

# Evaluation of polymeric coatings on their efficiency of inhibiting the adhesion of inorganic scale

M F B Sousa<sup>1,3</sup>, C A Bertran<sup>1</sup>, M O Penna<sup>2</sup>

<sup>1</sup>Universidade Estadual de Campinas, Instituto de Química, Campinas, SP, Brazil

<sup>2</sup>CENPES – Petrobras, Rio de Janeiro, RJ, Brazil

<sup>3</sup>to whom any correspondence should be addressed: mfabr@iqm.unicamp.br

**Abstract:** The use of polymer coatings allows modulating wettability and can contribute decisively to mitigate the formation of scale in pipes and equipment. In this work critical surface energy (CSE) and surface free energy (SFE) were determined for several polymer coatings (epoxy phenol novolac resins and fluoropolymers), aiming the evaluation of their anti-fouling capacity against brines reproducing formation waters from pre salt wells. Coatings with lower values for SFE and CSE presented the lowest degree of fouling as determined by wet analysis using inductively coupled plasma atomic emission spectroscopy (ICP - AES).

## 1. Introduction

Inorganic scale on the surface of equipment used in oil extraction originates from crystallization reactions involving ions present in the formation water. Scale deposition and adhesion are consequences of the properties of the interface between the solid surface and the scaling brine [1,6].

One of the interface features that contribute to the adhesion is wettability [7]. This property is determined by measuring contact angle, which is the angle that a drop of a probe liquid forms when in contact with a solid surface. Two quantities can be calculated from wetting data: the surface free energy (SFE) and the critical surface energy (CSE). The critical surface energy also known as the critical surface tension, characterizes the wettability of a surface by several liquids. Solids presenting high CSE are wettable by most liquids, while solids having low CSE are not wettable by most liquids. In turn, the surface free energy (SFE) is defined as the excess energy at the surface of a material compared to its bulk.

The use of polymer coatings allows modulating wettability and can contribute to mitigate the formation of scale in pipes and equipment, however the literature reports only few studies dealing with the application of polymeric coatings as anti-fouling surfaces for use in the oil and gas industry. In this work the critical surface energy and surface free energy were determined for seven polymer coatings from four different suppliers aiming the evaluation of their anti-fouling capacity when exposed to brines reproducing formation waters from pre salt wells in Brazil. Five epoxy phenol novolac resins (EPNA and EPNB from supplier 1; EPNC and EPND from supplier 2; EPNE from supplier 3) and two fluoropolymer resins (FPA from supplier 4 and FPB from supplier 2) were investigated. Stainless steel (SS) was used as reference.

## 2. Experimental

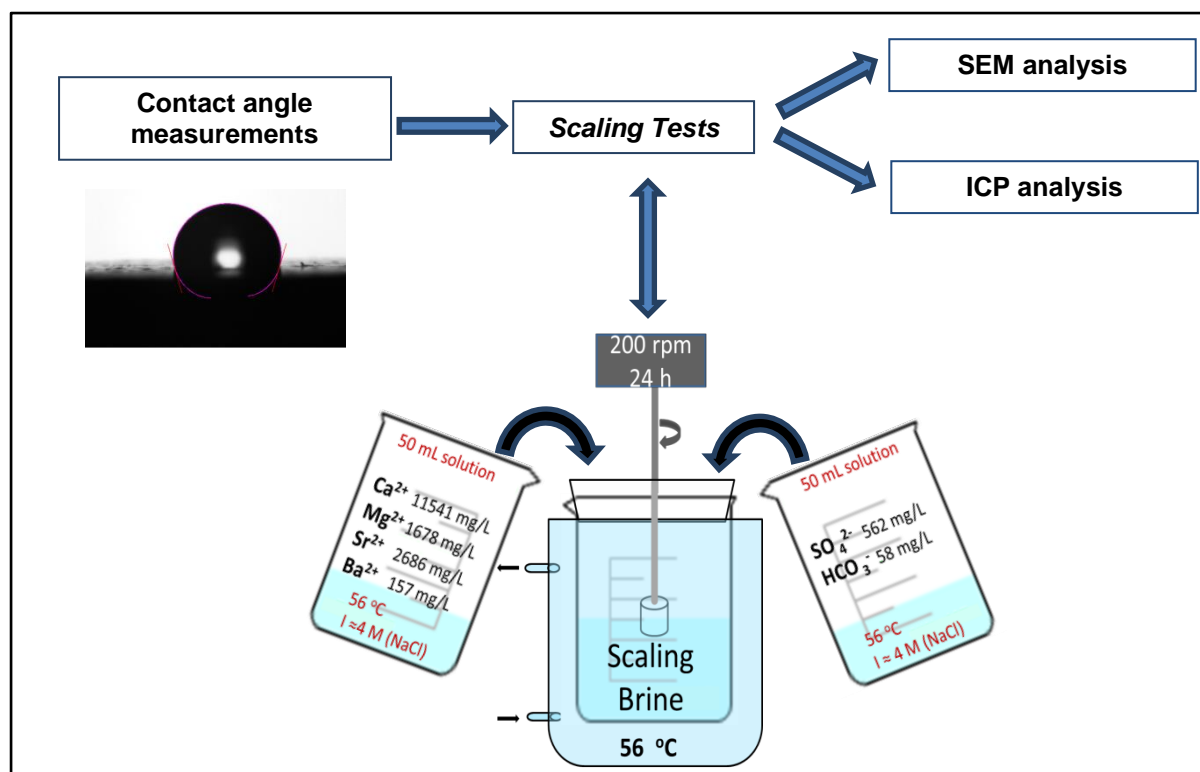
### 2.1. Contact angle measurements



Contact angle measurements were performed on the flat base of cylindrical coupons or on flat plates applying the sessile drop technique using a tensiometer/goniometry Attention Theta (BiolinScientific). Samples were rapidly cleaned with ethanol, rinsed with deionized water and ultrasonicated for 5 min in deionized water, then the contact angles were measured for three probe liquids. The used liquids and their average volumes were: water (5.5  $\mu\text{L}$ ), glycerol (4.4  $\mu\text{L}$ ) and ethylene glycol (7.0  $\mu\text{L}$ ). Hamilton syringe with stainless steel needle (out diameter = 0.72 mm; inner diameter = 0.21 mm) was used to dispense the drops.

## 2.2. Tests for the formation of scale deposits

Separated synthetic cations- and anions-containing brines, simulating composition of formation water (FW) with high sulfate and strontium content, were mixed and used for conducting scaling experiments (figure 1). Cations- and anions- containing solutions were prepared using analytical grade reagents dissolved in deionized water, and were filtered by membranes with pore size of 0.45 micrometers. Equal volumes (50.00 mL) of each of these two solutions were mixed and only the bottom of the coupon, connected to a rotor from PINE was exposed to the resulting mixture for 24 hours at 56 °C. A rotational speed of 200 rpm was applied. After being removed from the scaling medium, the coupon was slowly and carefully washed 4 times by immersion into deionized water. Then it was kept in an oven at 60 °C during 4 hours before preparation for ICP analysis.



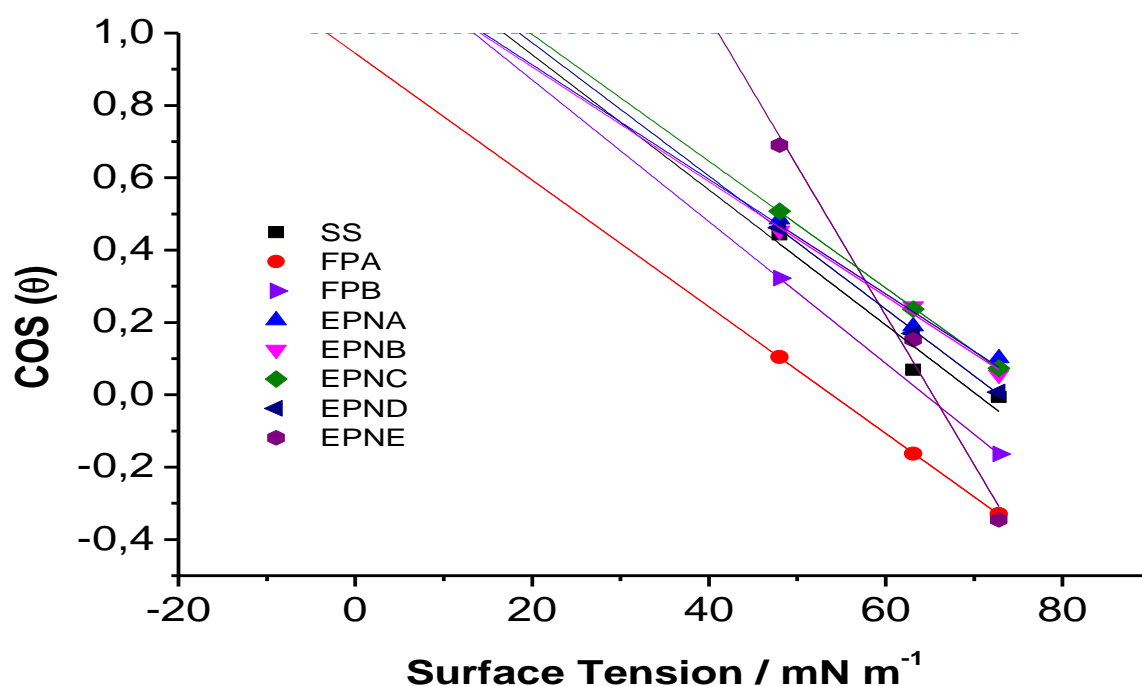
**Figure 1.** Overall experimental set-up.

## 2.3. Analysis by Scanning Electron Microscopy (SEM)

After the scaling experiments the coupons with scale deposits were washed with deionized water, dried at 60 °C and examined in a scanning electron microscope (JEOL SM-6360LV - JEOL Ltd.). Samples were imaged by SEM secondary electrons applying an accelerating voltage of 2 kV or 5 kV.

### 3. Results and Discussion

For the estimation of critical surface energies (CSEs), Zisman plot – type graph (figure 2) were done by plotting liquid surface tension ( $\gamma$ ) on the X-axis, and the cosine of the corresponding contact angle on the Y-axis [8]. The extrapolation of the  $\cos \theta$  vs  $\gamma$  curve to  $\cos \theta = 1$  (corresponding to the zero contact angle, or the complete wetting limit) gives the value of the CSE of the tested surface. Three pure probe liquids were used with surface tensions ranging from 72,8 mN m<sup>-1</sup> to 48,0 mN m<sup>-1</sup> (water, glycerol and ethylene glycol), which allowed a good precision in the extrapolation process as described above. The surface tension values used were:  $\gamma_{\text{water}} = 72.8 \text{ mN m}^{-1}$ ;  $\gamma_{\text{glycerol}} = 63.1 \text{ mN m}^{-1}$ ;  $\gamma_{\text{ethylene glycol}} = 48.0 \text{ mN m}^{-1}$ . It is necessary to point out that the critical surface energy (CSE) is in fact a wettability range showing the maximum surface tension a liquid may have to ensure complete wetting of a given material.



**Figure 2.** Zisman plot – type graph: extrapolation of the  $\cos \theta$  vs  $\gamma$  curve to  $\cos \theta = 1$  (corresponding to the zero contact angle, or the complete wetting limit for each coating).

It can be observed in Figure 3 that the fluor-based coatings, FPA and FPB, are hydrophobic, i.e., each of them presents water-contact angle higher than 90°, this behavior is expected for fluoropolymers coatings [9], but their ECS and SFE values are very similar those presented by epoxy phenol novolac resins EPNA and EPNB. All other coatings form one block with exception of EPNE, which shows a peculiar behavior, i.e. it presented high CSE, but has good discrimination for the probe liquids with hydrophobicity similar to FPA coating.

Although in theory only two liquids would be enough for the determination of CSEs, in practice, this is not true; if only few different liquids are used, incorrect results and even negative values can be obtained, as it occurred to FPA. For this reason, another approach to characterize these surfaces considering their surface energy was also applied.

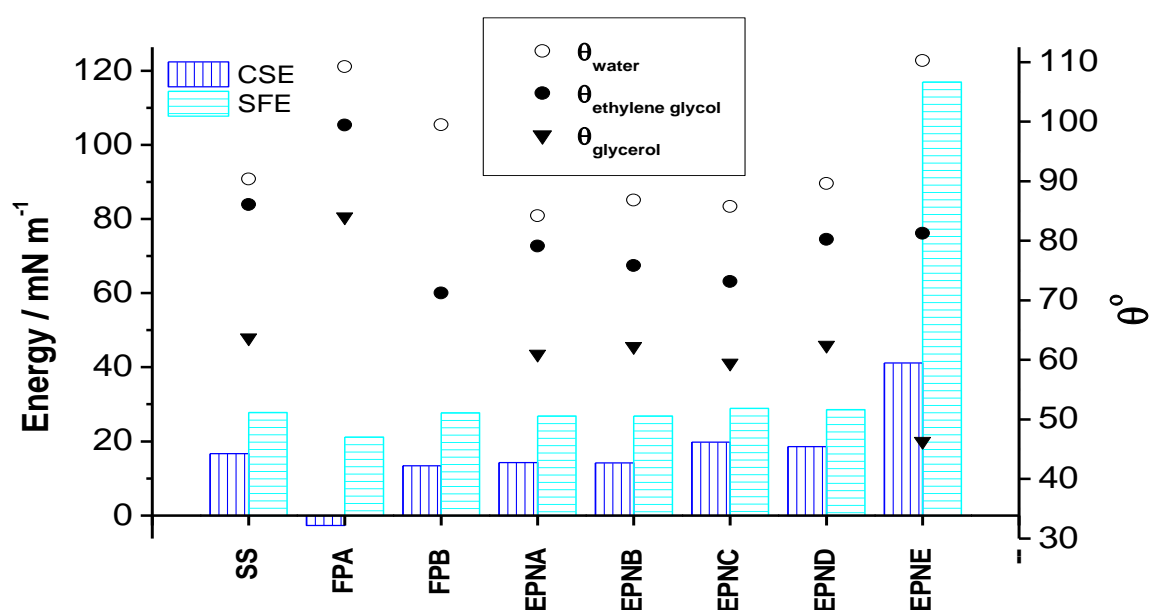
Many theories using different approaches are used for these calculations [10-12] involving testing the solid against two liquids whose polar and dispersive components of their surface tension are known. In this work the surface free energy (SFE) was calculated by using the OWRK/Fowkes equation (1). In this case, the adhesion energy is a sum of two partial contributions, each of which is expressed as the geometric mean of two adhesion parameters,  $\gamma_L$  and  $\gamma_S$ , characterizing the powers of

adhesion of the liquid and of the solid, respectively. The superscripts “*d*” and “*p*” refer to the dispersive and polar components of the probe liquids (Table 1) and of the solid surfaces (to be calculated). Results for this later methodology are presented in figures 3 and 4.

$$\gamma_L(1 + \cos\theta) = 2 \left[ (\gamma_L^d \gamma_S^d)^{\frac{1}{2}} + (\gamma_L^p \gamma_S^p)^{\frac{1}{2}} \right] \quad (1)$$

**Table 1** - Surface tension parameters for water and ethylene glycol [4]

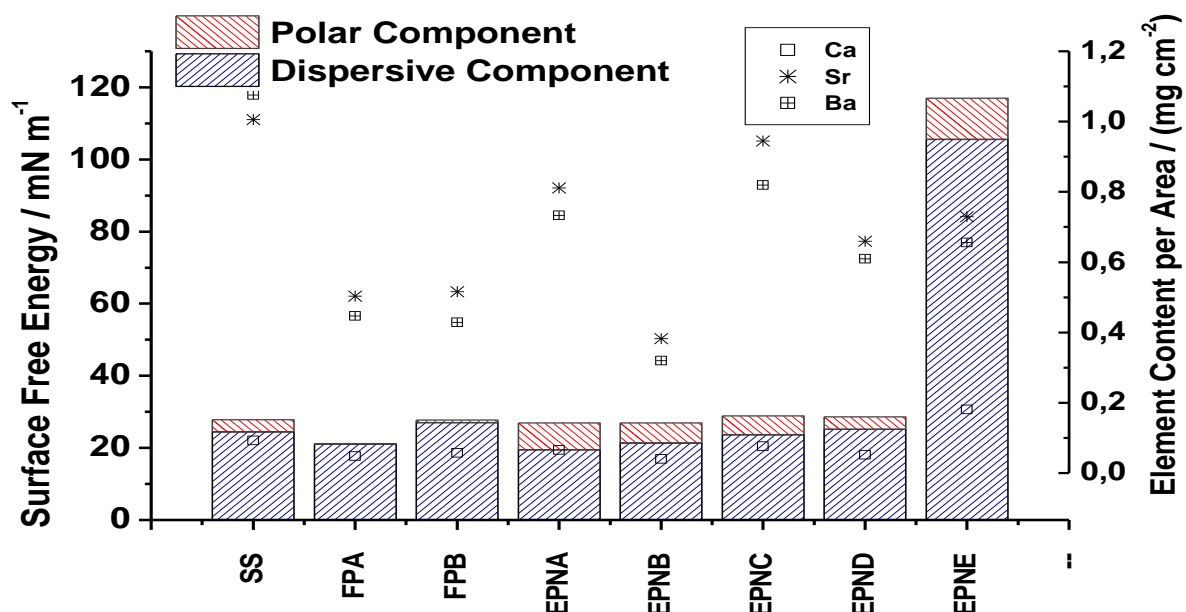
Probe liquid	$\gamma_L$ (mN/m <sup>-1</sup> )	$\gamma_L^d$ (mN/m <sup>-1</sup> )	$\gamma_L^p$ (mN/m <sup>-1</sup> )
Water	72.8	21.8	51.0
Ethylene glycol	48.0	29.0	19.0



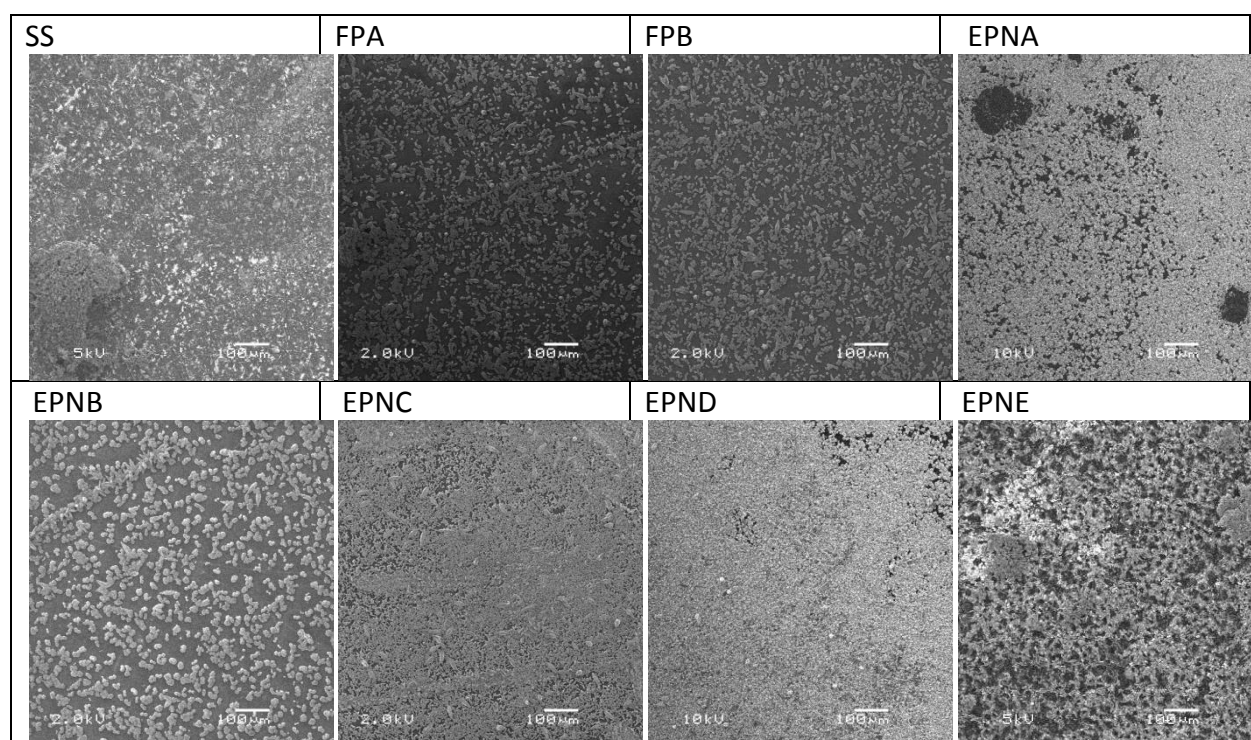
**Figure 3.** Values of contact angles, Critical Surface Energy (CSE) and Surface Free Energy (SFE) for each coating and the reference SS.

In figure 4 SFE for each coating is shown divided into its two components (polar and dispersive), as well as the content of Ca, Sr and Ba present in the deposits formed onto these coatings after their contact with the synthetic formation water for 24 hours. Coatings FPA, FPB and EPNB achieved higher inhibition efficiency, and EPNE was the coating with the highest degree of fouling.

Coatings presenting lower values for the polar component generally showed the lowest degree of scale compared to stainless steel as can be seen by ICP results (figure 4) and also in the micrographs presented in figure 5. In general, the deposit formed is not uniformly distributed over the surface of the coupon, therefore one should keep in mind that the analysis by ICP takes into account the total deposit while a SEM image is more sectorial and, depending on the magnification, shows only a small part of the whole.



**Figure 4.** Surface free energy and its components. Elemental composition of scale deposit per coating area, for each coating



**Figure 5.** SEM images showing scale deposited onto bare SS and coated coupons.



#### 4. Conclusion

Taking into account that all specimens were exposed to the formation water under the same conditions of temperature, stirring and time, it can be concluded that in relation to the deposition of calcium carbonate only SS presents some selectivity. However for barium and strontium sulfates there is a significant variation in the degree of deposition onto each of the evaluated coatings. Fluor-based coatings FPA and FPB presented lowest values the polar component in SFE. In general, considering the results of ICP and SEM, there are two groups of coatings. For the same manufacturer, coatings with lower SFE polar component presented less scale deposition. Coating with microscopically rougher surface like EPNE presented higher scale deposition.

#### Acknowledgments

The authors wish to acknowledge Petrobras-CENPES and ANP for their funding (Grant No. 0050.0077857.12.9)

#### References

- [1] Gunn D J 1980 Effect of surface roughness on the nucleation and growth of calcium sulphate on metal surfaces *J. Cryst. Growth* **50** 533-7.
- [2] Lin N H, Shih W-Y, Lyster E and Cohen Y 2011 Crystallization of calcium sulfate on polymeric surfaces *J. Colloid Interf. Sci.* **356** 790-7.
- [3] Al-Anezi K, Johnson D J and Hilal N 2008 An atomic force microscope study of calcium carbonate adhesion to desalination process equipment: effect of anti-scale agent *Desalination* **220** 359-70.
- [4] Cai Y, Liu M and Hui L 2014 Observations and mechanism of CaSO<sub>4</sub> fouling on hydrophobic surfaces *Ind. Eng. Chem. Res.* **53** 3509-27.
- [5] Zisman W A 1963 Influence of constitution on adhesion *Ind. Eng. Chem.* **55** 18-38.
- [6] Kazi S N, Duffy G G and Chen X D 2010 Mineral scale formation and mitigation on metals and a polymeric heat exchanger surface *Appl. Therm. Eng.* **30** 2236-42.
- [7] Szymczyk K, Zdziennicka A, Krawczyk J and Jańczuk B 2012 Wettability, adhesion, adsorption and interface tension in the polymer/surfactant aqueous solution system. I. Critical surface tension of polymer wetting and its surface tension *Colloid Surface A* **402** 132-8.
- [8] Kabza K, Gestwicki J E and McGrath J L 2000 Contact angle goniometry as a tool for surface tension measurements of solids using Zisman plot method *J. Chem. Edu.* **77** 63-5.
- [9] Chaudhuri R G and Paria S 2009 Dynamic contact angles on PTFE surface by aqueous surfactant solution in the absence and presence of electrolytes *J. Colloid Interf. Sci.* **337** 555-62.
- [10] Kwok D Y, Lam C N C, Li A, Leung A, Wu R, Mok E and Neumann A W 1998 Measuring and interpreting contact angles: a complex issue *Colloid Surface A* **142** 219-35.
- [11] Siboni S, Della Volpe C, Maniglio D and Brugnara M 2004 The solid surface free energy calculation II *J. Colloid Interf. Sci.* **271** 454-72.
- [12] Della Volpe C, Maniglio D, Brugnara M, Siboni S and Morra M 2004 The solid surface free energy calculation I. In defense of the multicomponent approach *J. Colloid Interf. Sci.* **271** 434-53.