

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,  $\text{mJ/m}^2$ ;  $\gamma_L$  = surface tension of the liquid,  $\text{mN/m}$ ;  $\Theta$  = contact angle,  $^\circ$ .

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,  $\Delta G_i^\circ$  = 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,  $\gamma_S^{LW}$ , was calculated from contact angle measurements with methylene diiodide, a nearly non-polar liquid ( $\gamma_L^{LW} = 49.8 \text{ mN/m}$ ,  $\gamma_L^P = 1 \text{ mN/m}$ ) 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  $\gamma_S^{LW}$ ,  $W_{SL}^{LW}$  with water was calculated from the dispersion component of the surface tension of water ( $\gamma_L^{LW} = 21.8 \text{ mN/m}$ ) 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  $64 \text{ mJ/m}^2$  (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]).

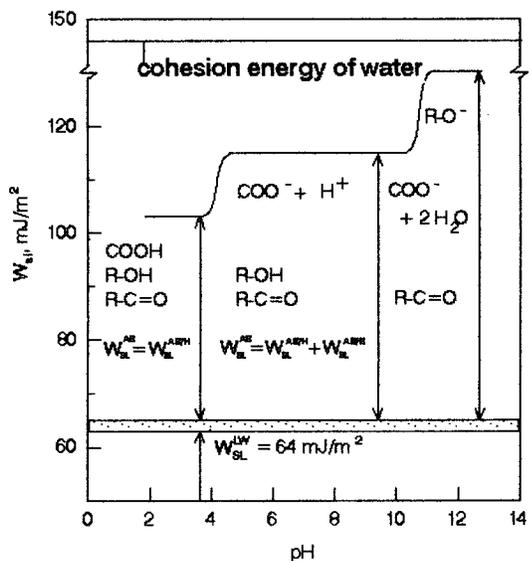


Fig. 1:  $W_{SL}$ -pH diagram of a surface activated carbon fibre.

## 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].

## ACKNOWLEDGEMENT

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## REFERENCES

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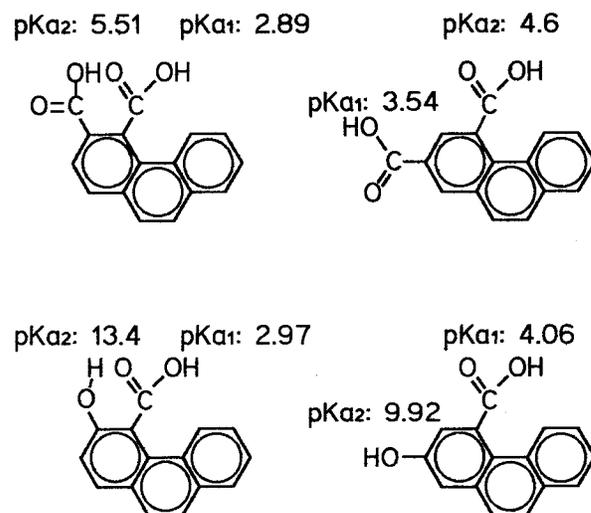


Fig.2: pKa values of carboxyl and hydroxyl groups showing the influence of neighbored groups.