization processes

The ball-milled ANBp were dried at 105 °C for 24 h, prior to reaction with the organosilane coupling agent, to remove physically adsorbed water. Anhydrous toluene (CAS No: 108-88-3) was used as the solvent since the ANBp is less soluble in toluene than water.

The order in which the silane, the ANBp, and the solvent are to be mixed during the coating process was determined by the preliminary experiments accordingly with the similar studies in the literature. The past studies show that silane (e.g., 3-APTES) is to be

incorporated before [20] or after [21] the addition of the raw material to the solvent (e.g., toluene, ethanol). Besides, the silane is added into the mixture of solvent and raw material in diluted state and at specified intervals [21] or in undiluted state and at one time [20], and accordingly, the mixing time is changing between 1 and 24 hours. Both methods have been tried with TMSPM silane to form a suitable coating procedure for the surface modification of the ANBp. While the solvent and raw material were mixed in a magnetic stirrer, 1 mL of diluted silane was added every 15 minutes. This necessitated the addition of 2.5 mL of silane in 25 mL of dilution, needing a mixing time of more than 6 hours (25 times x 1 mL x 15 minutes). It was determined that some of the ANBp were dissolved during this process. As a result of preliminary experiments, it was found that the most effective results were achieved when the silane was added to the solvent directly, before the addition of the raw material. Therefore, it was decided to add the raw materials after the silane was mixed in the solvent.

ANBp were treated with 2.5 mL of TMSPM coupling agent in toluene with the following procedure. The silane coupling agent was directly dropped into the 100 mL of solvent (toluene) in a 1000 mL three-neck flask. One hundred grams of ANBp were added into the silane-doped toluene solutions for each set of experiments, and the resulting mixture was magnetically stirred under the different silanization times (1, 6, 12, and 24 hours) to realise the surface modification of borax powders. To assure the completion of the silane-powders surface reaction, the mixed solutions were vigorously stirred at 750 rpm in a closed system for designed processing periods at room temperature. The schematic presentations of the experimental set-ups used in the experiments are shown in Figure 1.

At the end of the modification treatment, the solvent was removed by filtration using a filter paper having a pore size of 2-4  $\mu\text{m}$ , and then surface-modified anhydrous borax powders were obtained after drying for 2 h at 60 °C. The amount of anhydrous borax that was dissolved during the silanization process was measured to be  $0.2\pm 0.05$  wt.%, and this mass loss was assumed to be negligible. The separated powders from filter paper were kept to be used for further measurements and characterisations.

### 2.3. Characterisation of silane-modified anhydrous borax powders

The efficiency and success of the effort to modify the surface-related properties of ANBp were evaluated in terms of their interactions with water. In this context, the solubility and wettability properties of silane-modified ANBp are investigated.

#### 2.3.1. Determination of the solubility of silane-modified ANBp

The efficiency of silane coatings was analysed through variations in the solubility of powders caused by variations in the processing periods. Due to the inherent hydrophilic nature of water-soluble boron compounds, when natural ANBp remain in the aqueous medium for a long time, some part of them dissolve, and some part of them convert into hydrated forms, while the rest remain pristine. However, the surface-modified ANBp will float or suspend on the same condition if its surface becomes hydrophobic. Admittedly, the better the surface modification effect provides, the higher the coating efficiency, resulting in lower solubility.

The coating yield of the organosilane coupling agent on ANBp was evaluated by solubility tests. The powders

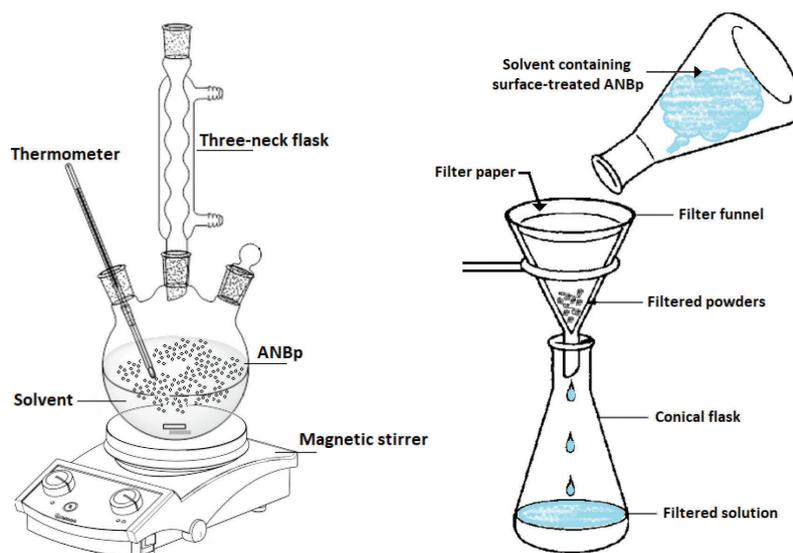


Figure 1. Experimental set-ups for silanization and filtration process.

were first dispersed into 10 grams of coated material and added to 100 mL of distilled water and vigorously mixed by a magnetic stirrer at 750 rpm for 60 min at room temperature. The pristine and surface-treated powders were washed with distilled water, followed by filtered and dried. The operation was repeated three times to ensure whether the same yield is achieved on each sample series.

The amounts (g) of maximum soluble powders ( $m_1$ ), insoluble parts of surface-coated ( $m_2$ ) and uncoated ANB powders ( $m_3$ ) were weighed accurately for each set of parameters, and coating yield (%) was determined using the following equation (Eq.1).

$$\text{Coating yield (\%)} = \left( \frac{m_2 - m_3}{m_1} \right) \times 100 \quad (1)$$

### 2.3.2. Determination of the surface wettability of silane-modified ANB powders

The hydrophobicity of the surface-modified ANBp samples obtained under the different silanization time was compared so as to determine the optimal processing period for surface modification. For comparison, the pristine anhydrous borax sample was also prepared and tested under the same conditions.

The tablet discs with 1.5 cm diameter were made by compression under a load of 10 kN using a uniaxial manual hydraulic press, and labelled discs were kept in a desiccator until contact angle measurements. The water contact angles (WCA) on tablets shaped from powder were recorded with a liquid-solid interface analyser (KSV Attension ThetaLite TL 101 Optical Tensiometer), and at least three repeat measurements were conducted for each to be tested sample.

## 3. Results and discussion

The silanization of the oxide surfaces is known to proceed via solvent-dependent mechanisms. In the presence of sufficient water in the system, the silanes produce monolayer structure by the horizontal orientation of its functional groups (e.g., 3-APTES), while the water in the system is wholly consumed or the environment is anhydrous (e.g., toluene), the silanes can produce multilayer and partial miscellaneous complex formations [22,23]. As a particular case different from the literature, the ANB powders have a very low solubility in toluene, whereas they may contain some hydroxyl sites on the surface, where the silanes may approach. In this situation, an assumption of the monolayer silane formation occurring until the consumption of the hydroxyl groups may arise, and later the multilayer silane formation in toluene may take place. In the latter condition, the uniformity of the silane films may weaken.

As mentioned in the literature, the agents of various silane families can also be oriented in different densities on the same oxide surface [22]. The density of the silane film may affect the abrasion resistance of the ANB powders. If the layer of silane coating is weak, or with low surface coverage density, then the silane films become more vulnerable to the abrasion or other effects under the stringent physical conditions, and thus, they are not able to hinder the hydration and dissolution of the ANB powders (Figure 2).

On the other hand, Kyaw et al. claim that the silane chemicals can be oriented in different ways to attach an oxide surface, and each orientation offers a different contact angle. In the case where the amino end group ( $\text{NH}_2$ ) does exist in silane structure (e.g., 3-APTES)

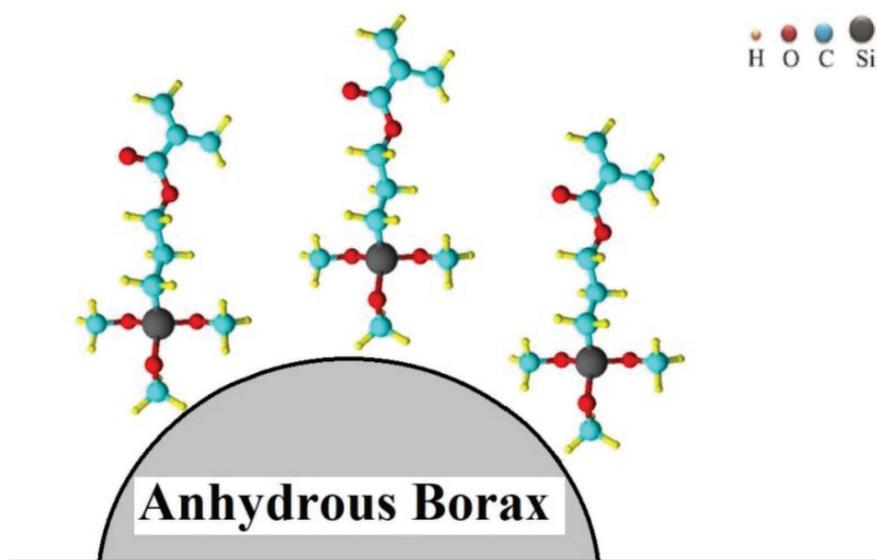


Figure 2. The surface of anhydrous borax with TMSPM silane coating.

interacts with the oxide surface, and the other end group ( $\text{Si}-\text{CH}_3$ ) oriented to water; the highest contact angle is  $59^\circ$  where water is repulsed most, and the lowest contact angle observed is  $41^\circ$  [24]. It has been stated that the wettability value of the surfaces modified with TMSPM silane has contact angle values ranging from  $70$  [25] -  $107^\circ$  [26] depending on the coating environment in similar studies in the literature.

Anhydrous borax powders were silanized in toluene, which containing  $2.5$  mL solution of TMSPM at  $25^\circ\text{C}$  for at  $0$ ,  $1$ ,  $6$ ,  $12$ , and  $24$  h. The values of  $m_0$ ,  $m_1$ ,  $m_2$ , and  $m_3$  used to determine the solubility values of the samples modified with various silanization times are given in Table 2. The experimental error was less than  $0.1\%$  for all the solubility measurements.

The changes in the solubility values of ANB powders depending on the processing period according to the data in Table 2 are plotted as Figure 3. In addition, the coating efficiency values calculated according to the formula in equation 1 by using the data in Table 2 are plotted as Figure 3.

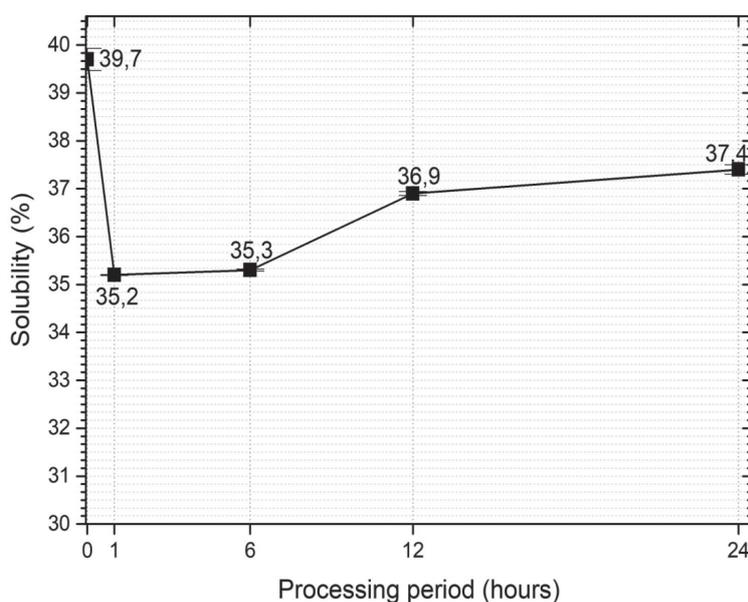
According to the graph in Figure 3, while the solubility values of uncoated ANB powders was about  $40\%$ , this value decreased to  $35\%$  after  $1$  hour of silanization, thus, the solubility of ANB powders was reduced by  $5\%$  after  $1$  hour of silanization. However, the solubility of ANBp increased again with an increasing processing period, and the silanization time of  $24$  h resulted in the solubility of  $37.14\%$ . This result indicates that as long as borax powders remain in the coating environment for more than  $1$  hour, the efficiency of coating their surfaces with silane decreases or there may be deterioration of the silane layer on the surface.

According to the graph in Figure 4, the coating efficiency of TSMPSM silane on the ANB powders surface appears to decrease with increasing processing period. The coating efficiency, which was determined as  $12.78\%$  after  $1$  hour of the processing period, decreased by approximately half after  $24$  hours and decreased to  $6.15\%$ .

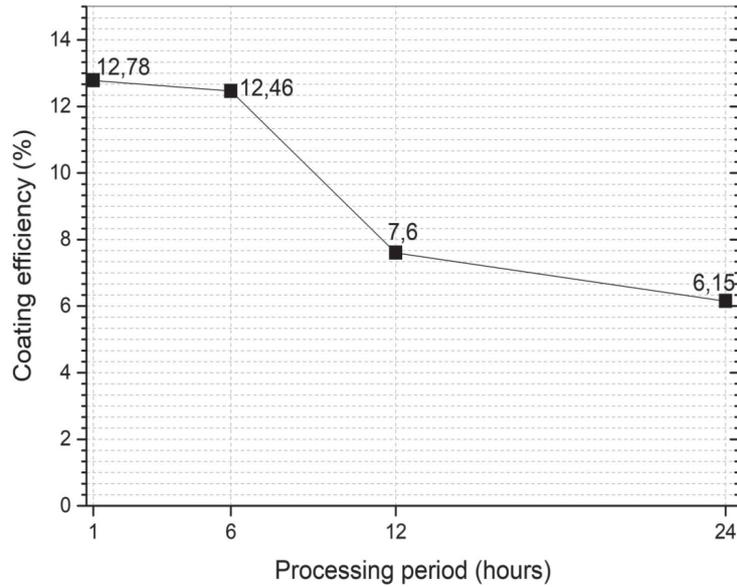
The reduction in coating efficiency and solubility values due to the increase in coating time can be explained

**Table 2.** ANB powder amounts in solubility tests as a function of processing period.

Processing period (h)	The amount of processed powder ( $m_0$ ), (g)	The amounts of maximum soluble powders ( $m_1$ ), (g)	The insoluble parts of surface-coated powders ( $m_2$ ), (g)	The insoluble parts of uncoated powders ( $m_3$ ), (g)
0	10	$3.97 \pm 0.23$	-	$6.03 \pm 0.23$
1	10	$3.52 \pm 0.01$	6.48	$6.03 \pm 0.23$
6	10	$3.53 \pm 0.02$	6.47	$6.03 \pm 0.23$
12	10	$3.69 \pm 0.04$	6.31	$6.03 \pm 0.23$
24	10	$3.74 \pm 0.10$	6.26	$6.03 \pm 0.23$



**Figure 3.** Solubility values of ANB powders as a function of the processing period.

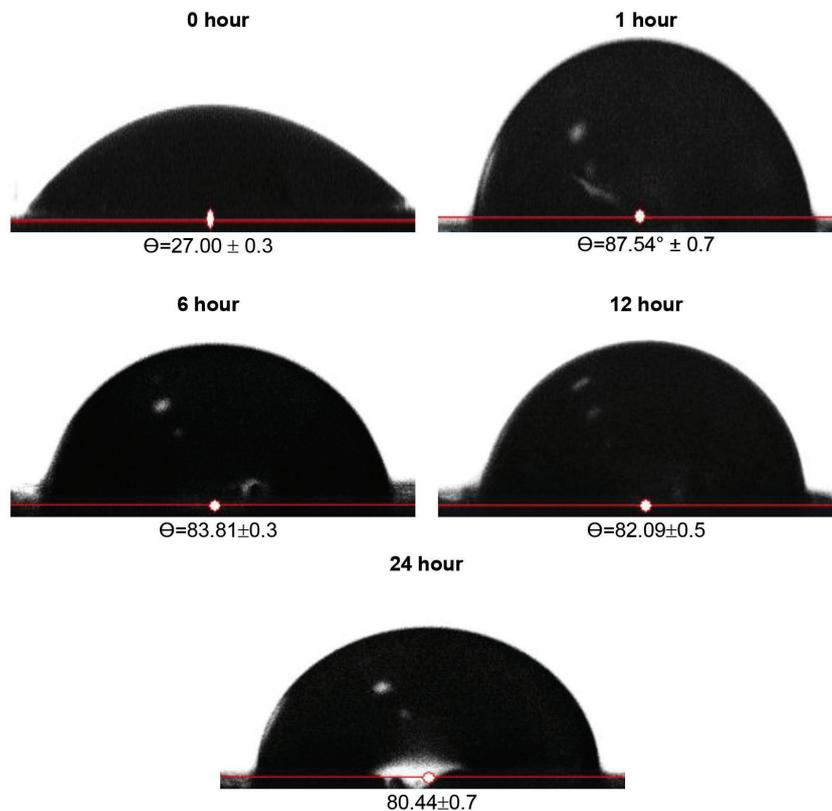


**Figure 4.** Coating efficiency of ANB powders as a function of the processing period.

as follows. It is well known that the silanes are sensitive to moisture, and they tend to be aggregated and can form lumps on the surface in the presence of moisture [27]. Besides, some authors stated that sufficient time is required for silanization on the surface, and longer time results in silane polymerisation and non-uniform coverage [28-29-30]. As a result of its interaction with water for a long time, the agglomerated or lumped TMSPM silane is thought to cause a decrease in solubility of ANB powders.

Water contact angles of ANB powders that are silanized in the constant concentration of TMSPM in toluene as the function of silanization time are presented as Figure 5.

As presented in Figure 5, the contact angles of the samples were in the range of 27° to 87.54°, with a standard deviation below 1°. Water contact angle (WCA) of the surface-treated ANBp notably increased as a function of silanization time, from 27° for the uncoated ANBp to



**Figure 5.** Water contact angles of ANBp that are silanized in the constant concentration of TMSPM in toluene as the function of silanization time.

87.54° after 1 hour of silanization. However, the WCA values of the ANBp were observed to decrease slightly with the increasing silanization time, and eventually reach the minimum (80.44°) at the highest processing period (24h). In general, high contact angles were observed in all the coated samples that reveal significant hydrophobic behaviour compared to the uncoated state. These results suggest that the ANBp surface could be switched from hydrophilic to hydrophobic with changing contact angle from wetting 27° to less-wetting 88°. On the other hand, the long processing period for silanization caused also a reduction in the wetting angle of ANBp, as observed in the result of solubility and coating efficiency values. This result suggests that the surface-modified powders with high hydrophobicity value will not guarantee that they may possess a low solubility in the aqueous environment.

#### 4. Conclusions

The surface functionalization of ANBp with TMSPM silane is investigated under different processing periods in order to reveal the best coating performance. The silanization process of ANB powders at a constant TMPSM concentration was carried out in anhydrous toluene solvent for 1, 6, 12, and 24 hours. The revealed results in terms of the solubility, coating efficiency, and wetting angles indicate that the processing period of 1 hour is the best silanization time under the given condition. However, the long processing period for silanization caused a reduction in the values of solubility, coating efficiency, and the wetting angle of ANBp. It is contemplated that prolonged staying of ANBp in the coating environment may lead to agglomeration or lumping of the TMSPM silane on the ANBp surface, thereby reducing coating efficiency, eventually leading to a decrease in solubility of ANB powders. In addition, it was well understood that the surface-modified powders with high hydrophobicity value would not guarantee that they have a lower solubility in the aqueous environment. Consequently, the surface modification was observed to invert the inherent hydrophilic nature of boron compounds and provided a hydrophobic surface having a water contact angle ~90°. So, such modified-surfaces for boron-containing minerals not only prevent to dissolve, but they also keep themselves even from moisture, thereby preventing uncontrolled structural changing and offer mass balance.

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