INTERACTION OF SURFACE OXIDIZED CARBON FIBRES WITH HIGH TEMPERATURE THERMOPLASTICS

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INTRODUCTION

In a recent study a very strong adhesion of high temperature thermoplastics (PC, PES) to surface activated carbon fibres was observed; it was explained by chemical bonds being formed in the interface during processing of the composites above a temperature of 300°C, where carboxyl groups are decomposed [1]. This remarkable phenomenon was further studied with carbon fibres of different nature (HT, IM and HM fibres), polyethersulfone (PES) and polyetherimide (PEI) as matrix resins, and by direct analyses of the interphase. For angle resolved XPS some additional experiments with surface oxidized glass like carbon were performed.

EXPERIMENTAL

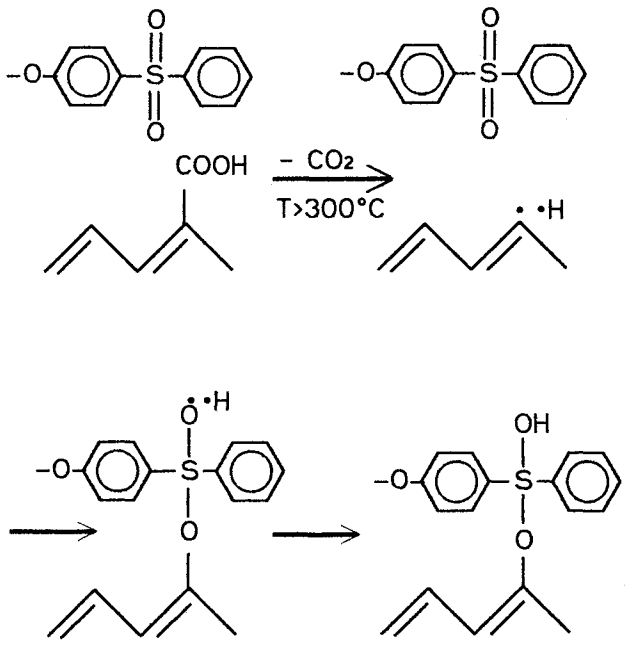
UD-composites with a fibre volume fraction of 60% were fabricated with the following fibres: Tenax HTU (uu), (A);Tenax HTA (ou), (B); fibre (A)/ozone treated, (C); AS4 (ou), (D); T800 (ou), (E); M40 (ou), (F); (uu = unoxidized, unsized); (ou = oxidized, unsized). Fibres C_1, C_2 and C_3 were treated with methanol/HCl (C_1), reduced with $LiAlH_4$ (C_2), and heat treated at 500°C in pure argon (C_3). The composites were investigated by measuring the strength with the short beam shear test, σ_{ST}, and the flexural strength with the three point bending test, σ_{BT}. For analysis of surface attached or bound polymer the matrix was extracted from the composites with dichloromethane (Soxhlet technique) and the fibre surface was subsequently studied by XPS. The same procedure was applied to polymer coated glass like carbon.

Glass like carbon was surface activated by a 1 hour treatment with boiling 50% HNO_3, coated with films of PES and PEI, and treated in argon at the processing temperature of the polymers at 340°C. Contact angles with water were measured on the activated sample, after treatment at 340°C in flowing argon, after coating with the polymers, and after removal of the coating with dichloromethane.

RESULTS AND DISCUSSION

Fig. 1 shows the apparent interlaminar shear strength σ_{ST} in dependence of the maximum work of adhesion, $W_{SL,max}$, determined from contact angle measurements with a basic solution of pH 13 [2]. Composites with the HT fibres (B), (C) and (D) do not show a dependence of σ_{ST} on $W_{SL,max}$, in other words the surface activity of the fibre; these composites failed by plastic deformation, and not by shear, because the adhesion energy in the interface is higher than the cohesion energy of the polymer. The composites with all further fibres were found to fail in a complex manner, most probably by a combined compression/shear mechanism. A linear relationship between σ_{ST} and $W_{SL,max}$ was found for these fibres. In the case of fibre (E), σ_{ST} was corrected to account for the lower diameter of 5 µm, giving the value referred to fibre E*. Fig. 2 shows the work of adhesion, W_{SL}, with water (pH = 7) on various surface treated glass like carbon samples without and with polymer coating. It is remarkable that equal W_{SL} values were found on the polymer coating before and after extraction and especially after additional treatment of the extracted sample at 340°C. It means that at least a monolayer of the polymer could not be removed by exhausting extraction. This result is a first direct indication on the strong adhesion of the polymer to the surface oxidized carbon.

XPS studies before and after extraction of the samples showed the following changes: (1) a strong decrease of double bound oxygen and a corresponding increase of single bound oxygen (PES), (2) a decrease of imide nitrogen and a new peak at 401.5-402.3 eV (PEI). This nitrogen peak is known from literature, but it has not yet been attributed to a well defined binding state of nitrogen [3]. Possible structural units are tertiary amine, oxazine, or quaternary nitrogen. With PES the following surface reaction is most probable:



Possible reactions with PEI will be presented elsewhere [4].

SUMMARY

The results of this study give a strong support for the earlier suggestion that chemical bonds can be formed between surface oxidized carbons and HT thermoplastics. The reason may be seen in the high processing temperature at which the carboxyl groups are decomposed.

ACKNOWLEDGEMENT

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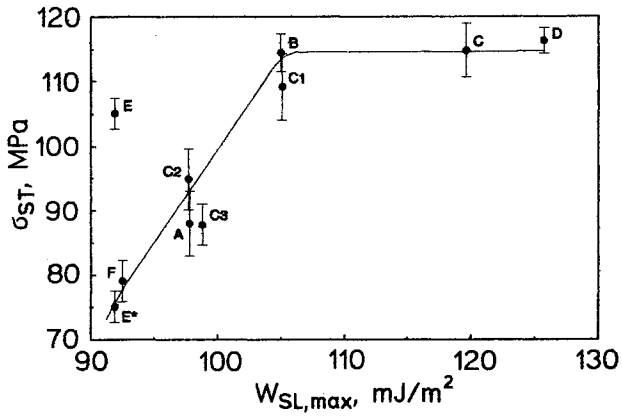

Fig.1: σ_{ST} in dependence of $W_{SL,max}$ (W_{SL} of an aqueous solution with pH = 13) at the carbon fibre surface.

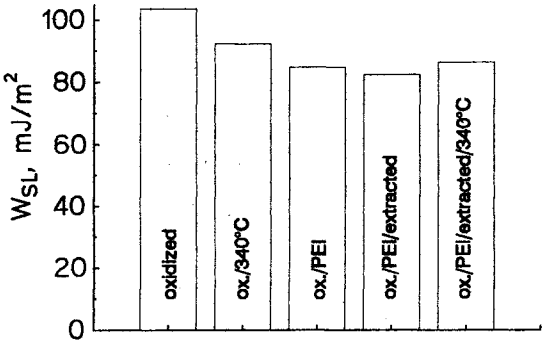

Fig. 2: W_{SL} with water on various glass like carbon samples; after coating with PEI the sample was treated at 340°C in argon.