

CHARACTERIZATION OF THE CARBON FIBRE SURFACE CHEMISTRY
BY THE WORK OF ADHESION - pH DIAGRAM

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INTRODUCTION

The work of adhesion - pH value diagram was introduced for characterization of the acidity and basicity, in other words the chemistry of a solid surface [1,2]. It is based on the fortunate fact that the surface tension of basic and aqueous solutions covering the pH range from 1 to 14 is nearly constant and equal to the surface tension of water (72.8 mN/m). With a polar surface, water can make not only dispersive interactions, but also various kinds of non dispersive interactions, at least by hydrogen bonds and Brønstedt acid - base complexes. By addition of acids and bases, additional Brønstedt acid - base complexes can be formed.

The work of adhesion, W_{SL} , is determined from contact angle measurements by eq. (1):

$$W_{SL} = \gamma_L \cdot (1 + \cos \Theta) \quad (1)$$

W_{SL} = work of adhesion between a solid S and a liquid L, mJ/m²; γ_L = surface tension of the liquid, mN/m; Θ = contact angle, °.

It is composed of the following terms (eq.(2)):

$$W_{SL} = W_{SL}^{LW} + W_{SL}^{AB/H} + W_{SL}^{AB/B} \quad (2)$$

W_{SL}^{LW} = W_{SL} due to Lifshitz/van der Waals forces, $W_{SL}^{AB/H}$ = W_{SL} due to hydrogen bonds, and $W_{SL}^{AB/B}$ = W_{SL} due to Brønsted acid -base complexes.

W_{SL} can be calculated by eq. (3):

$$W_{SL}^{AB} = - n_i \Delta G_i^\circ \quad (3)$$

n_i = number of acid -base pairs, ΔG_i° = Gibbs free energy of formation of an acid base pair.

Earlier interpretations of the W_{SL} -pH value

diagram of surface oxidized carbon surfaces were not complete [1,2]; therefore, an extended interpretation will be presented.

RESULTS AND DISCUSSION

For determination of W_{SL}^{LW} with water, the dispersive fraction of the surface free energy of the various carbon fibres, γ_S^{LW} , was calculated from contact angle measurements with methylene diiodide, a nearly non-polar liquid ($\gamma_L^{LW} = 49.8$ mN/m, $\gamma_L^P = 1$ mN/m) by the geometric mean relationship (eq.(4)):

$$W_{SL} = \gamma_L \cdot (1 + \cos \Theta) = 2(\gamma_S^{LW} \cdot \gamma_L^{LW})^{1/2} \quad (4)$$

With the known value of the surface free energy of the carbon fibres γ_S^{LW} , W_{SL}^{LW} with water was calculated from the dispersion component of the surface tension of water ($\gamma_L^{LW} = 21.8$ mN/m) by eq. (4). It was found that W_{SL}^{LW} for water or the aqueous solutions is not strongly influenced by the degree of surface oxidation; the values are in the range of 64 mJ/m² (see Fig. 1). The differences between the W_{SL} values measured with the various carbon fibres and W_{SL}^{LW} have to be attributed to acid -base interactions given by $W_{SL}^{AB/H}$ and $W_{SL}^{AB/B}$.

Fig. 1 shows a typical W_{SL} -pH diagram of a surface oxidized carbon fibre; it usually exhibits two steps, namely one in the lower and another one in the higher pH range. It follows from Fig. 1 that W_{SL}^{AB} at low pH values results from various types of hydrogen bonds. The first step indicates a Brønstedt acid - base complex formed with strongly acidic carboxyl groups. The second step in the range of high

pH values indicates another Brønsted acid - base complex; it is attributed to phenolic hydroxyl groups. Sometimes a third step is observed around pH = 7 resulting from weakly acidic carboxyl groups which correspond to lactoles.

The steps were identified by two different methods: (1) stepwise decomposition of the functional groups by thermal treatment of the carbon fibre at the relevant decomposition temperatures, (2) chemical modification of the relevant functional groups; in both cases XPS analyses were performed before and after the treatment.

Fig. 2 shows the relevant functional groups and the corresponding pKa values. It is important to point out that the acidity of a functional group is generally influenced by a neighbored group. These mutual influences are the reason why a step in the W_{SL} - pH diagram caused by a Brønsted acid - base complex cannot be correlated with a well defined pH - value (see Fig. 13, reference [3]).

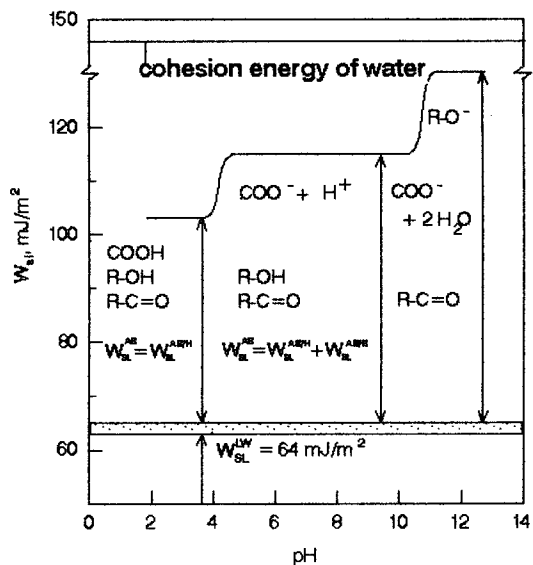


Fig. 1: W_{SL} -pH diagram of a surface activated carbon fibre.

SUMMARY

The W_{SL} - pH diagram now seems to be clear. This fact is useful because W_{SL} is an excellent correlation parameter with the adhesion of a polymer to a carbon fibre surface [4].

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REFERENCES

1. K.J. Hüttinger, S. Höhmann-Wien, G. Krekel, *Carbon* **29**, 1281 (1991).
2. K.J. Hüttinger, S. Höhmann-Wien, G. Krekel, *J. Adhes. Sci. Tech.* **6**, 317 (1992)
3. U. Zielke, W.P. Hoffman, K.J. Hüttinger, *Carbon*, to be submitted.
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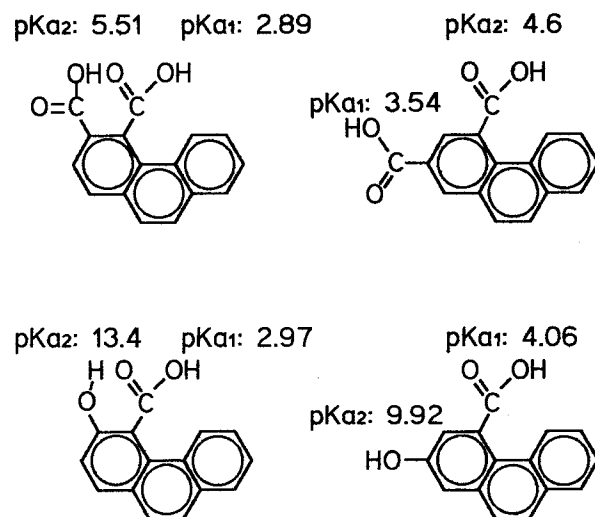


Fig.2: pKa values of carboxyl and hydroxyl groups showing the influence of neighbored groups.