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Wetting Behavior of Dental Implants

In-Hye Kim, Tae-Yup Kwon and Kyo-Han Kim

Abstract

Titanium (Ti) and titanium alloys are widely used in biomedical devices and components, because of their desirable properties, such as relatively low modulus, good fatigue strength, formability, machinability, corrosion resistance, and biocompatibility. However, Ti and its alloys cannot meet all of the clinical requirements. Therefore, surface modification of Ti has been often performed to improve the biological, chemical, and mechanical properties. Various modifications of surface properties have been investigated to predictably improve the osseointegration of Ti implants. The rate and quality of osseointegration in Ti implants are related to their surface properties. A multiplicity of implant surface forms exist engineered with mechanical features that physically interlock the implant with bone. Various strategies have been utilized to improve bone integration of Ti-based implants. For example, surface grit blasting, acid-etching and anodization methods enhance cell growth, improving implant fixation through increases in interlocking surface area and alterations of oxide thickness. On the other hand, surface composition and hydrophilicity are parameters that may play a role in implant-tissue interaction and osseointegration. Highly hydrophilic surfaces seem more desirable than hydrophobic ones in view of their interactions with biological fluids, cells and tissues. Several recent studies have shown that the surface energy of biomaterials strongly has influence the initial cell attachment and spreading of osteoblastic cells on the biomaterial surfaces. Hallab et al. said that surface energy might be a more important determinant of cell adhesion and proliferation, and might be more useful than surface roughness for generating cell adhesion and cell. It may have the influence on protein adsorption and the structural rearrangement of the proteins on the material. Therefore, understanding the relationship between surface energy and cell adhesion on different biomaterials will facilitate the design of optimized implant material surfaces and subsequently the
cell attachment. Surface energy is an important parameter of the material surface. It is affected by several surface characteristics, such as chemical composition, surface charge, and microstructural topography. Many papers reported that surface energy is one of important surface characteristics parameter of modified titanium surfaces. Given the importance of surface wettability of dental implants surfaces in the achievement of osseointegration, the surface free energy values for a given material, obtained by various methods and with use of different measuring liquids, are not consistent. Thus, we provided a review article of the surface modification on titanium surface and the surface wettability. The relationship between CAs and surface preparations was determined in this review.

**Keywords:** surface free energy, contact angle, dental implant

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1. Introduction

Titanium (Ti) and titanium alloys are widely used in biomedical devices and components because of their desirable properties, such as relatively low modulus, good fatigue strength, formability, machinability, corrosion resistance, and biocompatibility. [1] However, Ti and its alloys cannot meet all of the clinical requirements. Therefore, the surface modification of Ti has been often performed to improve the biological, chemical, and mechanical properties. [2] Various modifications of surface properties have been investigated to significantly improve the osseointegration of Ti implants. [3] The rate and the quality of osseointegration in Ti implants are related to their surface properties. A multiplicity of implant surface forms exists, which are engineered with mechanical features that physically interlock the implant with bone. Various strategies have been implemented to improve bone integration of Ti-based implants. [4, 6] For example, surface grit blasting, acid etching, and anodization methods enhance cell growth, improving implant fixation and thereby increasing interlocking surface area and altering oxide thickness.

On the other hand, surface composition and hydrophilicity are parameters that play an important role in implant–tissue interaction and osseointegration. [7] Radiofrequency glow discharge has been implemented to increase surface energy and to enhance cell binding. Highly hydrophilic surfaces seem more desirable than hydrophobic ones in view of their interactions with biological fluids, cells, and tissues. [8] Recent studies have shown that the surface energy of biomaterials strongly has influence on the initial cell attachment and spreading of osteoblastic cells on the biomaterial surfaces. [9, 10] Hallab et al. [11] suggested that surface energy may be a more important determinant of cell adhesion and proliferation and may be more useful than surface roughness for generating cells. It may have the influence on protein adsorption and the structural rearrangement of the proteins on the material. Therefore, understanding the relationship between surface energy and cell response on different biomaterials will facilitate the design of optimized implant surfaces and subsequently enhance cell responses. [12]
Surface energy is an important parameter of the material surface. [12] It is affected by several surface characteristics, such as chemical composition, surface charge, and microstructural topography. [13, 14] It has been reported that surface energy is one of important surface characteristic of modified titanium surfaces. [7, 15, 17] The relationship among surface factors, including surface roughness, surface energy, contact angle (CA) values, and cell adhesion to biomaterial surfaces, is presented in Figure 1. Each relationship was supported by a number of studies, which are referenced in the diagram. The understanding of surface factors, cell adhesion, and their relationships is mandatory for better understanding of the bone-implant interface.

Figure 1. The relationship among contact angle, surface preparation, surface energy, roughness, and cell adhesion.

Given the importance of surface wettability of dental implants in the achievement of osseointegration, the surface free energy (SFE) values for a given material obtained by various methods using different measuring liquids are not consistent. Thus, the current review article deals with the relationship between CAs and surface preparations.

2. Surface Free Energy (SFE) and Contact Angle (CA)

Surface free energy (SFE) is defined as the work required for increasing the surface area of a substance per unit area. SFE is induced from the unfulfilled bonding potential of molecules at a surface. These are different molecules within a material, which have less energy because they are affected by interactions with like molecules in all directions. Moreover, SFE is dictated by the surface roughness, topography, and composition of the implant and is crucial in determining which proteins are absorbed onto the surface. Surface energy, which is intimately related to wettability, [18] is a useful quantity that has often correlated strongly with biological interaction. Thus, it is usually reported that biomaterial surfaces with moderate hydrophilicity improves cell growth and higher biocompatibility. [19] This points out to the existence of a range of optimal surface energies. [20]
SFE can be determined by measuring the contact angle formed by a range of liquids on a given surface, using several diverse approaches. [21] The most useful methods for characterizing wettability on solid surfaces are static CA measurements. CA measurements are quantifiable, readily acquired using relatively low-cost instruments and simple procedures, amenable for use in environments from academic research laboratories to industrial manufacturing facilities, and an extremely powerful method for characterizing surfaces. A drop of liquids in contact with a surface will display a contact angle, traditionally measured through the liquid. Thus, examination of wetting behavior draws the conclusion that a liquid usually shows a wide range of angles on a measured solid surface. [22] The physical surface properties and the surface energy can be quantified by the wettability and by the CA of liquids with the surface. [23] The values of the CA indicate whether the surface is hydrophilic or hydrophobic. [24] Several authors have suggested that CA measurements give values ranging from 0° (hydrophilic) to 140° (hydrophobic) for titanium implant surfaces. [25, 26]

3. Calculations of surface free energy

The modified form of the Young equation is as follows:

\[ \gamma_s = \gamma_s^p + \gamma_s^\text{ab} + \gamma_s^h + \gamma_s^i \]

where the SFE of a solid (and of a liquid) is a sum of independent components, associated with specific interactions:

\[ \gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^\text{ab} + \gamma_s^h + \gamma_s^i + \gamma_s^o \]

where \( \gamma_s^d, \gamma_s^p, \gamma_s^\text{ab}, \gamma_s^h, \text{ and } \gamma_s^i \) are the polar, dispersion, acid–base components, hydrogen (related to hydrogen bonds), and inductions, respectively, while \( \gamma_s^o \) refers to all interactions. Moreover, the dispersion component of the surface free energy is related with the London force interactions, resulting from the electron dipole instability according to the theory. These interactions occur normally between neighboring atoms and molecules. The forces depend on the kind of similarly attracting elements of the matter but are independent of other types of
interactions. The remaining van der Waals interactions have been regarded by Fowkes [27] as a
division of the generation interactions. He investigated a solid or liquid in which the
dispersion interactions appear. Considering such systems, he found out the surface free energy
corresponding to the interface of a solid and liquid as follows:

\[
\gamma_d = \gamma_s + \gamma_l - 2\left(\gamma_s^d \gamma_l^d\right)^{0.5}
\]  
(3)

Eq. 3 is limited to the interfacial London interactions.

Owens and Wendt [28] changed the Fowkes idea while assuming that the sum of all the
components occurring on the right-hand side of Eq. 2, except \(\gamma_{s}^{l}\), can be considered as
associated with the polar interaction (\(\gamma_{s}^{p}\)). Thus, they suggested the following equation:

\[
\gamma_d = \gamma_s + \gamma_l - 2\left(\gamma_s^d \gamma_l^d\right)^{0.5} - 2\left(\gamma_s^p \gamma_l^p\right)^{0.5}
\]  
(4)

Because the polar interaction definition by Fowkes [27] differs from that by Owens and Wendt,
the meanings of \(\gamma_{s}^{p}\) and \(\gamma_{l}^{p}\) in Eq. 2 are different than those in Eq. 4.

The latest idea of the partition of surface free energy of solids and liquids into components is
that presented by van Oss, Chaudhury, and Good. [29] The authors separated \(\gamma_{s}\) into two
components, one containing the long-range interactions (London, Debye, and Keesom) called
the Lifshitz–van der Waals component (\(\gamma_{s}^{LW}\)) and the other that includes the short-range
interactions called the acid–base component (\(\gamma_{s}^{AB}\)). The latter component associated with the
acid–base interactions is equal 2(\(\gamma^{+}\gamma^{-}\))^{0.5}, where \(\gamma^{+}\) and \(\gamma^{-}\) mean the acidic and basic components,
respectively. Consequently, the following relationship was created:

\[
\gamma_d = \left(\gamma_{s}^{LW}\right)^{0.5} + \left(\gamma_{l}^{LW}\right)^{0.5} + 2\gamma^{+}\gamma^{-}\left(\gamma_{s}^{LW}\right)^{0.5}\left(\gamma_{l}^{LW}\right)^{0.5}
\]  
(5)

4. Owens–Wendt method

In the Owens–Wendt method, [30] they made the assumptions similar to those in the Fowkes
method. The two methods, being identical in the mathematical aspect, differ slightly in the
way of calculating the surface free energy. The combination of Eq. 1 with Eq. 4 leads to the
following relationship:

\[
\left(\gamma_s^d \gamma_l^d\right)^{0.5} + \left(\gamma_s^p \gamma_l^p\right)^{0.5} = \gamma_l^l (1 + \cos \Theta)
\]  
(6)
5. van Oss–Chaudhury–Good method

The component $\gamma_{ab}$ is equal $2(\gamma^+\gamma^-)^{0.5}$ and combining Eq. 1 with Eq. 5, van Oss, Chaudhury, and Good obtained the following relationship: [30]

$$
\left(\gamma_{sLW}^{LW} - \gamma_{sLW}^{LW}\right)^{0.5} + \left(\gamma_{s+}^{+} - \gamma_{s+}^{+}\right)^{0.5} + \left(\gamma_{s-}^{-} - \gamma_{s-}^{-}\right)^{0.5} = 0.5 \left(1 + \cos \Theta \right)
$$

(7)

Since three unknowns, $\gamma_{sLW}^{LW}$, $\gamma_{s+}^{+}$, and $\gamma_{s-}^{-}$, appear in Eq. 7, the solution of a system of three independent linear equations is needed to establish these quantities. When three different liquids are used to measure the contact angle of a material, such a system is obtained. Moreover, two bipolar and one non-polar liquid should form the set of the three measuring liquids. The values of the coefficients appearing in such a scheme of equations have been given somewhere else. The key of the scheme of three equations shown, as used in the van Oss–Chaudhury–Good method, cannot always be appropriate and undoubtedly interpreted. This follows from the presumed conditions and limitations, related with both the selected measuring liquids and the methods of determination of the surface free energy components such as $\gamma_{s}^{LW}$, $\gamma_{s}^{+}$, and $\gamma_{s}^{-}$.

6. Methods based on determination of the contact angle hysteresis

This approach is one of the latest methods for calculating the SFE of polymeric materials. [31, 32] It consists of the measurements of both the advancing CA ($\Theta_a$) and the receding one ($\Theta_r$) by using the same measuring liquid of a known value of $r$. The surface free energy of a tested solid can be calculated from the following equation:

$$
r_s = r_i \left(\cos \Theta_a - \cos \Theta_r\right) \left[\left(1 + \cos \Theta_a\right)^2 / \left(1 + \cos \Theta_r\right)^2 - \left(1 + \cos \Theta_a\right)^2 - 1 + \cos \Theta_r\right] + \cos \Theta_a
$$

(8)

Unlike the approaches presented above, Eq. 8 takes into account adsorption at the interface. The contact angle appearing in Eq. 1 is the advancing contact angle. Thus, this equation transforms into the following one:

$$
r_r = r_i + r_i \cos \Theta_a
$$

(9)

The SFE of a solid ($r_s$), which considers adsorption occurring during the measurement of $\Theta_a$, can be expressed by the following relationship:

$$
r_{sf} = r_i + r_i \cos \Theta_r
$$

(10)
The following relation is valid:

\[ r_{sl} = r_{s} + \pi \]  \hspace{1cm} (11)

where \( \pi \) is the equilibrium pressure of the surfaces of the measuring liquid. The adhesion can be determined from the following equation:

\[ W_{sl} = r_{s} + r_{l} - r_{sl} \]  \hspace{1cm} (12)

in which \( \Theta_a \) or \( \Theta_r \) is used, depending on the kind of the interfacial system.

When applying the Young and Dupre equations, the parameter \( \Phi \) defined by Girifalco and Good as well as making suitable substitutions. While finding this relationship, its authors neither asked nor confirmed the basics of the knowledge in this area. Finding new relations are unquestionable contribution of the authors of this method.

The determination of the polymeric material surface energy with the use of Eq. 8 needs the measurements of \( \Theta_a \) and \( \Theta_r \) and the information of \( r \) of the measuring liquid. Nonetheless, as the authors of the method highlighted, the calculated values of the surface free energy rely on the tested measuring liquid. Therefore, they verify the results of studies regarding other methods for calculating the surface free energy of polymeric materials. [33–34]

7. Analysis methods of wetting behavior of different dental implant surfaces

There are a number of techniques to measure the contact angle of a liquid on a substrate, including optical reflectometry, contrast interferometry, capillary rise technique, Wilhelmy plate tensiometry, and various goniometric methods (Table 1).

| Surface modifications                  | Conditions of measurement | Ref.      |
|----------------------------------------|---------------------------|-----------|
| Calcium phosphate coating              | Drop diameter from 5 to 10 mm Water, glycerol Static drop Owens and Wendt | [35]     |
| Nitric acid etching                    | Drop diameter from 5 to 10 mm Water, glycerol Static drop Owens and Wendt | [35]     |
| Acid etching                           | 10 mm/min Water, fibronectin solutions Wilhelmy plate | –        | [6]       |
### Table 1. Contact angle and surface free energy calculation analysis of various treated dental implants on previous studies.

| Surface modifications | Conditions of measurement | Ref. |
|-----------------------|---------------------------|------|
| **Thermal oxidation** | N/A | Benzylethanol, diiodomethane, formamide, and water | Owens and Wendt [3, 6] |
| **Physical vapor deposition** | N/A | Water, Dulbecco’s modified Eagle’s medium | Dynamic contact angle – | [37] |
| Acid, sandblasted, and anodized treatment | N/A | Water, NaCl, DMSO, and human blood | Static drop – | [38] |
| Acid, blasted, and blasted + etched | 1–2 s | Water | Sessile drop | Wenzel law | [39] |
| None | N/A | Water, formamide, and diiodomethane | Captive air bubble | van Oss–Good | [40] |
| Plasma spray | 10 s–20 min | Water, diiodomethane | Sessile drop | Owens and Wendt | [5] |
| Plasma immersion ion implantation | N/A | Glycol, glycerol, water, formamide, methylene iodide, and tricresyl phosphate | Static drop | Owens and Wendt | [41] |
| RGDS-coated anodized Ti | 1 μL/s | Water | Sessile drop | N/A | [42] |

7.1. Static drop method

The most commonly employed technique for measuring the contact angle of drops on liquid repellent surfaces is the sessile drop method coupled with digital image analysis. A liquid drop of a volume (calculated) is silently dropped on the substrate and a camera captured the boundary of the drop. Many imaging analysis algorithms can be utilized to estimate the contact angle from the drop outline, such as rough spherical cap calculations [43] or direct fitting to arithmetical keys of the Young Laplace equation. [44]

7.2. Advancing and receding angle

The advancing contact angles of water and other liquids (diiodomethane, formamide, etc.) were measured after settling 6 μL droplets on the surface. Then after sucking of 2 μL from the droplet into the syringe, the receding contact angle was measured. On the other hand, a drop on a tilted plate is shown schematically, in which the front angle is close to the advancing angle and the rear angle is close to the receding angle on the drop before descending. When the
hysteresis is small, the droplet is close to a spherical cap. Moreover, the contact angle passes from the advancing value to the receding one along the contact line. Because these angles are considered to be close to each other, it just is written that the upper half of the droplet makes the angle $\Theta_r$, while the lower half meets the angle $\Theta_a$.

7.3. Captive air bubble method

Although most studies addressing (super)hydrophobic behaviors have so far dealt with the wetting of low surface energy and textured substrates in air environment, the captive air bubble method, the so-called two liquid phase method, is a totally novel system and configuration involving the wetting of highly hydrophilic, textured metallic materials in liquid alkane medium.

7.4. Wilhelmy plate method

The dynamic contact angle measurements are performed on the basis of the Wilhelmy plate technique. The force acting on plates immerse (wetting) and emerge (dewetting) in a liquid is recorded by means of an electrobalance. The hysteresis force loops are used to calculate advancing and receding contact angles (CAs) during immersion and emersion according to the following equation:

$$\cos \Theta = \frac{F}{L \gamma} \quad (13)$$

where $\Theta$ is the advancing or receding CA, $F$ is the wetting force, $L$ is the wetted length (sample perimeter), and $\gamma$ is the surface tension of the wetting liquid. Thus, the CA and the wettability of a solid can be determined from the known surface tension and the measured weight of the liquid meniscus. $F/L$ is the so-called wetting tension and equals to the product of $\cos \Theta$ and $\gamma$, which is itself part of the fundamental Young equation for sessile drops in thermodynamic equilibrium. The difference between the advancing and the receding CAs is referred to as CA hysteresis. [45]

The hysteresis force loops are qualitatively described in terms of thermodynamic and kinetic hysteresis. For CA calculations, linear portions of the respective $F/L$ lines are extrapolated to zero immersion depth by linear regression. Before each tensiometry wetting experiment, water surface tension $\gamma$ was measured by means of the Wilhelmy method using a standard roughened platinum Wilhelmy plate. [46]

8. Influence of surface cleaning on contact angle analyzing

Surface cleaning method has a quantitative and qualitative influence on the results of contact angle (CA) measurements. An author studied the evolution of contact angle values versus the roughness for the three different cleaning methods [47]:

...
Type 0: water rinsing followed by nitrogen drying

Type I: successive soakings in ultrasonic baths of acetone, cyclohexane, and acetone, followed by water rinsing and nitrogen drying

Type II: “Type I” cleaning followed by an argon plasma cleaning

Based on the study, CAs around 150° was observed with type 0 cleaning, and no trivial correlation with the roughness was found. Type 0 cleaned surfaces are still covered by usual organic contaminants from ambient air, and no significant influence of the roughness on CA values is observed. The contact angle remained even around 140° in the roughness range between 2.5 and 12 μm, before it begin to reduce for $Ra$ higher than 12 μm. Finally, type II cleaning strongly decreased contact angle values [48] compared to type I and type 0 ones. When the roughness increased up to a threshold value $Ra = 10 \mu m$, an increase in contact angle was detected. Above this threshold, the contact angle remained constant at 120°.

It thus clearly appears from these results that the more efficient the surface cleaning, the more strong and measurable the correlation between CA and roughness. To determine the Young equilibrium angle, CAs were measured on mirror polished titanium surfaces in the “two liquid phase” configuration, after the three different cleaning methods.

Figure 2. Ti surfaces of the untreated (a) and plasma-treated (b) for cleaning. Reproduced with permission from Kim et al. (49).
Plasma treatment also can be used as a cleaning method. Appropriate plasma processes render the surfaces more hydrophilic and modify the oxide layer. Also, the application of plasma to metal implants can clean the surface of materials as shown in Figure 2. Among the wide range of plasma techniques, atmospheric plasma is one of the simplest and most efficient processes. We studied to evaluate the effects of atmospheric pressure plasma on the Ti surface. In this study, the plasma treatment did not affect the surface roughness. Therefore, atmospheric plasma is a powerful way of creating a functionalized hydrophilic surface of Ti implants as a simple and highly efficient method. An atmospheric plasma treatment has the potential as a surface modifying technique to clean the Ti implant surface.

9. Surface roughness and contact angle

The surface roughness is also an important parameter to be considered. To enhance our understanding of liquids in contact with rough surfaces, a systematic study was carried out in which water contact angle measurements were performed on a wide variety of rough surfaces with precisely controlled surface chemistry.

A uniform surface (Θ) does have a unique value only if perfectly flat. On genuine surfaces, depending on how a drop is deposited, the contact angle can differ from advancing and receding contact angles. This hysteresis can be attributed to inhomogeneities in the division of adsorbents or the existence of contaminants, to surface roughness, or to time-dependent surface reorganizations. The value of Θ is strongly influenced on the surface morphology on rough surfaces. On rough and hydrophobic surfaces, the liquid can either go after the surface topography or show strong pinning or can connect from sharpness to asperity while surrounding air below and presenting almost no hysteresis in the contact angle.

9.1. Wenzel

A roughness factor, describing the roughness influenced on Θ (Eq. 11), was introduced by Wenzel, as follows [51]:

$$\cos\Theta^W = r \cdot \cos\Theta$$  (14)

where $r$ is calculated by dividing the actual roughness-enhanced surface area by its projection. This behavior is often referred to as Wenzel-type wetting.

9.2. Cassie–Baxter

For the second case, Cassie and Baxter [52] modified Wenzel’s equation by introducing the fractions $f_1$ and $f_2$, where $f_1$ corresponds to the area in contact with the liquid divided by the projected area and $f_2$ to the area in contact with the air trapped beneath the drop, also divided by the projected area:
Structured surfaces that exhibit superhydrophobicity can also show an effect known as hemiwicking [53] or superwetting if they are surface-chemically functionalized to be hydrophilic. Hemiwicking is a complete wetting due to the presence of capillary forces in two dimensions. [54]

When the surface energy is high, the surface roughness indeed enhances wettability, causing hemiwicking in many cases caused by capillary forces. The pinning of the contact line results in a move to more hydrophobic $\theta$ values at lower surface energies. It was found that the surface topography outlines the pinning strength and with it the energy barrier working against the wetting behavior of the drop.

10. Contact angle and roughness of modified Ti implant surfaces

Although the increasing contact angle is in accordance with roughness on nontreated surfaces, modified surfaces have shown different consequences. In physical states, grit-blasting and etching treatments decrease the contact angle of the surfaces, except sandblasting and the acid-etching (SLA) treatment (Table 2). SLA-treated surface has nanosized features. This surface also contains two major roughness scales. The microscale roughness originates from the sandblasting step, leading to troughs. The superimposed nanoscale roughness was created by the acid-etching process. Thus, the apparent contact angle on the SLA surface is hydrophobic. This phenomenon can be explained by pinning the contact line. [48] On the other hand, anodizing treatment makes surface hydrophilic.

| Modifications of surface          | Degrees of water contact angle (°) | Surface roughness (μm) | Ref. |
|-----------------------------------|------------------------------------|------------------------|------|
| Nontreated (ground surfaces)      | 85.2 ± 3.6                         | 0.65                   | [38] |
|                                   | 76.3 ± 3.0                         | 0.45                   | [7]  |
|                                   | 55.4 ± 4.1                         | 0.26                   |      |
|                                   | 43.0 ± 2.0                         | 0.25                   |      |
| Physical state                    | 32.5 ± 3.5                         | 1.64                   | [55] |
| Grit-blasting                     | 69.3 ± 3.0                         | 0.37                   | [38] |
| Etching                           | 96.2 ± 9.2                         | 0.51                   |      |
| Sandblast with large grit and acid etch (SLA) | 138.3 ± 4.2 | 2.40 | [6] |
|                                   | 120.1 ± 15.2                       | 3.12                   |      |
| Thermal spray                     | 57.4 ± 3.2                         | 1.06                   | [56] |
|                                   | 0.0                                | -                      |      |
| Chemical state                    | Electro chemical deposition         | 75.0 ± 1.0             | [37] |
|                                   |                                    | 3.50                   |      |
| Modifications of surface | Degrees of water contact angle (°) | Surface roughness (μm) | Ref. |
|-------------------------|------------------------------------|------------------------|------|
| Ion implantation        | 81.5 ± 1.5                         | -                      | [57] |
| Anodizing               | 47.25 ± 2.9                        | 0.87                   | [38] |
| Plasma-based fluorine ion implantation | 90.0 ± 1.5                         | -                      | [58] |
| Hydrothermally oxidation| 38.5 ± 10.8                        | -                      | [12] |
| rhBMP-2-immobilizing    | 13.7 ± 0.2                         | -                      | [59] |
| Biological state        |                                    |                        |      |
| RGDS-coated anodized Ti | 29.9 ± 3.3                         | 0.38                   | [42] |
| Heparin and fibronectin adsorption | 17.3 ± 3.5                         | 0.31                   | [60] |

Table 2. Surface contact angle and roughness value of modified titanium surfaces.

11. Conclusions

Surface composition and hydrophilicity are parameters that play a major role in implant–tissue interaction and osseointegration. In biological state, interfacial reactions in vivo change relevant physical and chemical surface parameters, such as the surface energy, affecting the long-term stability of implants. [61] In addition to surface topography, the properties of implant materials that affect cellular behavior include mechanical rigidity and wettability (SFE). The wettability of the surface plays an important role with respect to protein adsorption, cell attachment, and spreading. [62, 63] In some recent works, surfaces with a high surface free energy are reported to be more adhesive than those with a low surface free energy. [36] Thus, the understanding of surface factors, particularly surface wettability, is mandatory for better understanding of the bone implant biomaterial interface.

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