

Evaluation of surface free energy of bioactive coatings on magnesium and titanium alloys

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The contact of the implant surface with the body tissues is important for osseointegration [1]. The chemical composition of the implant directly determines biocompatibility with the body; the relief and roughness affect the contact area of the material with the biological medium and cell adhesion [2]. In addition, the adhesion rate of the serum components related to the wettability, which depends on the surface free energy (SFE) [1].

SFE characterizes the energy of the intermolecular interaction of the contacting phases. Many authors note that high-energy surfaces are more desirable to increase osseointegration and osteogenesis [2]. One of the reasons is to increase the interaction of biomolecules with the surface of implantation materials, which reduces the risk of scarring and a negative immunological reaction [2].

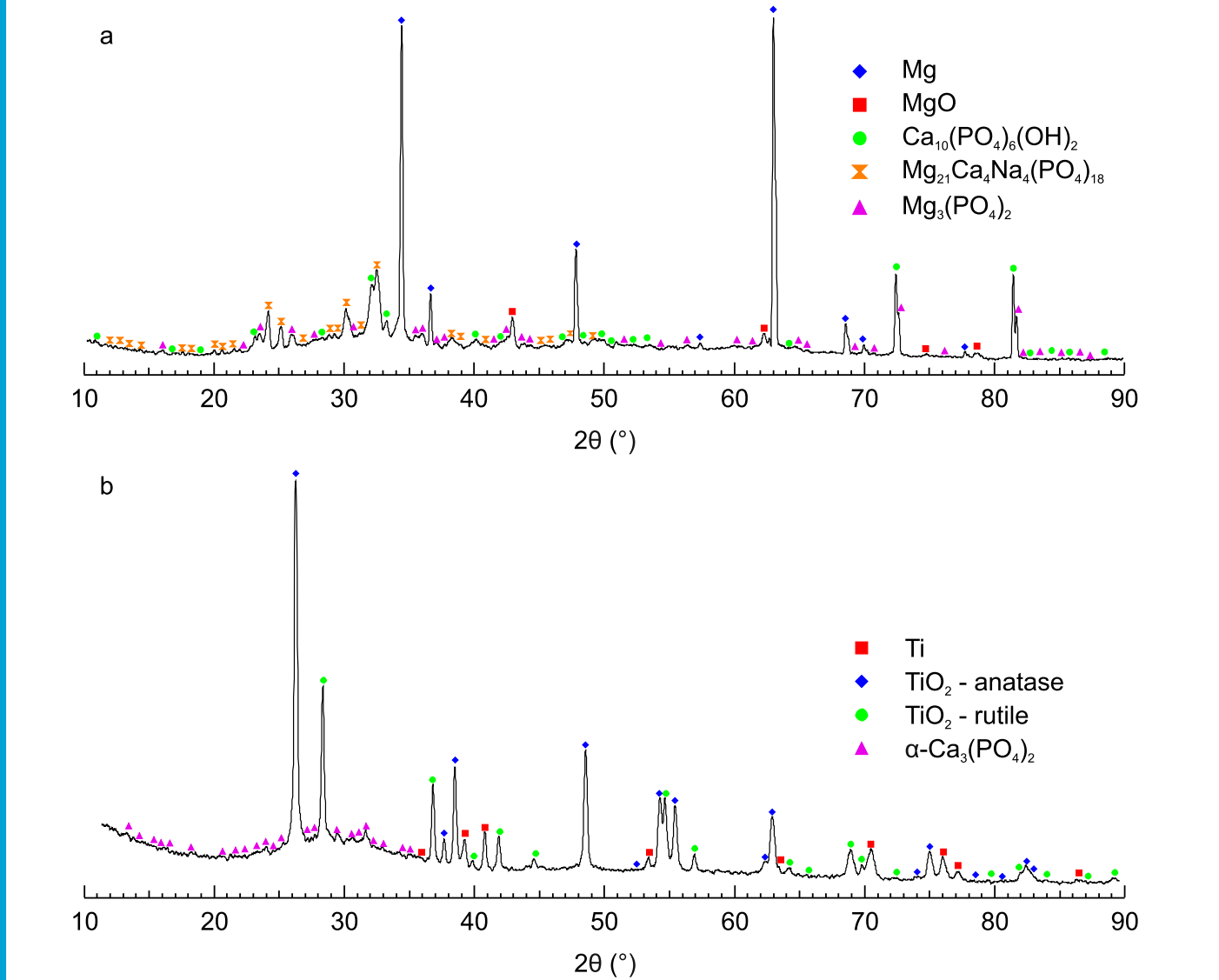


Fig. 1. XRD-patterns of bioactive PEO coatings on magnesium (a) and titanium (b)

PEO of the pure titanium was carried out in an electrolyte containing 30 g L⁻¹ calcium glycerophosphate (C₃H₇CaO₈P) and 40 g L⁻¹ calcium acetate (Ca(CH₃COO)₂) in a monopolar potentiodynamic mode. The voltage during the oxidation process varied from 150 to 300 V for 300 s. The pulse duration was 0.01 s [3].

PEO of the magnesium alloy was carried out in an electrolyte containing 25 g L⁻¹ calcium glycerophosphate (C₃H₇CaO₈P), 5 g L⁻¹ sodium fluoride (NaF), and 7 g L⁻¹ sodium metasilicate (Na₂SiO₃) in a bipolar mode. In the anode phase, the voltage was fixed at 380 V; in the cathode phase, the current density was increased from -0.40 to -0.28 A cm⁻². The duration of the cathode and anode phases was 0.01 s. The duration of the oxidation process was 100 s [4].

Based on the data of X-ray phase analys (Fig. 1), biactive PEO coatings include calcium-phosphate compounds prone to the formation of hydroxyapatite in body fluids. In addition to calcium phosphate, the coatings consist of titanium dioxide (in the modification of rutile and anatase) for pure titanium (Ti-PEO), magnesium oxide and triphosphate for magnesium alloy (Mg-PEO).

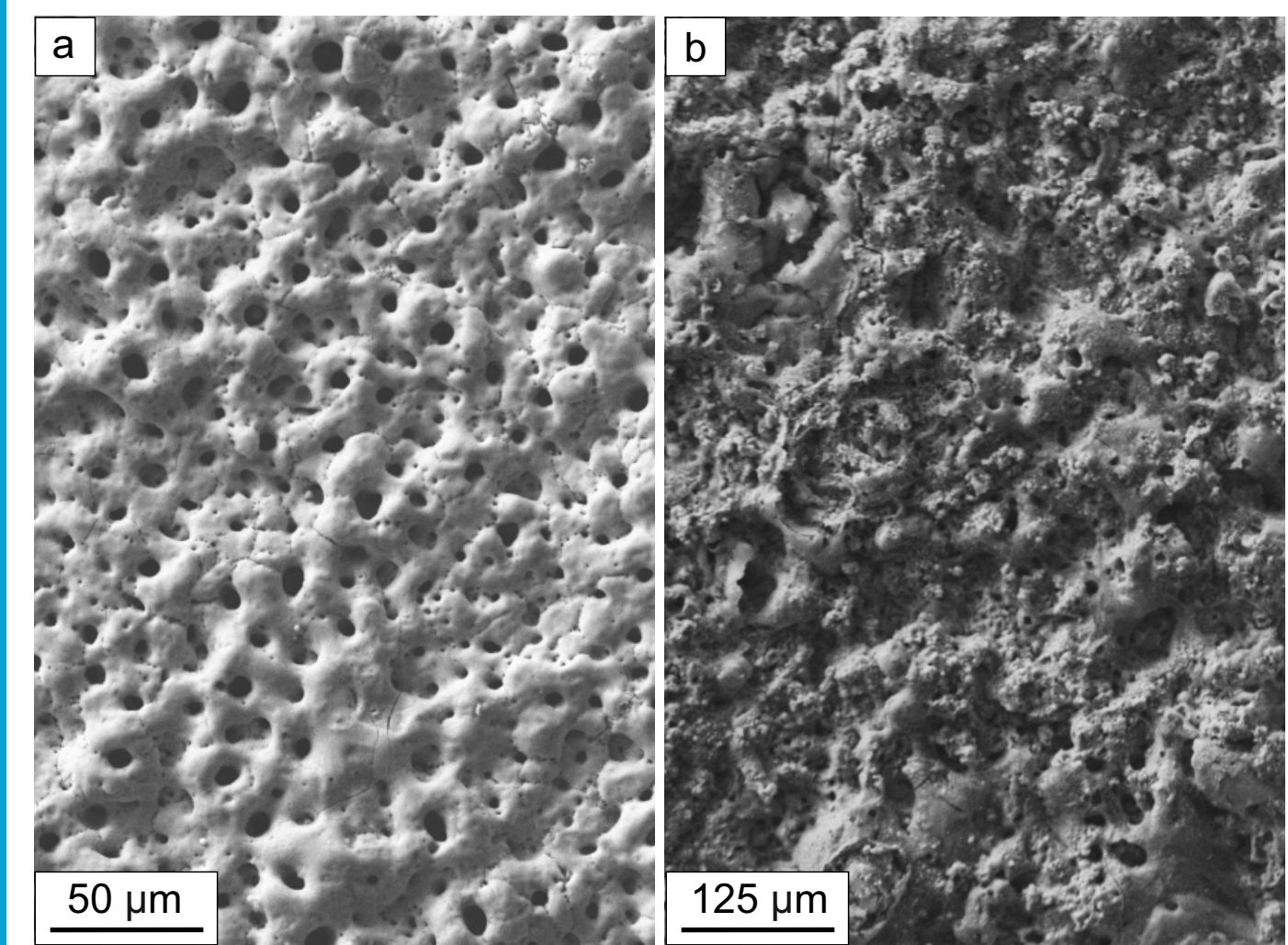


Fig. 2. SEM images of bioactive PEO coatings on titanium (a) and magnesium (b).

The surface of PEO coatings has high roughness and porosity. Moreover, the most developed PEO surface on magnesium alloy. Coatings on titanium are smoother and have a larger number and size of pores, unlike coatings on magnesium alloy (Fig. 2).

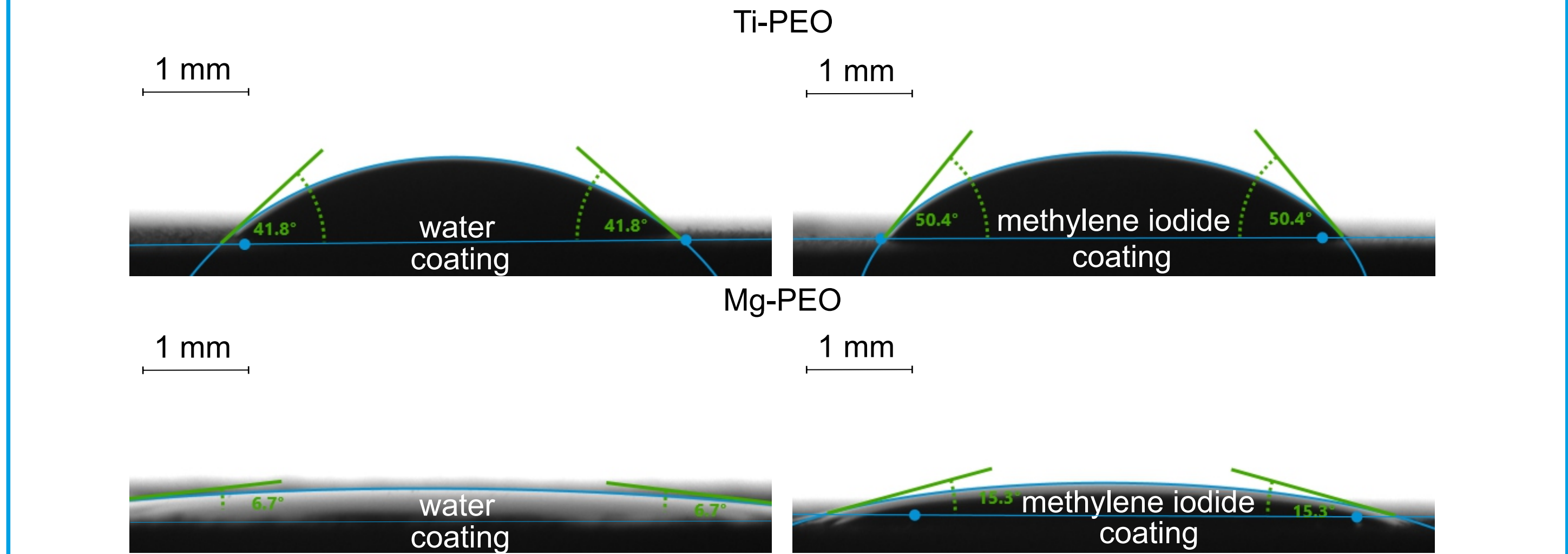


Fig. 3. Optical images of liquid (water and methylene iodide) drop on bioactive PEO coatings on magnesium and titanium.

Analysis of the wettability of bioactive surface layers on titanium and magnesium indicates a significant decrease in contact angle (CA) in comparison with the metal surface (Table 1). In particular, coatings on magnesium alloy exhibit properties close to superhydrophilicity when wetted with water (for a superhydrophilic surface, the equilibrium CA should not exceed 5° for 0.2 s). For formed surfaces, the CA value is in the range 4.2 – 6.5°. However, these values are approximate, since the drop spreads at a high speed and is absorbed by the material, because of which it is difficult to register the real CA.

Surface	Contact angle [°]		Surface free energy [mJ m ⁻²]		
	H ₂ O	CH ₂ I ₂	γ ^p	γ ^d	γ
Mg	82.57±0.61	54.91±1.07	5.23±0.12	28.34±0.26	33.57±0.38
Mg-PEO	5.35±1.18	15.70±0.99	31.35±0.16	48.92±0.23	80.27±0.40
Ti	75.07±0.32	43.66±0.43	5.73±0.14	37.72±0.23	43.45±0.37
Ti-PEO	41.37±1.12	50.02±1.20	25.96±0.77	34.26±0.67	60.22±1.44

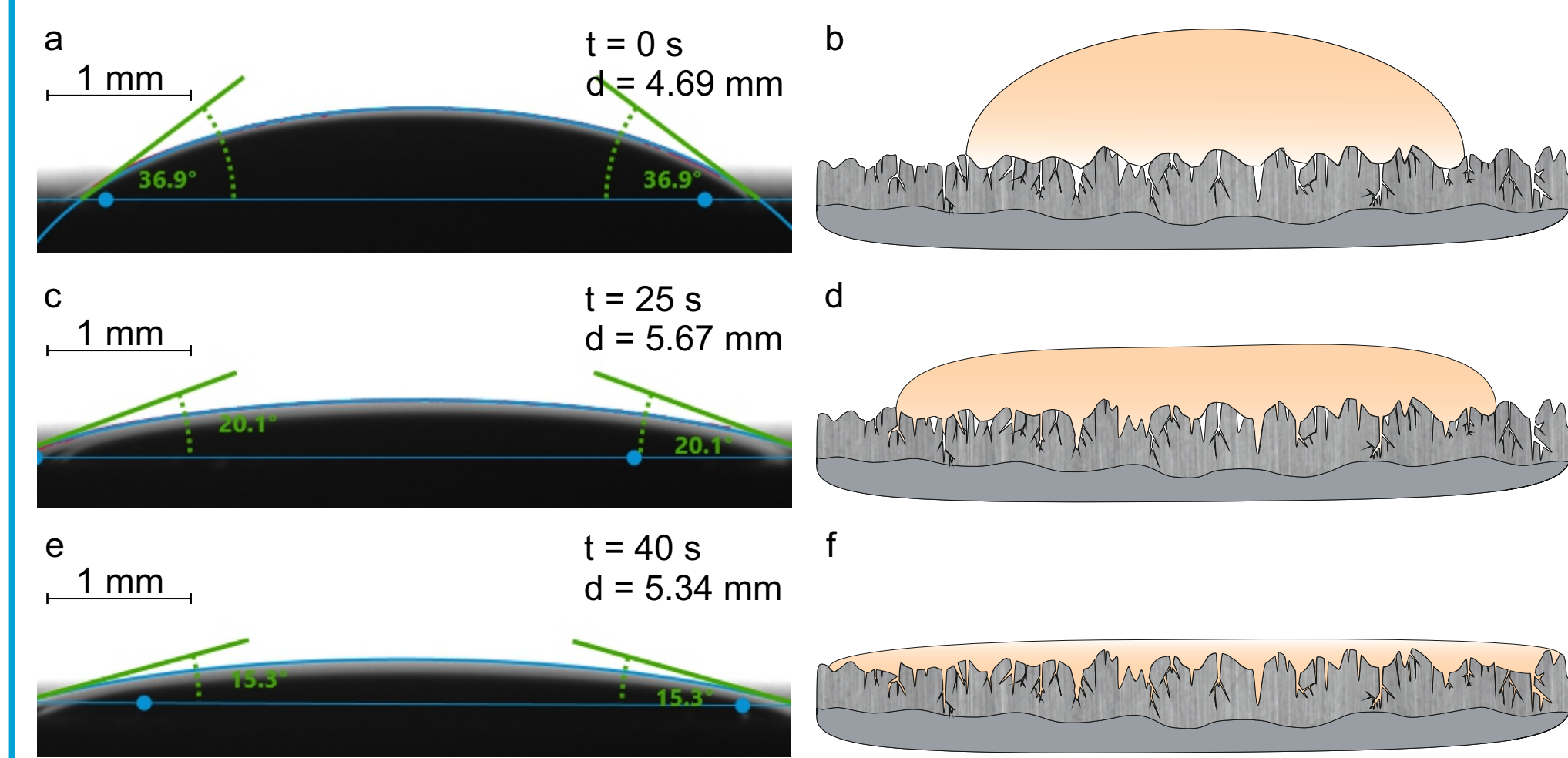


Fig. 4. Optical images (a, c, e) and wetting model (b, d, f) of methylene iodide CA for Mg-PEO surface after 0 s (a, b), 25 s (c, d) and 40 s (e, f)

When wetting Mg-PEO with methylene iodide, the equilibrium CA = 15.7° is not established immediately, but for some time, approximately ranging 30–60 seconds (Fig. 4). This behavior of liquids on the surface of bioactive coatings on magnesium alloy is a reflection of high roughness, large porosity and a developed pore system (Fig. 2), as a result of which, due to capillary effects, the drop gradually penetrates deep into the texture of the coatings, and spreads over the surface, and the CA in turn decreases (Fig. 4).

At the initial stage of wetting (Fig. 4a,b), the liquid-material contact boundary contains both liquid / solid and liquid / vapor sections contained in the pores of the PEO layer. Then the contact boundary increases (Fig. 4 c,d), which can be judged by the increase in the length of the contact line (d). Accordingly, the proportion of liquid-solid contact increases, which indicates partial filling of the coating pores.

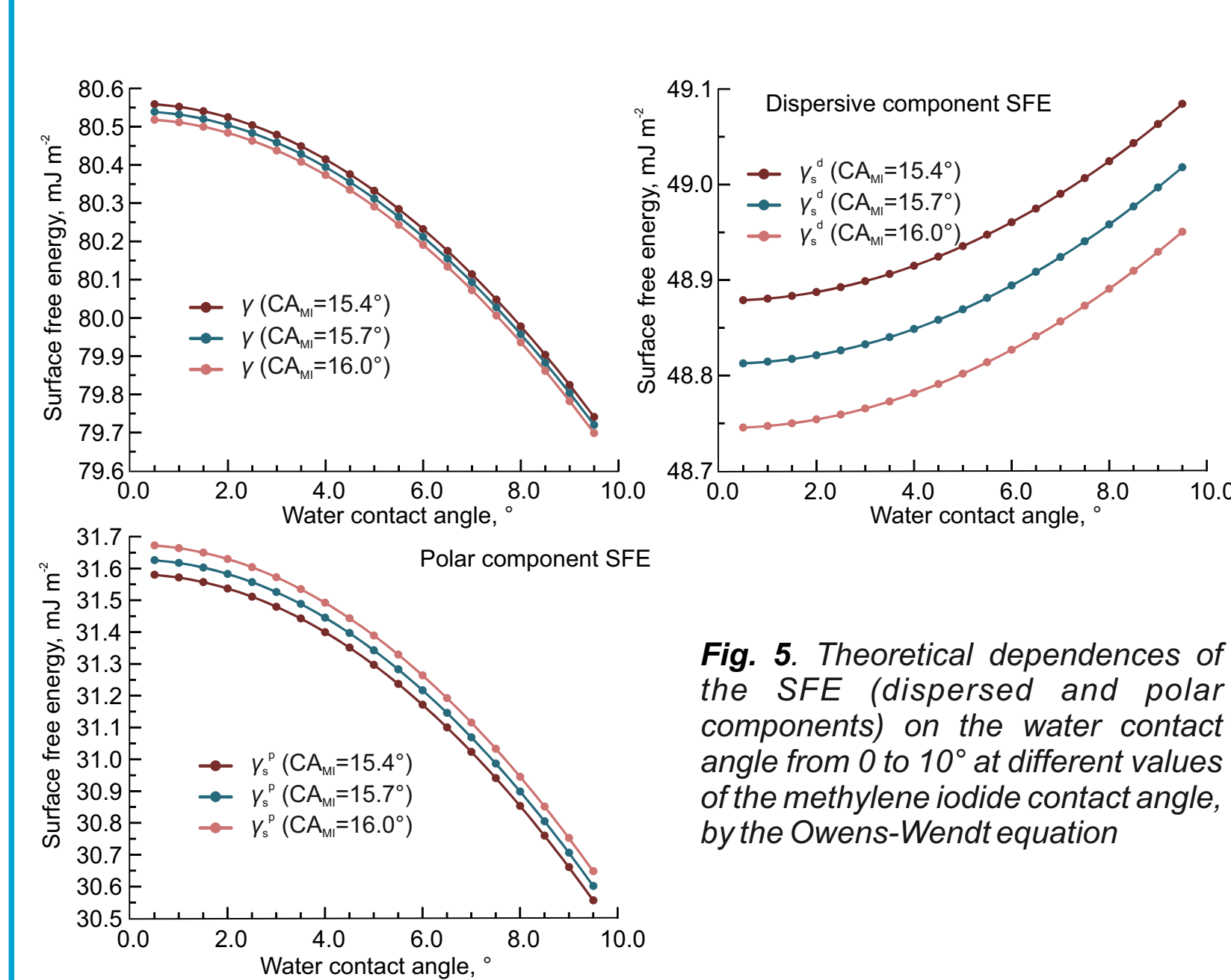


Fig. 5. Theoretical dependences of the SFE (dispersed and polar components) on the water contact angle from 0 to 10° at different values of the methylene iodide contact angle, by the Owens-Wendt equation

For Ti-PEO, a stable state is achieved immediately, and the wettability of such a surface improves compared to untreated metal. Water CA decreases by almost half, and methylene iodide CA increases (Table 1), which is probably a consequence of the presence of titanium oxide on the surface in advantage. A significant difference in the wetting of Mg-PEO and Ti-PEO is due to differences in the morphology of the surface (Fig. 2).

In accordance with the change in CA due to the formation of PEO coatings on the surface of titanium and magnesium, the value of SFE also changes. To a large extent, the value of the polar component of the SFE changes for PEO coatings, which is due to a significant difference in the energy of interaction of the liquid with metal and metal oxides.

Since it is difficult to estimate the real water CA with the surface of Mg-PEO due to its high hydrophilicity, determining the value of SFE by the OWRK method is also non-trivial. Therefore, we graphically presented the Owens-Wendt equation in the area of the water CA 0 – 10° (Fig. 5), with the value of the methylene iodide contact angle 15.7±0.3°. The results show that at this site the value of the SFE is determined with an accuracy of 1 mJ m⁻², which is less than 1% of the specified value. Also, decomposing the SFE by components, it is clearly seen that the polar component (0.9 mJ m⁻²) makes the greatest contribution to this difference, and the dispersed component lies within the error (0.2 mJ m⁻²). According to the graphs' data, it can be assumed that the SFE of the Mg-PEO surface is 87.27±0.40 mJ m⁻².

It is possible to judge the positive effect of the treatment of the metal surface by plasma electrolytic oxidation, since the value of the SFE increases by 240% for magnesium and 40% for titanium. An increase in wettability and, as a consequence, the amount of surface energy is a favorable factor for the biocompatibility and adhesion of cells and tissues on the surface of the implantation material [1].

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