CARBON FIBRE SURFACES WITH GRAFTED FUNCTIONAL GROUPS AND SIZINGS AND ITS INTERACTION WITH DIFFERENT MATRICES

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ABSTRACT

The aim of this research is to investigate the influence of different fibre surface modifications on the adhesion between carbon fibre and thermoplastic or thermoset matrices following different approaches. Carbonized, additionally oxidized and extra amino functionalized as well as epoxy sized and plasma modified single fibres were embedded into epoxy resin, polyamide 66 (PA66), polybutylene terephthalate (PBT), and maleic anhydride grafted polypropylene. Single fibre composites were produced in order to characterize the adhesion strength by the single fibre pull-out test. The failure behavior was investigated using scanning electron microscopy. The results show that the adhesion between fibre and matrix could be improved due to the installed amino groups in PA 66, the removal of the epoxy sizing, and applied oxygen containing groups in maleic anhydride modified PP. In the case of carbon fibre the epoxy sizing is supposed to seal the different functional groups on the fibre surface, however, an improved fibre-matrix adhesion in epoxy and PBT matrix was found.

1 INTRODUCTION

Carbon fibres (CF) are used increasingly in fibre reinforced composites because of their excellent properties such as high tensile strength, Young's modulus, chemical resistance, and low density. However, the poor interfacial adhesion between reinforcing CF surface and the polymer matrix limits the crucial properties of the composites toughness as well as longitudinal and transverse strength for the application in aerospace, wind energy, sports, and the automotive industry [1]. To overcome this critical issue, different ways of surface treatments have been applied during the last few years to enhance the adhesion between fibre and matrix [2-4] on the one hand and to guarantee the processability on the other. At industrial scale, this was achieved by a wet chemical two-step process. First, the activation of the fibre with electrochemical oxidation in an electrolytic bath to apply functional groups leading to improved chemical reactivity, and second, the application of a sizing layer to enhance the compatibility to the matrix polymer and to protect the fibre during processing. To achieve the aim of a good fibre-matrix adhesion, the applied functional groups must be selected accurately to enable the best possible matrix compatibility. Besides the carbon fibre surface, also the modification of the matrix polymer with additional coupling agents is a possible way to obtain good adhesive strength due to an increased number of interactions especially for polymers without reactive or polar functional groups (e.g. polypropylene) [5]. The presented results give a summary of different approaches to effect the fibre matrix interaction and its outcome regarding the adhesion strength.

2 EXPERIMENTAL

Our work is related to two main issues: (i) the effect of well matrix-adapted functional groups directly grafted on the carbon fibre surface and (ii) the fundamental understanding of the interaction of grafted functional groups in combination with additionally applied sizings on the fibre-matrix adhesion. Therefore, we used carbon fibres which were carbonized (CFC) and additionally electrolytically oxidized (CFO) provided by Carbon Nexus, Australia. The functionalization of these

fibers with amino groups ($CFONH_2$) was realized by an electrochemically reduction process of a synthesized diazonium salt described in [2]. The carbonized fibre and the oxidized fibre were treated with the same epoxy sizing (CFCEP1 and CFOEP1). Furthermore, a commercial available electrolytically oxidized and epoxy sized carbon fibre (CFOEP2) was used for plasma treatment. As matrix material polyamide 66 (PA66), polybutylene terephthalate (PBT), maleic anhydride grafted polypropylene (PPgMAH), and an epoxy resin (EP) were used. The interfacial adhesion strength was evaluated by single fiber pull out (SFPO) test using embedding equipment for sample preparation that was designed and constructed at the Leibniz-Institut für Polymerforschung Dresden e.V.. All treated fibres were embedded computer-assisted into different matrices under argon atmosphere. Afterwards, the fibre was pulled out by a self-made pull-out device [6] with a velocity of 0.01 µm/s and the force displacement curve was recorded. The evaluation with regard to the adhesion strength was carried out with the help of the measured characteristic forces and the material properties of fibre and matrix. The apparent interfacial shear strength (τ_{app}) and the local interfacial shear strength (τ_d) were calculated using the equations given in [7]. The post pull-out fibres were analyzed by SEM.

3 RESULTS AND DISCUSSION

The SFPO test results with polyamide 66 (see Table 1) showed that carbon fibres with grafted amino groups ($CFONH_2$) reveal higher values for τ_{app} and τ_d than the oxidized control fibres (CFO). Comparing the force displacement curves in Figure 1, $CFONH_2$ reveals higher max forces at less embedding lengths. At the same time, the max forces were reached at higher displacements which lead to a greater work of debonding. Comparing the SEM images of the fracture surfaces after the SFPO (see Figure 2) for both fibre types a nearly clean surface can be observed that indicates an adhesive failure behavior, however, the NH_2 modified fibre show some residual polymer at the surface.

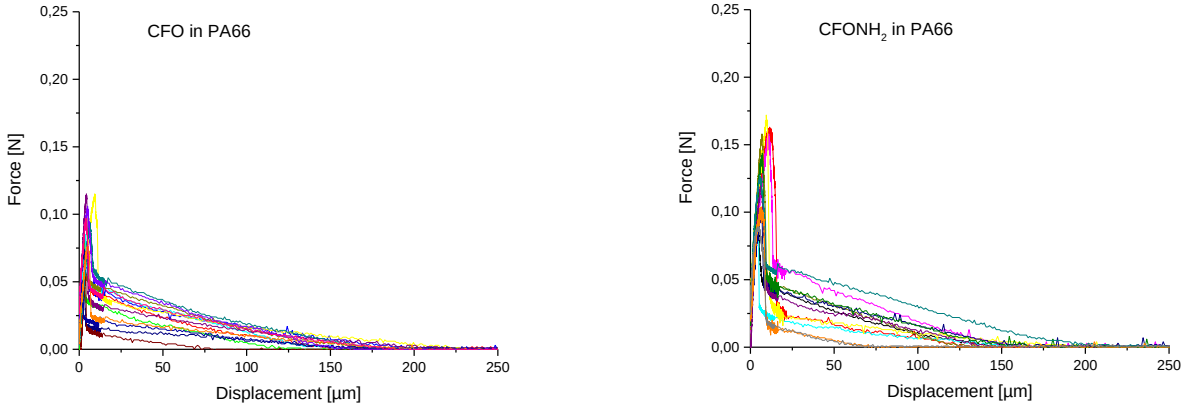

Figure 1: Force displacement curves for oxidized (CFO) and additionally NH_2-modified ($CFONH_2$) fibres pulled out of PA66

Using a polypropylene matrix, the epoxy sized carbon fibres (CFOEP2) were used due to their predictable low adhesion. As expected the adhesion strength in a maleic anhydride crafted polypropylene was rather low (Table 1). The incompatible epoxy sizing was removed during O_2 plasma treatment and functional surface groups were applied, which was evinced by XPS (see [8]). Therefore, the values for τ_{app} and τ_d increased (see Table 1).

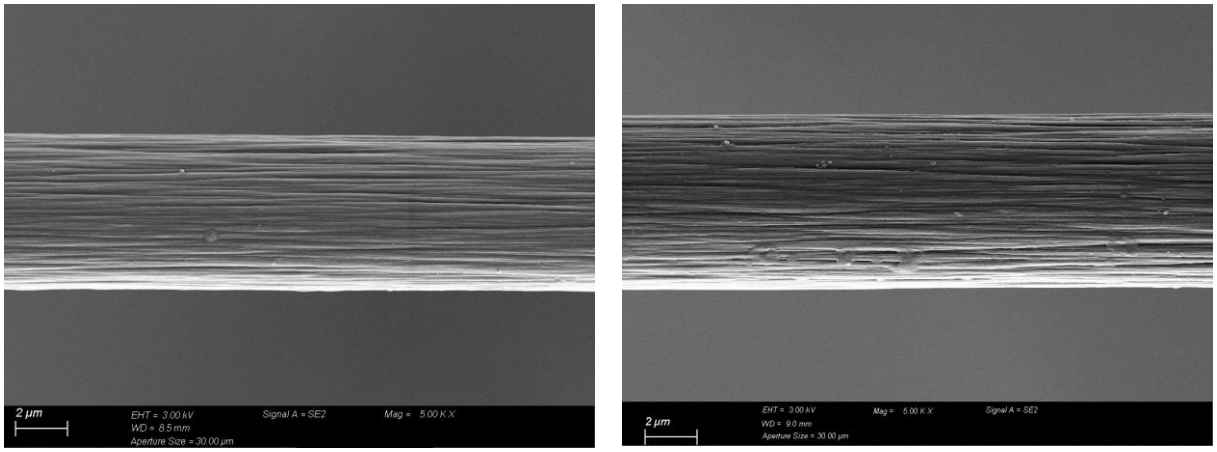

Figure 2: SEM of oxidized (CFO) and additionally NH_2-modified ($CFONH_2$) fibres pulled out of PA66

Fibre	Matrix	Apparent interfacial shear strength τ_{app} [MPa]	Local interfacial shear strength τ_d [MPa]	Embedding length l_e [µm]
CFO	PA66	21.5 ± 5.0	53.5 ± 11.9	177 ± 37
$CFONH_2$	PA66	37.2 ± 11.4	58.9 ± 10.8	153 ± 40
CFOEP2	PPgMAH	19.6 ± 9.5	22.1 ± 11.9	131 ± 36
$CFOEP2/PO_2$	PPgMAH	27.8 ± 5.8	33.1 ± 9.5	126 ± 37
CFO	PBT	22.0 ± 7.9	39.1 ± 7.6	156 ± 31
CFOEP1	PBT	44.8 ± 9.1	61.8 ± 13.0	123 ± 35
CFCEP1	PBT	39.1 ± 7.2	60.8 ± 19.2	123 ± 25
CFO	EP	47.6 ± 9.2	50.2 ± 8.6	68 ± 17
CFOEP1	EP	60.6 ± 4.2	63.4 ± 10.7	75 ± 17
CFCEP1	EP	57.4 ± 6.5	61.9 ± 9.6	77 ± 18

Table 1: Results of the quasistatic single fibre pull-out test

The experiments based on different polymer matrices reveal that grafted functional groups as well as functional groups applied by plasma are able to enhance the fibre-matrix interaction without involving any sizing (aqueous solution containing at least a polymer film former). In another experiment an epoxy sizing was applied on CF with different functional groups, so that in this case the sizing remains the same but the functional groups of the fibre surface are changed. Carbonized (CFCEP1) and additionally oxidized (CFOEP1) carbon fibres were embedded in polybutylene terephthalate. Both fibre types lead to nearly the same values in the SFPO test with no significant differences (see Table 1). This behavior was also observed when embedding the fibres in epoxy resin which also revealed no difference with relation to the grafted functional groups. It is assumed, that the functional surface groups were fully covered by the sizing and therefore do not straightly effect the fibre-matrix interaction. However, the shear strength values of the additionally EP-sized fibre CFOEP1 are significantly higher compared to the oxidized control fibre (CFO). It can clearly be seen that the applied sizing strongly contributes to the fibre-matrix adhesion. With regard to the local interfacial shear strength this means an increase of approximately 58%.

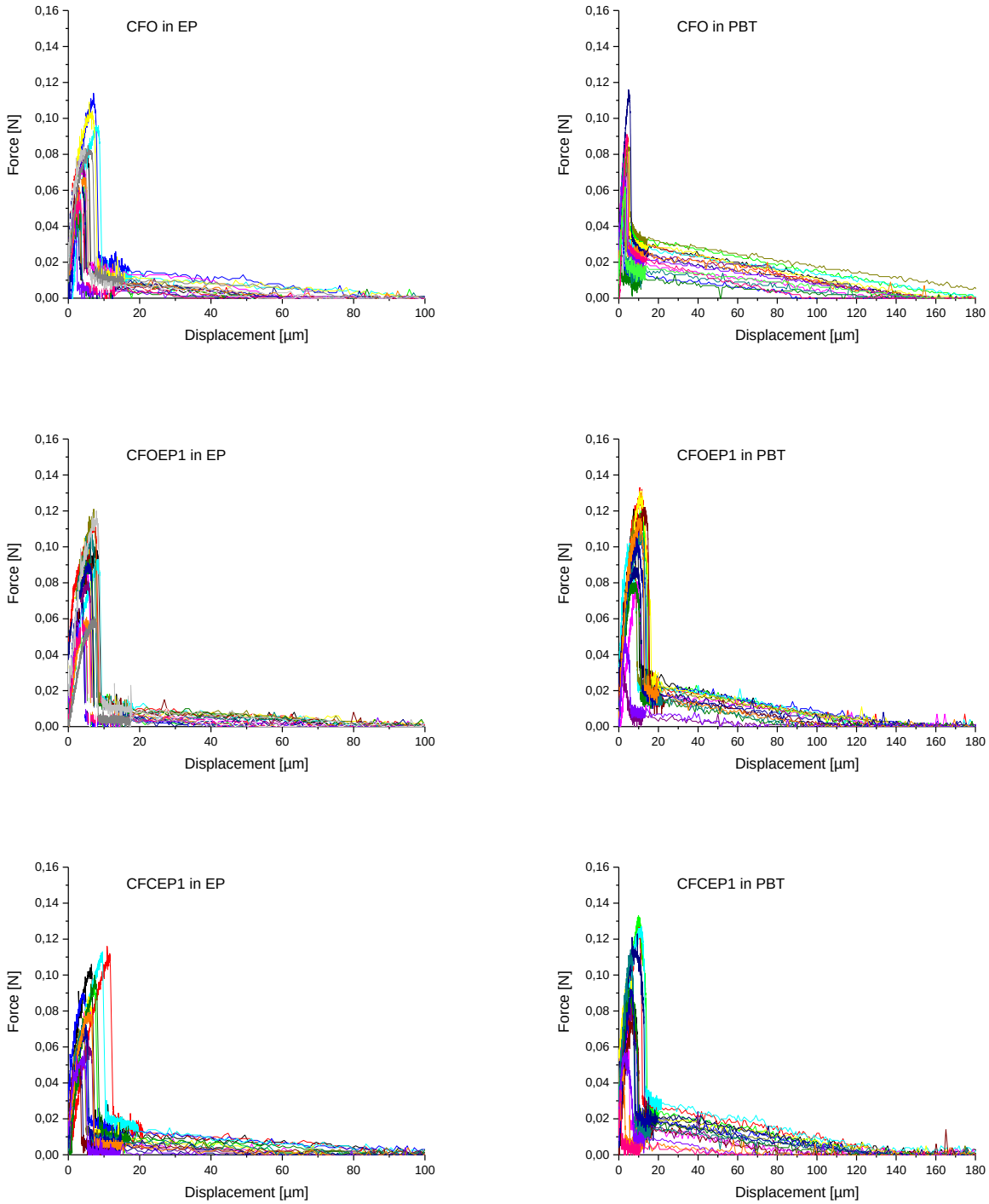

Figure 3: Force-displacement curves for the oxidized (CFO), additionally EP-sized (CFOEP1) and carbonized and EP-sized (CFCEP1) fibre in EP (left side) and PBT (right side)

This difference can also be seen when comparing the force displacement curves given in Figure 3. Despite the larger embedding lengths of CFO the average maximum force (F_{max}) compared to CFOEP1 was lower. Also the area under the curve up to the point F_{max} which corresponds to the work of debonding was much lower. By comparison, only slight differences in the shape of the force displacement curves of CFO and CFOEP1 can be seen in epoxy matrix. This is also noticeable in the

values for the shear strength which show an increase due to the applied sizing, but the percentage increase is not as high as in PBT.

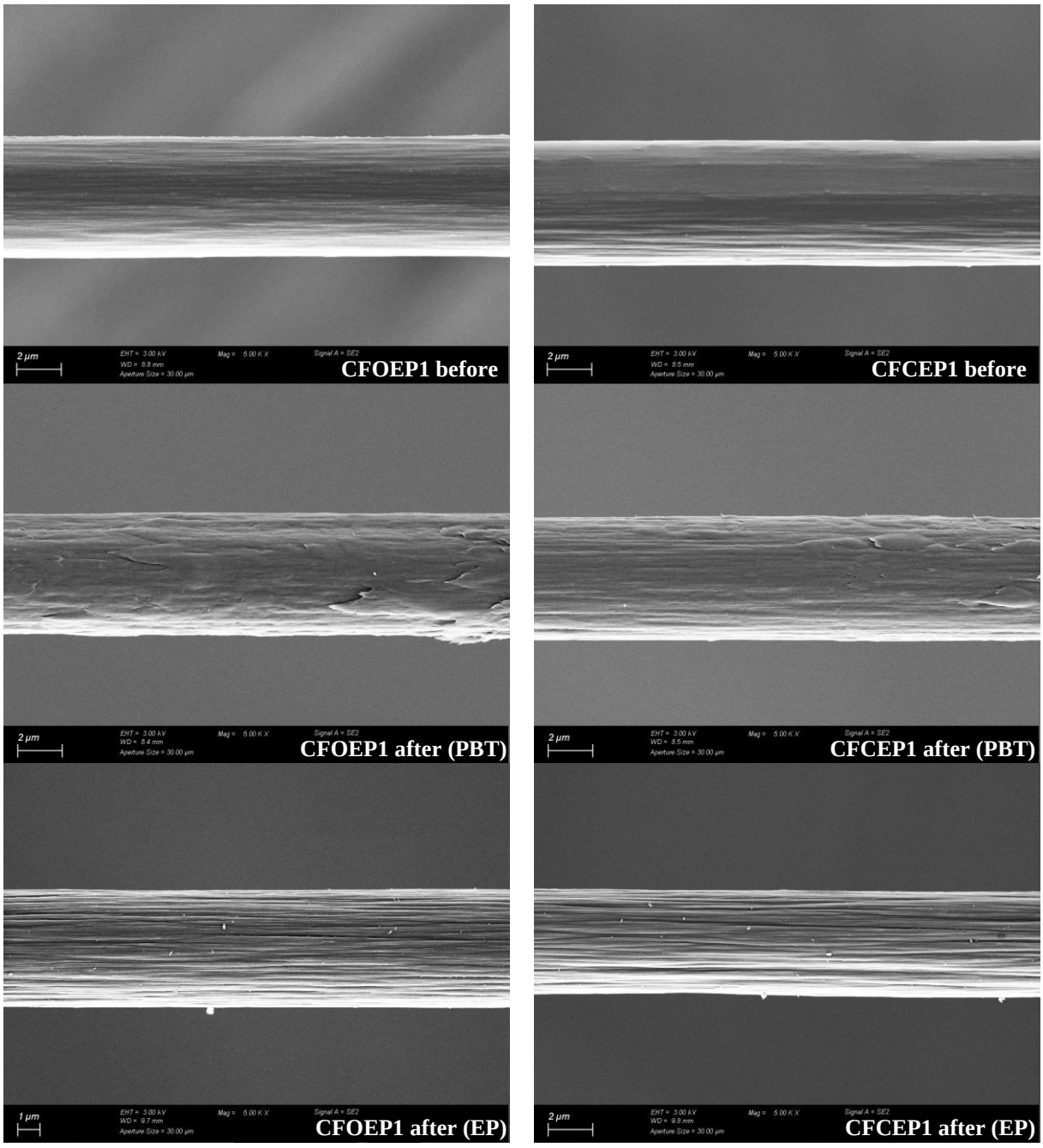

Figure 4: SEM of fibre CFOEP1 before embedding in PBT and epoxy resin and after SFPO

The comparison of the SEM images of the fibre CFOEP1 before and after the SFPO (see Figure 4) revealed that the failure behavior in PBT and epoxy resin was quite different. The fibre surface after being pulled out of PBT is covered with the sizing and remained matrix material which indicates a cohesive failure. In comparison the pulled out fibre from the epoxy resin revealed an original and clean surface without any sizing or matrix material which displays adhesive failure behavior. The reason for the different behavior might be the better compatibility between epoxy sizing and matrix and the integration of sizing constituents during the hardening process. The SEM images after SFPO of the fibre CFCEP1 embedded into epoxy and PBT exhibit similar fracture behavior like the fibre

CFOEP1. The surface after the SFPO of the unsized fibre CFO embedded into PBT was mainly clean comparable with the image of CFOEP1 in epoxy but with little spots of residual polymer (not shown).

4 CONCLUSION

This work shows that the grafting of functional groups on the carbon fibre surface enables enhanced fibre-matrix interaction. Applied amino groups on carbon fibre surface lead to an increased shear strength determined by SFPO which indicates an improved fibre-matrix adhesion in PA66. The detachment of the incompatible epoxy sizing and the introduction of functional groups containing oxygen during the plasma modification lead to higher adhesion strength between carbon fibre and maleic anhydride grafted PP. No difference was found for CF with different functional groups in combination with an additionally applied sizing. Trials with epoxy and PBT as matrix material reveal that the shear strength could be improved independently from the functional groups on the fibre surface. The SEM results exhibit the different fracture behavior in epoxy matrix – adhesive failure and PBT – cohesive failure.

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