Fabrication of Superhydrophilic TEOS-Lactic acid Composite Films and Investigation of Biofouling Behaviour

Tugce Ervan¹,a, Mehmet Ali Kucuker ²,b, Ugur Cengiz³,c,*

¹ORCID: 0000-0003-0723-4814  
²ORCID: 0000-0001-9648-8925  
³ORCID: 0000-0002-0400-3351

¹Istanbul Technical University, Faculty of Construction, Department of Environmental Engineering, ITU Ayazağa Campus, 34467, Istanbul, Türkiye  
²Izmir Institute of Technology University, Faculty of Engineering, Department of Environmental Engineering, 35430, Izmir, Türkiye  
³Canakkale Onsekiz Mart University, Faculty of Engineering, Department of Chemical Engineering, Surface Science Research Laboratory, 17020 Canakkale, Türkiye

*Corresponding author.  
E-mail address: ucengiz@comu.edu.tr

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Abstract

Phytoplankton and diatom microalgae species cause biofouling by adhering to the surfaces, especially in closed cultivation systems such as tubular photobioreactors. This biofilm formation blocks the sunlight; after harvesting, it is necessary to clean the reactor. This cleaning process causes loss not only in time and finance but also in terms of environmental pollution due to using toxic chemicals and excess water usage. This study aimed to investigate the reduction of the microorganism cell adhesion on the hybrid surface. To succeed in this, the composite surface of tetraethoxysilane (TEOS) and lactic acid (LA) was prepared by the sol-gel process. Then the hybrid surfaces were coated on glass slides by the dip coating method. The wettability performance of the TEOS-LA hybrid surface was investigated using contact angle measurement and light transmittance. The wettability result showed that the superhydrophilic surface having 54 mJ/m² of surface free energy values was obtained. Furthermore, the increased lactic acid content of the composite films increased the surface free energy (SFE) values, decreasing the water contact angle. A pencil hardness test characterized the mechanical strength of the surfaces, and it was determined that the hardness of the composite films was decreased by increasing the LA content of the composite films. Resultantly, it is found that the TEOS-LA superhydrophilic composite film reduces the adhesion of microalgae.

Keywords: Sol-gel; Composite; Microalgae; Bioadhesion; Lactic acid; Eco friendly

1. Introduction

Stepping up day by day after the industrial revolution worldwide, industrialization has caused ecological problems such as environmental pollution, climate change, and various diseases. This situation has led scientists to research how to produce sustainable, eco-friendly, and economical materials. Usage of microalgae to bring down resource consumption is one of the most common green engineering trends of recent times. Microalgae are unicellular photosynthetic eukaryotic creatures, and there are 30000 species worldwide. They are lived in oceans and lakes. Diatom, phytoplankton, blue-green algae, brown and green flagella, and dinoflagellate are some of the species known as microalgae [1]. According to some investigations, they have been found that microalgae are unicellular; however, some species are multicellular. For example, Heimann and Huerlimann reported that microalgae are multicellular because they possess one plastid and chlorophyll a and b, mucus sheath [2]. Furthermore, their high nutritional value and organic components are used as feed for aquarium fish, poultry, cats, and dogs, as a natural dye in buildings, biocatalyst in genetic engineering applications [3]. In addition, they are utilized as the raw material of the bioplastic to decrease the petroleum-based plastics' adverse environmental impact [4].

Adhesion consists of three stages: primary adhesion, irreversible adhesion, and biofilm density. Depending upon the negative or positive surface charges of all microorganisms are affected by the adhesion strength between the cell and surface via
physicochemical interactions [5]. Microalgae harvesting occurs in closed and open systems, flat panels, stirred tanks, hybrid type, helical type, airlift, bubble column photobioreactors (PBRs), and raceway ponds [6]. Some optimum conditions are required for microalgae harvesting to take place. These can be listed as the light, CO₂, and PBR designs. As a result of limited scattering of light, biofilm layer and microalgae adhesion inside the PBR [7]. Besides little light, cell-surface interaction, microalgae surface free energy, and hydrophilicity or hydrophobicity of microalgae caused adhesion on any surface [8,9]. Microalgae adhesion formation is decreased by altering the thin films' wettability properties [10-12].

Superhydrophobic surfaces were defined as water contact angles lower than 10° and showed antifogging, self-cleaning, and antireflective properties [12,13]. However, microalgae behavior on superhydrophobic surfaces is also exciting [14]. Koschitzli et al. reported that the superhydrophilic surface successfully results against the microalgae adhesion, especially the pure culture of microalgae harvesting, due to the absence of the silt [14]. In this study, the TEOS-LA super hydrophilic composite thin films were fabricated containing different LA content having high light transmittance. The super hydrophilic TEOS-LA composite surfaces were also tested in pure microalgae cultures of Chlorella sorokiniana (C. sorokiniana), Nannochloropsis sp., and Chlorella vulgaris (C. vulgaris). Increasing the composite surface's LA content decreased the water contact angle from 79 to 8°. In addition, the surface hardness values of the composite surface changed from 9H hardness to 6B softness with increasing the LA content. The microalgae adhesion test indicated that the biofilm formation is decreased on superhydrophilic TEOS-LA surfaces.

2. Materials and Methods

2.1. Materials: Methanol (MeOH), Tetraethoxysilane (TEOS), and Lactic acid (LA) were purchased from Aldrich. The test liquids of ultra-pure water, Diiodomethane (MeI2), α-Bromonaphthalene (α-BN), and Formamide (F) were purchased from Merc.

2.2. Fabrication of transparent TEOS-LA Surfaces: The TEOS-LA solution was prepared with different ratios of LA content, as given in Table 1. Firstly, the TEOS, LA, MeOH, and water were mixed in 100 ml of the reactor, and then the reaction was heated from 60 °C. Next, the sol-gel reaction was stirred for 3 h at 60 °C, and 0.1 mL of NH₄F (0.1 M) was added to the reaction medium to catalyze. The sol-gel reaction lasted 4 h at 60 °C in reflux.

<table>
<thead>
<tr>
<th>Code</th>
<th>MTEOS (g)</th>
<th>MLA (g)</th>
<th>MMEOH (g)</th>
<th>Mwater(g)</th>
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<td>0</td>
<td>25.50</td>
<td>2.65</td>
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<tr>
<td>TLA₁₇</td>
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<td>1.06</td>
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<tr>
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<td>25.50</td>
<td>2.65</td>
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<tr>
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<td>25.50</td>
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<tr>
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<tr>
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<td>4.88</td>
<td>25.50</td>
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<td>8.48</td>
<td>25.50</td>
<td>2.65</td>
</tr>
</tbody>
</table>

The TEOS-LA composite thin films were fabricated with the dip coating method. First, the glass slide was cleared sequentially in ethanol and water and dried in an oven at 85 °C for 1 h. Next, the glass slides were stood for 2 minutes dipping with a vertically moving mechanical immersion at a speed of 6.53 mm/sec. Finally, the coated glass slide was kept in an oven at 85 °C (Referans istenmiş ancak, bu niz makaleden almamıştik hocam ben şöyle hatırlıyorum).

2.3. The surface characterization of composite films: The water contact angle (WCA) of the composite films was determined by the Attention Theta contact angle meter. The static WCA values were determined after removing the needle from 5 μL droplets [13]. Five different CA measurements were done on each copolymer film surface, and average CA values were reported with standard deviations of ± 1°. The Van-Oss Good method calculated the composite films' surface free energy (SFE) using test liquid contact angle values [15,16]. Light transmittance of the composite films was measured by Analytical-Jena model ultraviolet-visible spectroscopy (UV – VIS). Finally, the scratch resistance of the composite surface was characterized by a pencil hardness tester (Model 291, Erichsen) [13]. The scratch test was made using different hardness pencils having 6 mm lengths and flat tips. Another mechanical test is the peeling tape test of the coating surface. In this test, 3M-scotch tape (1 x 2 cm) was adhered to the composite surface. Then, 10 Pa pressure was applied to the tape for strong adhesion. Next, the bant was removed from the surface, and the tested surface was characterized by light transmittance compared to the untested region. The abrasion test of the composite coating was determined using H₂SO₄ (1M), NaCl (3.5 %), and NaOH (2.5 M) solutions. The composite coatings were immersed in test liquids for 2 - 3 weeks, and it was checked whether there was abrasion against test liquids on the coating surfaces [17]. Finally, the adhesion behavior of microalgae species (C. vulgaris, C. sorokiniana, and Nannochloropsis sp.) on the superhydrophilic TLA₁₈₇ composite film was determined to keep with microalgae medium for 14 days (Figure 1).
3. Results and Discussions

The light transmittance of the composite surfaces is given in Figure 2. This figure indicated the optical transmission of the TEOS-LA composite films with a bare glass slide. All composite films have exhibited higher optical transmittance, almost as bare glass.

![Fig 2. Optical transmission of the TEOS-LA composite films](image)

The contact angle of the water, MeI₂, α-BN and F result on the composite surface, and the SFE of the composite films are given in Table 2. This table indicated no linear connection with the rising LA content of the composite films. The lactic acid molecular structure has two –OH groups, so the LA surface tends to be hydrophilic. However, the number of the –OH group decreased with the sol-gel reaction’s progression, especially the LA’s lower content. Because the sol-gel reaction between TEOS and LA continues with the attack silanol structure of TEOS on the –OH group of LA. While the water contact angle value is high at low LA content, the water contact angle values decrease at high LA content due to the free –OH group, and superhydrophilic surfaces were obtained in Table 2.

![Table 2. The contact angle values of the test liquids and SFE values calculated by the Van Oss-Good Method](table)

<table>
<thead>
<tr>
<th>Code</th>
<th>Water</th>
<th>MeI₂</th>
<th>α-BN</th>
<th>F</th>
<th>χ_W</th>
<th>χ_H</th>
<th>χ_O</th>
<th>χ_AB</th>
<th>χ_Total</th>
</tr>
</thead>
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<td>48</td>
<td>34</td>
<td>26</td>
<td>36.4</td>
<td>1.7</td>
<td>35.8</td>
<td>15.7</td>
<td>52.1</td>
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<tr>
<td>TLA8.8</td>
<td>79</td>
<td>61</td>
<td>48</td>
<td>69</td>
<td>29.3</td>
<td>0.0</td>
<td>12.8</td>
<td>0.2</td>
<td>29.5</td>
</tr>
<tr>
<td>TLA15.0</td>
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<td>56</td>
<td>33</td>
<td>19</td>
<td>34.4</td>
<td>3.6</td>
<td>25.3</td>
<td>19.1</td>
<td>53.5</td>
</tr>
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<td>41.0</td>
<td>16.5</td>
<td>52.0</td>
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<tr>
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<td>17</td>
<td>36.9</td>
<td>1.4</td>
<td>55.6</td>
<td>17.3</td>
<td>54.3</td>
</tr>
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<td>44</td>
<td>18</td>
<td>19</td>
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<td>0.7</td>
<td>56.9</td>
<td>12.9</td>
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</tr>
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<td>24</td>
<td>15</td>
<td>38.0</td>
<td>1.2</td>
<td>55.4</td>
<td>16.6</td>
<td>54.5</td>
</tr>
<tr>
<td>TLA45.1</td>
<td>8</td>
<td>49</td>
<td>19</td>
<td>17</td>
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<td>56.1</td>
<td>15.3</td>
<td>53.8</td>
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<td>TLA50.2</td>
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<td>54.9</td>
<td>14.9</td>
<td>54.2</td>
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</table>

The variation of WCA depending on LA content decreased sharply up to 10 % (wt) LA content. However, a constant WCA plateau was obtained despite increasing the LA content from 10 to 25 % (wt) as given in Figure 3. In addition, total SFE values (χ_Total) of the composite films were calculated by the Van-Oss Good method using the test liquids tabulated in Table 2.
Fig 3. Changed with WCA and SFE values depending on the LA content of the composite films

Usually, the variation of SFE values changes opposite the contact angle values of the test liquids. An increasing contact angle results in a decreasing SFE value, as given in Figure 3. The mechanical stability of the composite film was tested by scratching [13], and the hardness test results are shown in Table 3.

<table>
<thead>
<tr>
<th>Code</th>
<th>9H</th>
<th>H</th>
<th>F</th>
<th>B</th>
<th>2B</th>
<th>3B</th>
<th>5B</th>
<th>6B</th>
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<td>x</td>
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<td>x</td>
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</tr>
<tr>
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<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
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<td>x</td>
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</tr>
</tbody>
</table>

The findings showed that while the hardest coating is T₀₀ having a 9H value, the softest coating is TLA₂₃₅ having 6B due to the rising organic part of the composite surface depending on LA content. An increasing organic amount of the composite layer resulted in a decrease in the hardness [18]. Miller et al. reported that higher PLA content results in softer films [18].

The TLA₁₈₇ surface was selected to investigate microalgae adhesion due to the lowest contact angle values. The test was carried out for 14 days in 3 types of microalgae. The microalgae concentration on day 14 is measured as 3.2 g/L for C. vulgaris, 2.8 g/L for C. sorokiniana, and 3.5 g/L for Nannochloropsis sp. The TLA₁₈₇ coated and uncoated glass slides were taken out in the microalgae medium after a harvesting period of 14 days, as shown in Figure 4. This figure showed that biofouling occurred on both surfaces. However, the biofouling of C. vulgaris is less than other microalgae. In addition, it is shown in Figure 4 that the TLA₁₈₇ coated surface showed partial success on biofouling.
Fig 4. The biofouling performance of TLA\textsubscript{18.7} interaction with microalgae species. The left side is coated, and the right side is uncoated on images a) \textit{Nannochloropsis sp}. b) \textit{C. vulgaris}, and c) \textit{C. sorokiniana}, respectively

4. Conclusions
The dip coating method successfully fabricated superhydrophilic TEOS-LA composite films in this study. The sol-gel reaction between TEOS and LA was prepared at constant TEOS content with increasing LA. The superhydrophilic composite films having 8° of the contact angle were obtained without nanoparticle adding. This point of view is important in terms of environmental sustainability for developing biocompatible materials with reduced chemical content. The Van-Oss Good method calculated the SFE values of the composite films. The SFE results increased from 28.5 to 54.5 by increasing the LA content due to the rising OH unit on the composite films. However, a decrease in the WCA and an increase in the SFE did not have a linear relationship to LA content. The hardness test indicated that an increase in the organic part of the composite films resulted in a decreasing hardness. As a result of the bioadhesion test showed that the superhydrophilic TLA\textsubscript{18.7} thin film reduced the biofouling formation in the microalgae.

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Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement
All graphs and data obtained or generated during the investigation appear in the published article.

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Author’s Contributions
Author #1 Tuğçe Ervan: Experimental, Methodology, Writing – original draft.
Author #2 Mehmet Ali Küçüker: Writing – review & editing.
Author #3 Uğur Cengiz: Writing – review & editing, Supervision.

Ethics
There are no ethical issues with the publication of this manuscript.
References


