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Multi-effect distillation – Wettability of polymeric falling film heat transfer surfaces

Introduction

Multi-effect distillation (MED) is a well-established process in seawater desalination. Heat transfer surfaces used in MED-plants are exposed to highly corrosive process conditions due to direct contact to a liquid falling film of evaporating seawater. This requires corrosion resistant and expensive metal alloys as heat transfer surfaces. Therefore, polymeric materials might be a low-cost and less-corrodible alternative to metals for energy efficient heat transfer. One drawback of polymers in falling film applications is their poor water wettability. Moreover, surface wettability is also an important aspect in distillation columns with polymer packings.

The high performance polymer polyetheretherketone (PEEK) was chosen as test material to study the wettability with water. It exhibits excellent mechanical and chemical properties and a high continuous operating temperature[1]. 25 μm thick Victrex aptiv 1000 and aptiv 1103 PEEK films as well as different surface modifications were investigated. PEEK film wettability was characterised by contact angle measurements with water, ethylene glycol and diiodomethane. Surface free energy was determined applying the method of Owens[2], Wendt[2], Rabel[3] and Kaelble[4] (OWRK) and the method of van Oss et al.[5,6], respectively.

Results

Surface free energy

Commercially available untreated and plasma treated PEEK films aptiv 1000 (PEEK unfilled, $R_a < 0.1$ μm) and aptiv 1103 (PEEK filled with 30 % talcum powder, $R_a \approx 0.9$ μm) were used. The untreated PEEK film aptiv 1000 was additionally conditioned in water for 30 days at 22 °C and dried afterwards for 7 days at 70 °C on air.

Model of Owens[2], Wendt[2], Rabel[3] and Kaelble[4] (OWRK)

The OWRK model is based on the geometric mean of dispersion (γ^d) and polar (γ^p) solid-liquid interaction components:

$$\gamma_{LV}^{tot} \cdot (1+\cos\theta) = 2 \cdot \left(\sqrt{\gamma_{LV}^d \cdot \gamma_{SV}^d} + \sqrt{\gamma_{LV}^p \cdot \gamma_{SV}^p} \right) \qquad \gamma^{tot} = \gamma^d + \gamma^p$$
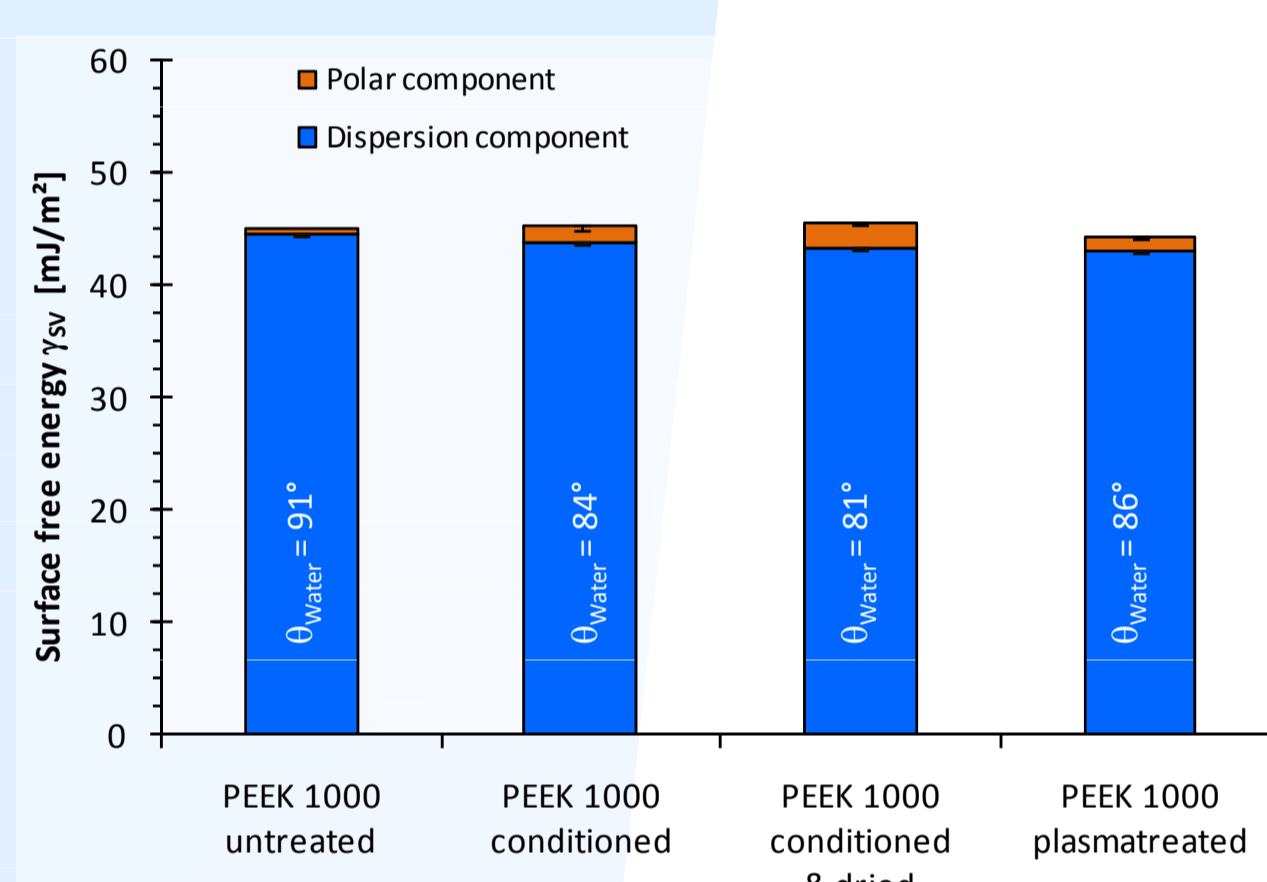

Fig. 1: Water contact angle θ and comparison of surface free energies for PEEK aptiv 1000 films calculated with the OWRK-method.
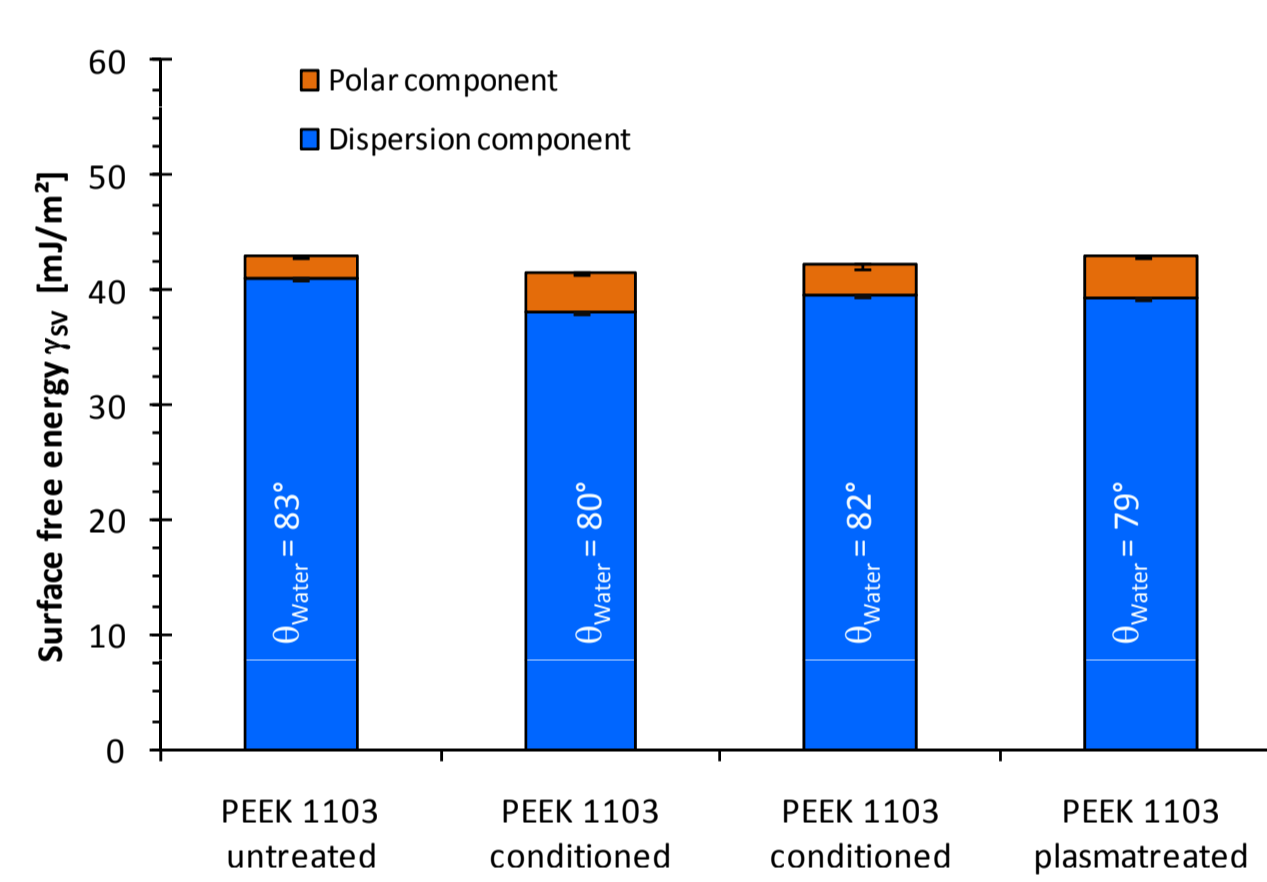

Fig. 2: Water contact angle θ and comparison of surface free energies for PEEK aptiv 1103 films calculated with the OWRK-method.

Model of van Oss et al.[5,6]

The van Oss model is based on a Lewis-acid-base approach where γ^{LW} describes apolar Lifshitz-van der Waals interactions. γ^A and γ^B represent polar Lewis acid (electron acceptor) and Lewis base (electron donor) interactions, respectively:

$$\gamma_{LV}^{tot} \cdot (1+\cos\theta) = 2 \cdot \left(\sqrt{\gamma_{LV}^{LW} \cdot \gamma_{SV}^{LW}} + \sqrt{\gamma_{LV}^B \cdot \gamma_{SV}^A} + \sqrt{\gamma_{LV}^A \cdot \gamma_{SV}^B} \right) \qquad \gamma^{tot} = \gamma^{LW} + \gamma^{AB} \qquad \gamma^{AB} = 2 \cdot \sqrt{\gamma^A \cdot \gamma^B}$$
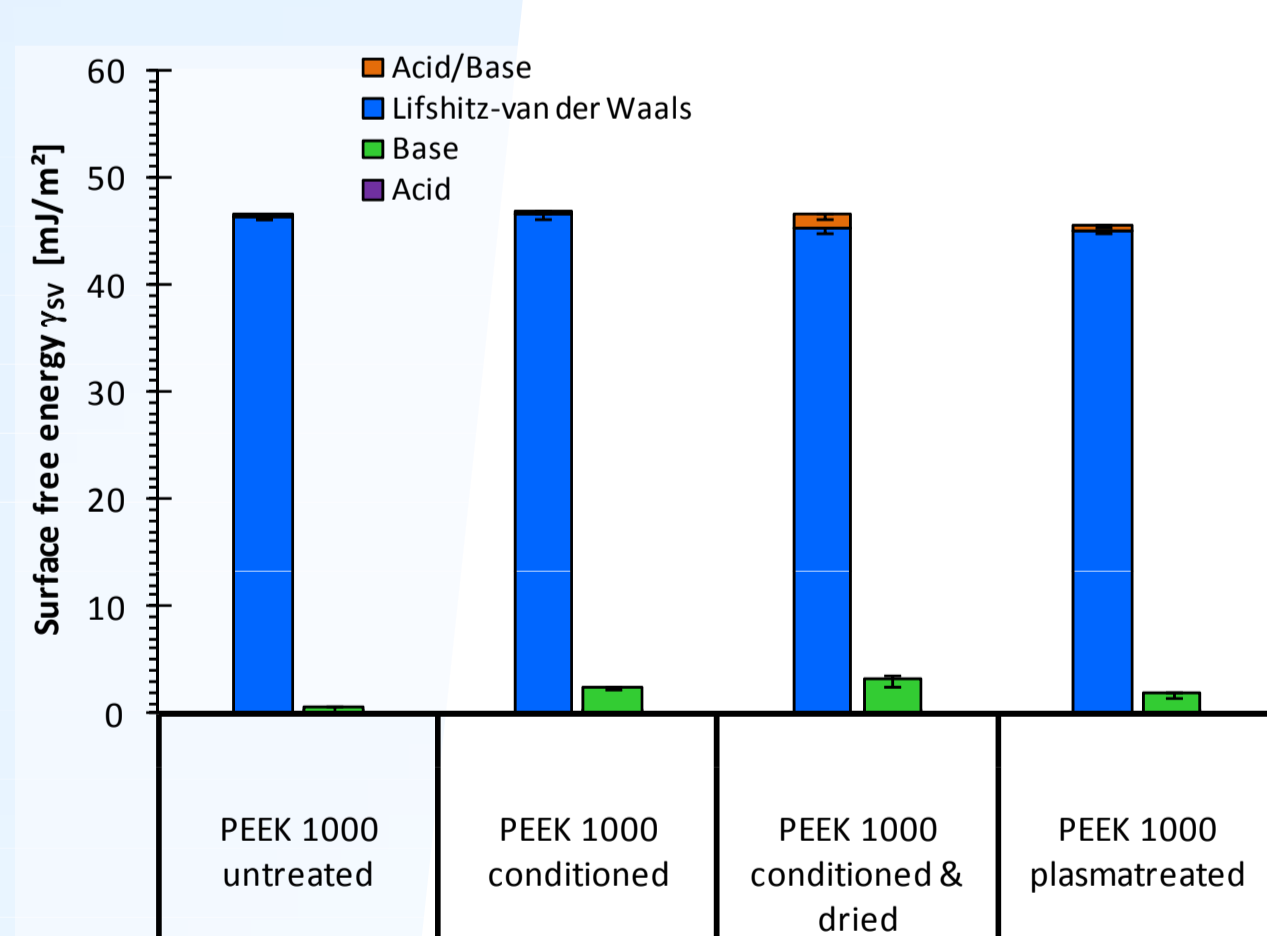

Fig. 3: Comparison of surface free energies of PEEK aptiv 1000 films calculated with the van Oss-method.
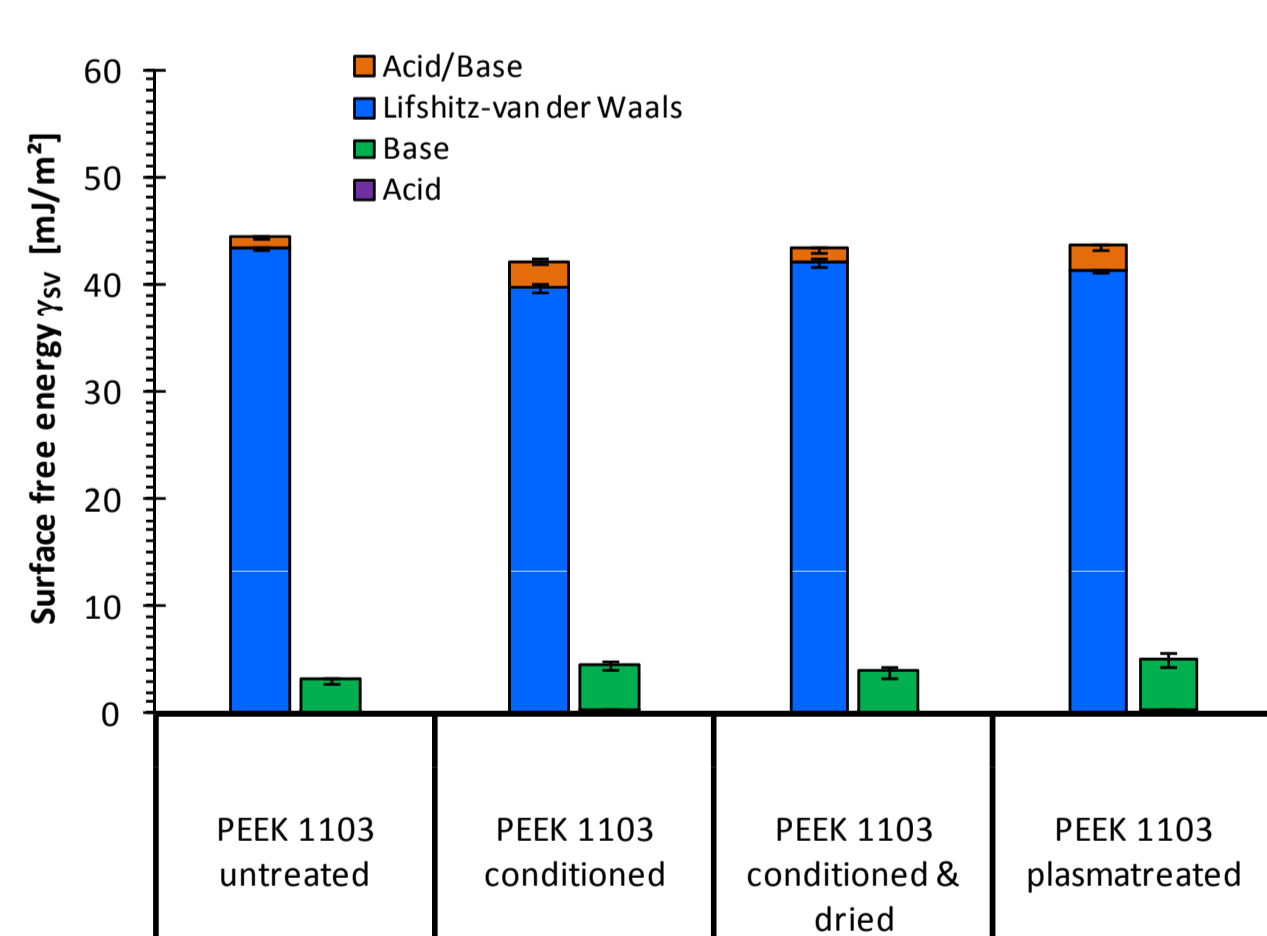

Fig. 4: Comparison of surface free energies of PEEK aptiv 1103 films calculated with the van Oss-method.

The results show a decrease of the contact angle with water and an increase of the polymer's polar (γ_{SV}^p) and basic (γ_{SV}^B) surface free energy fraction after conditioning in water. Hence, the polarity of the surface is increasing. The effect is still observable after drying and therefore it is not based on water absorption of the polymer matrix only. Plasma treatment of the surface leads to a similar effect. The acidic fraction of the surface free energy γ_{SV}^A is almost neglible for both surfaces.

Wetting envelope

The wetting envelope is the graphical presentation of the solutions for the surface free energy model equations. It represents the surface free energy fractions of the liquid (OWRK: γ_{LV}^d and γ_{LV}^p, van Oss et al.: γ_{LV}^{LW}, γ_{LV}^A and γ_{LV}^B) for a surface with known surface free energy contributions in the case of spreading of the liquid ($\theta = 0°$). With the wetting envelope and knowledge about the liquid's surface free energy fractions it is possible to predict whether a particular liquid will wet the solid completely (spreading).

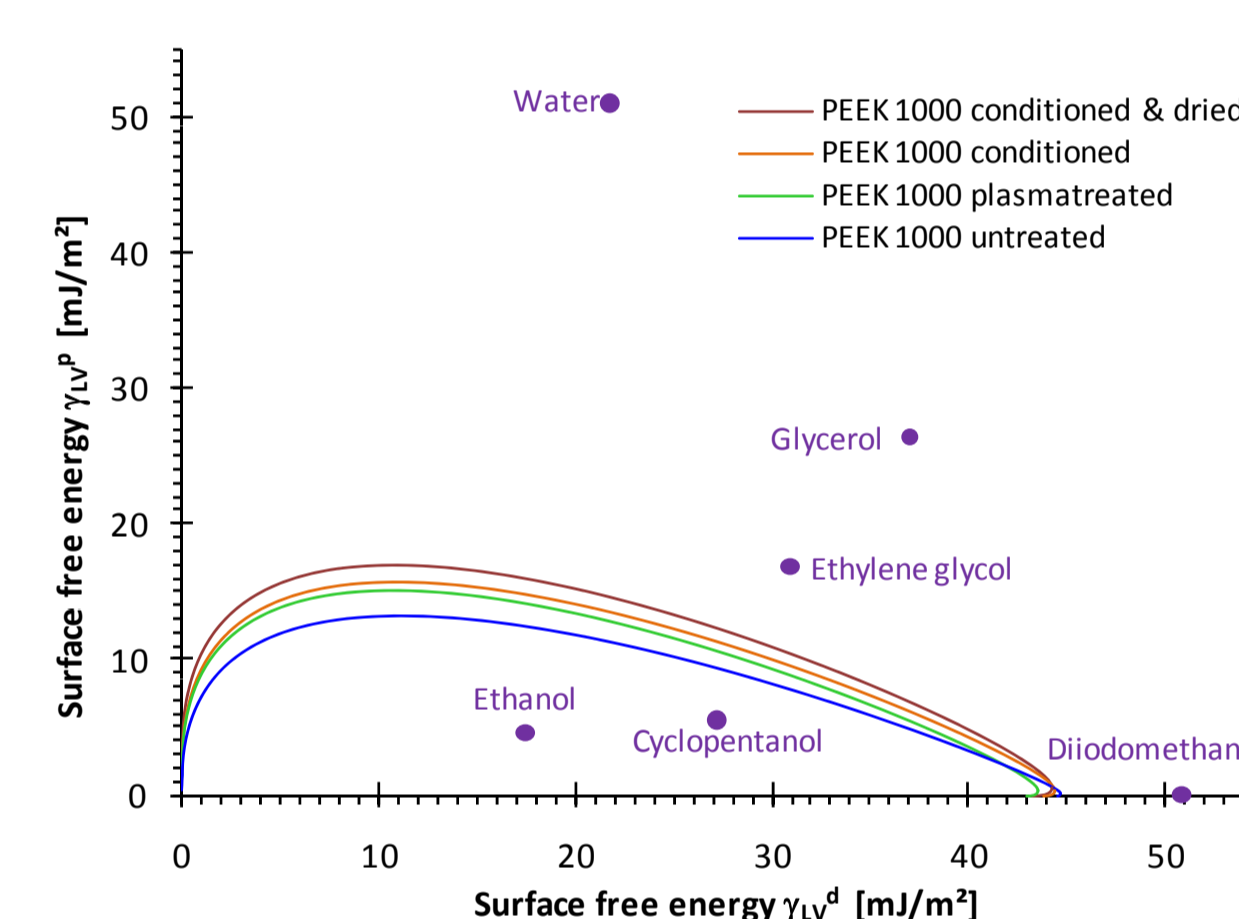#### Model of Owens[2], Wendt[2], Rabel[3] and Kaelble[4] (OWRK)

Fig. 5: Wetting envelope of different PEEK aptiv 1000 films and liquids based on the OWRK-method.
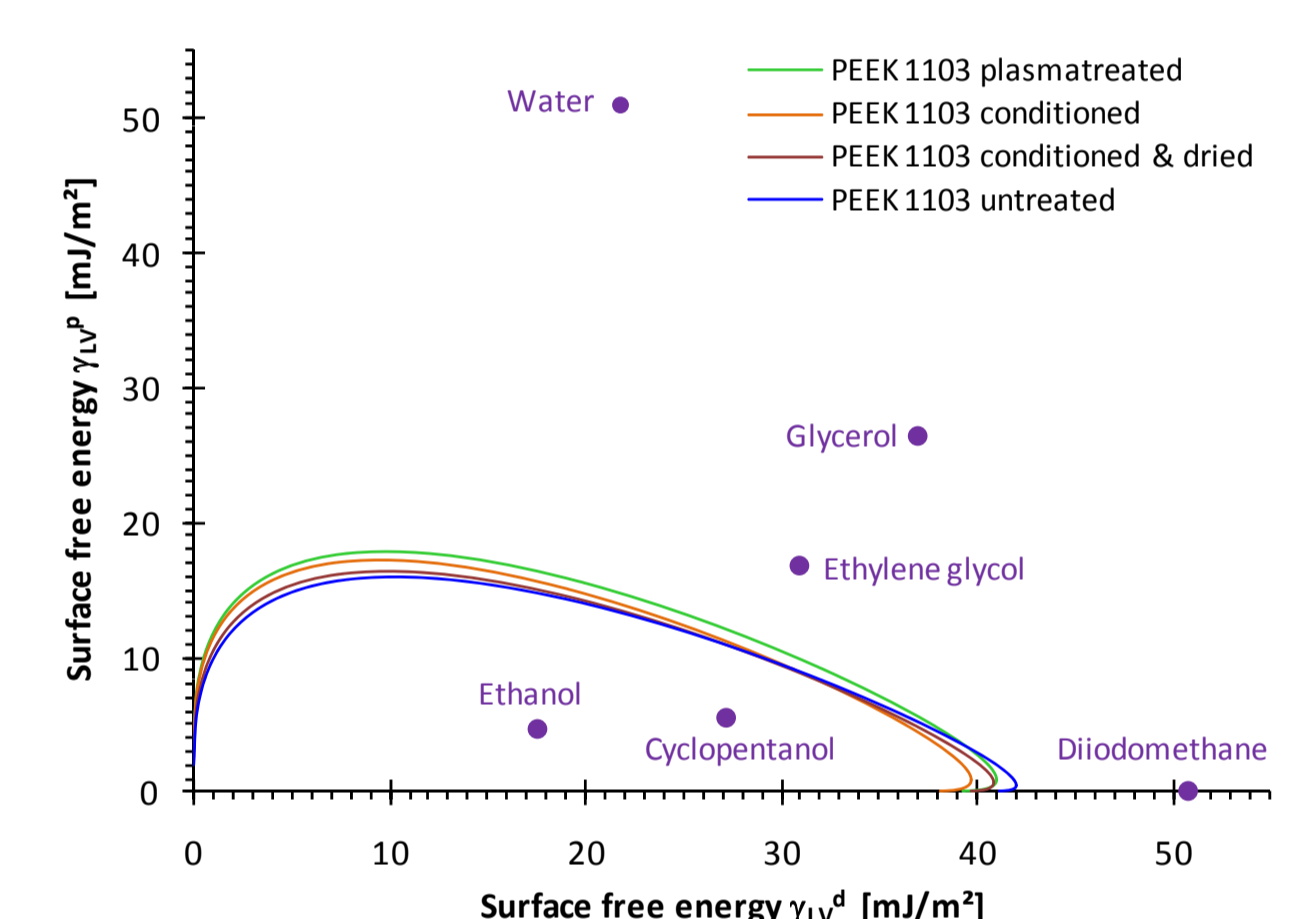

Fig. 6: Wetting envelope of different PEEK aptiv 1103 films and liquids based on the OWRK-method.

Model of van Oss et al.[5,6]

Fig. 7 and Fig. 8 show the wetting envelops derived by the model of van Oss et al. The diagramms compare the worst wettable surface (PEEK aptiv 1000 untreated) and the best wettable surface (PEEK aptiv 1103 plasma treated) tested.
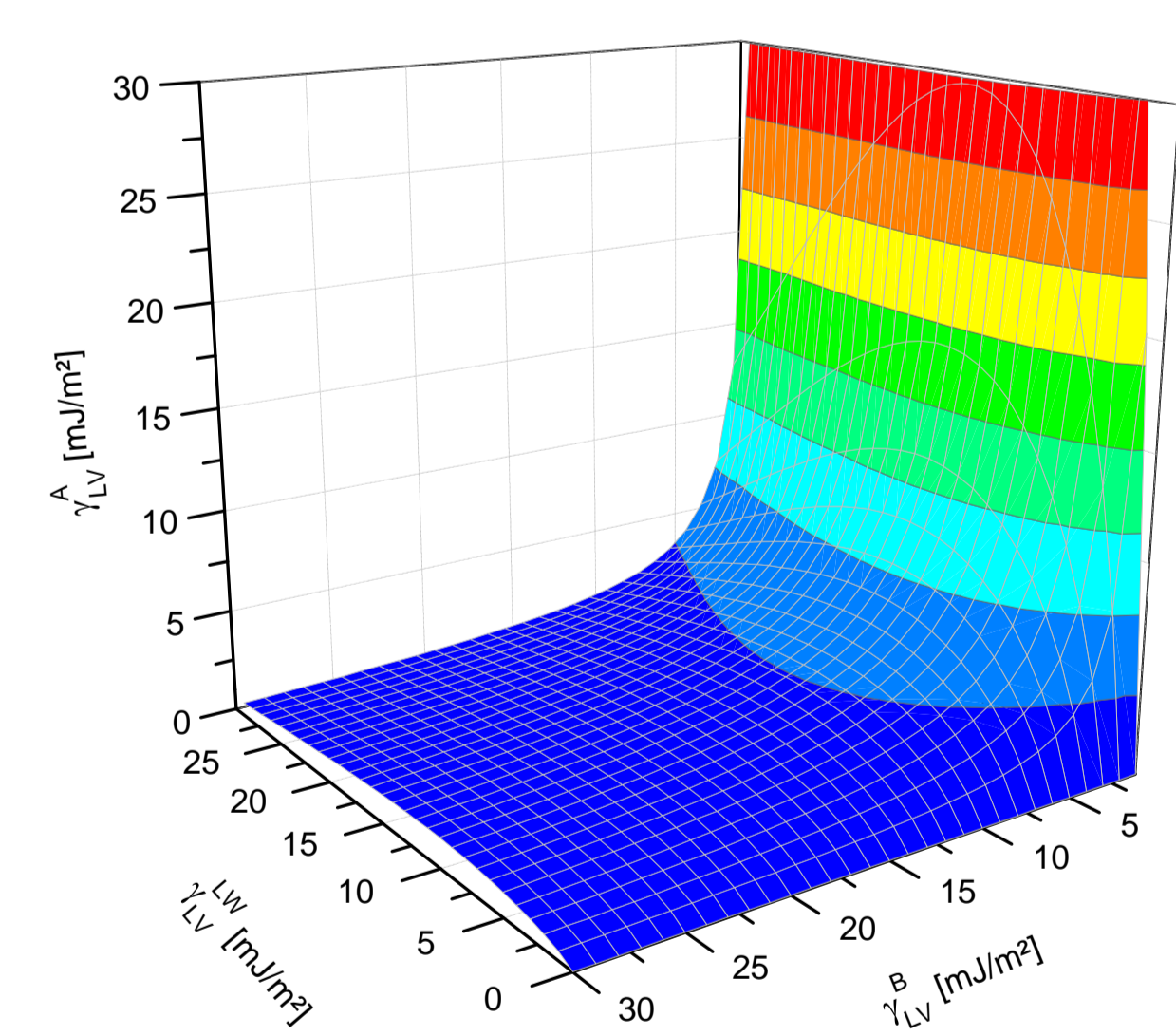

Fig. 7: Wetting envelope of PEEK film aptiv 1000 untreated based on the van Oss method.
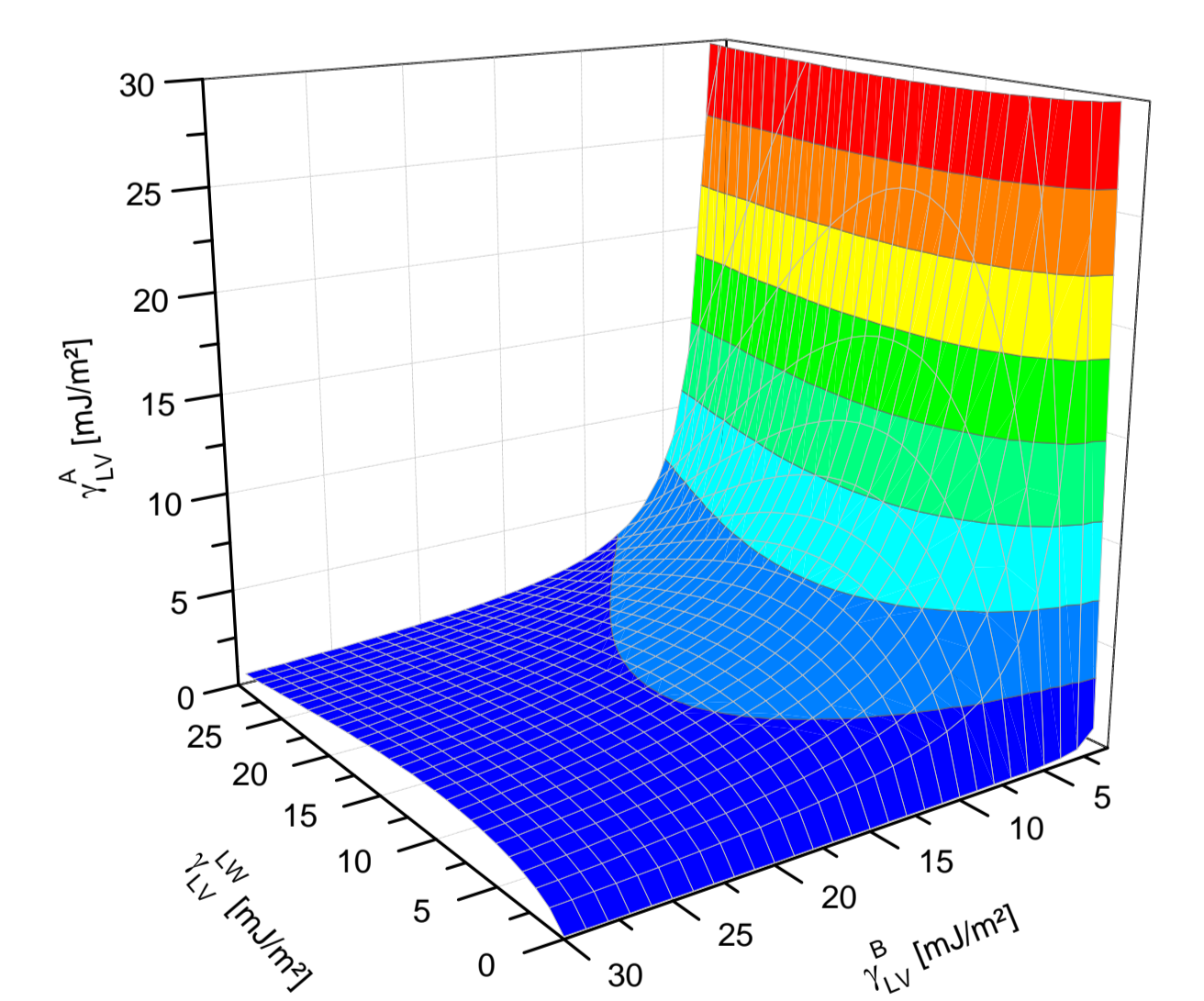

Fig. 8: Wetting envelope of PEEK film aptiv 1103 plamsateated based on the van Oss method.

The wetting envelopes show an enhancement of the wetting behaviour after pre-treatment by conditioning in water and plasma pre-treatment, respectively. The range of liquid surface free energies which lead to spreading of the liquid on the surface is expanding after pre-treatment. The impact of the type of pre-treatment is different for both PEEK films. Conditioning in water has a superior effect on PEEK aptiv 1000 films compared to PEEK aptiv 1103 films.

Conclusions

➤ The wettability of PEEK surfaces can be improved by conditioning with water or by plasma treatment. The reason leading to polarity increase is different for both types of pre-treatment. Plasma treatement it is leading to an oxidation of polymer molecules on the surface. With reference to the excellent hydrolysis resistance of PEEK, surface oxidation during water storage can be excluded.

➤ The lack of an acidic surface free energy fraction allows for the conclusion that both PEEK surfaces display monopolar basic surface properties.

➤ The increase of surface polarity after pre-treatment in water is an indication for polymer chain migration or reorientation. This is supported by the observed increase of the basic surface free energy fraction, which accounts for the presence of electron donors at the surface. PEEK contains oxygen atoms and benzene rings with delocalised π electrons, that can serve as electron donors exhibiting a monopolar basic character.

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