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Adhesion Problematic for Novel Non-Crimp Fabric and Surface Modification of Carbon-Fibres Using Oxy-Fluorination

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***Abstract*—**In the scope of application of technical textiles, Non-Crimp Fabrics are increasingly used. In general, NCF exhibit excellent load bearing properties, but caused by the manufacturing process, there are some remaining disadvantages which have to be reduced. Regarding to this, a novel technique of processing NCF was developed substituting the binding-thread by an adhesive. This stitch-free method requires new manufacturing concept as well as new basic methods to prove adhesion of glue at fibres and textiles. To improve adhesion properties and the wettability of carbon-fibres by the adhesive, oxy-fluorination was used. The modification of carbon-fibres by oxy-fluorination was investigated via scanning electron microscope, X-ray photoelectron spectroscopy and single fibre tensiometry. Special tensile tests were developed to determine the maximum force required for detachment.

***Keywords*—**Non-Crimp Fabric, adhesive, stitch-free, high-performance fibre.

I. Introduction

FOR lightweight construction, high-performance fibres are an integral part of constructive design and durability. Due to their excellent chemical resistance and physical properties, they are often more resistant than classic materials as metal. A common structure made of high-performance fibres are Non-Crimp Fabrics (NCF). NCF are widely used in the field of automotive, aircrafts or for reinforcing building structures. Such a rising demand of this fibre reinforced components lead to a revise of manufacturing process concerning different problems and improvement possibilities [1].

In general, NCF are assembled by several layers of unidirectional high-performance fibres set in load direction of the prospective structural element. The relevant position of high-performance fibres is ensured by stitch-bonding in a multiaxial warp-knitting machine. As known, the stich-bonding provides adverse secondary effects, i. e. damage of single filaments and a decreased cross-section of the yarn, which enforces an enrichment of resin[1]. The resulting gap respectively fish-eye is presented in Fig. 1. Caused by the deflection of the narrowed cross-section of yarn, the accurate position of the load bearing structural element (fibre) is not any longer ensured and also it represents the starting point of cracks. Additionally, the delamination process themselves at cracks is affected by the presence of stitching [2]

To receive optimal load bearing properties and use a non-destructive joining method, an increased application of adhesives for composite applications is recognised, i.e. tapes or chemical stitching for rapid preform-manufacturing of glass fibre ply [3]. In this work, it is a novel approach to use a binder to substitute the binding yarn in a NCF. This has several advantages. Firstly, composite structures are enhanced by avoiding ondulation of fibres. Secondly, the weight proportion in the NCF of the used binder is much lower than the amount of binding yarn. And lastly, a punctual fixation enables different geometries of composite by more flexible NCF. Therefore, the draping properties can be improved.



Fig. 1 Fish-Eye in a NCF in matrix made of carbon fibre; polyester binding yarn

Caused by their conspicuous chemical resistance, it is also a field of interest to improve the surface properties to achieve acceptable adhesion properties and an excellent wettability by the used binder respectively adhesive. Next to the use of a sizing, there are different methods to modify the surface, i.e. cold plasma treatment [4], nitric acid treatment [5], [6], oxy-fluorination [7], as well as acid anode treatment [8]. In this study, the oxy-fluorination was used to improve the surface properties of carbon fibres. For high-performance carbon fibres, the oxy-fluorination is not in common use in this point.

The oxy-fluorination process is driven by the reactivity of the fluorine gas which departs under normal conditions into his radicals. Surfaces expose possible reaction partners for fluorine radicals. Therefore, hydrogen radicals will occur after the reaction with fluorine radicals on polymer surfaces. In the presence of other reaction partners and with fluorine radicals,

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functional groups will appear at the surface. Moreover, oxygen containing surface functional groups can be induced by a reaction mixture including air.

Different advantages characterize the oxy-fluorination process. To start with, diffusion of the gaseous reaction medium supports the treatment difficult geometries. Additional, the energy consumption of the process is well defined caused by absent heating and drying steps.

II. Materials

A. Carbon Fibres

Different high-performance carbon fibres were used. They were all based on polyacrylonitrile (PAN) precursor and differ in tensile strength and sizing. The high-tensile carbon fibres were taken: HTS 40 F13 (polyurethane sizing) 12K roving and HTS 45 E23 (epoxy sizing) 12K roving. All 800 tex carbon fibre rovings were purchased from Toho Tenax Europe GmbH, Germany.

B. Adhesives

To comply with the requirements of matrix for fibre reinforced plastics, different adhesives were taken in account for use in thermoplastic and thermosetting matrix. A Griltex® CE 21 was used for the use in thermosetting matrix. The compatibility between thermosetting matrix and Griltex® CE 21 was tested in a previous work [9]. The Griltex® CE 21 exhibits a melt-viscosity at 160°C of 220 Pa·s. This adhesive was purchased from EMS-Chemie AG, Switzerland.

III. Methods

A. Oxy-Fluorination

The oxy-fluorination was performed at Fluor Technik System GmbH in Lauterbach, Germany. For oxy-fluorination, carbon fibres were used sized and desized. The preparation of desizing took place at 500°C for four minutes in a ceramic oven. The oxy-fluorination process is a batch process and was done at room temperature with 5% fluorine gas for 10 minutes. The reaction chamber was evacuated to a pressure of 200 hPa. Afterwards, the chamber was filled with fluorine gas mixture (F_2/N_2 10:90). Finally, the reaction chamber was flushed with fresh air and evacuated several times to remove the remaining fluorine gas. The fluorine gas was fed to a CaO chamber where it was converted to CaF_2. Subsequently, the reactor is opened and the samples can be removed.

B. SEM Measurements

The scanning electron microscope (SEM) was used to examine the surface in the micrometre range. A high-resolution low-voltage SEM with a field emission cathode Zeiss DSM 982 Gemini was used. The investigated samples were reference carbon fibres, desized carbon fibres as well as oxy-fluorinated carbon fibres. The desizing and the oxy-fluorination takes place as described above.

C. XPS

X-ray photoelectron spectroscopy (XPS) is a common technique to understand the surface chemistry and to estimate the interface behaviour [10]. A Physical Electronics PHI 5700 ESCA System with an Al Kα anode was used for X-ray photoelectron spectroscopy to achieve information about the surface elemental composition. The reached sample depth was less than 9 nm and the X-ray irradiation was set under 250 watts. Single peaks were measured with the pass energy of 29.35 eV for high resolution spectra. The binding energies of the XPS-spectra were analysed at 284~291 eV for carbon (C1s). Quantitative analysis was performed with the standard PHI software. The used vacuum was at $5 \cdot 10^{-10}$ torr. All XPS investigated carbon fibre samples oxy-fluorinated under same conditions and exhibit the same processing time.

D. Wettability Tests, Single Fibre Tensiometer

The surface tension describes the wettability properties of a substrate. To estimate the surface tension of a fibre material, the contact angle θ was determined to calculate the surface energy ϒ according to (1). This method is based on Owens, Wendt, Rabel and Kaelble [11].

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\left(\frac{\gamma_l^p}{\gamma_l^d}\right) + \sqrt{\gamma_s^d} \quad (1)$$

With this model, single filaments can be evaluated in its wettability. The contact angle is a parameter of the degree of attraction of the liquid by the substrate and gives the levels of hydrophobicity. The surface tension is composed of the polar component (^{p}) and the disperse component (^{d}). Dipol-dipol interactions, hydrogen bonds and acid-base interaction affect the polar component. The disperse component is defined by van-der-Waals forces [11]. The used tensiometer was a Krüss K 100 (Krüss GmbH, Germany).

E. Tensile Tests

According to ISO 3341 and by determining the optical variation, the tensile tests were performed at a tensile testing machine Z100 (Fa. Zwick und Roell, Germany). The maximum tensile force, deformation behaviour and the elastic modulus were calculated by the typical force strain diagram. The measurement was done with the half clamping length (250mm).

F. Maximum Force for Detachment

To determine the adhesion behaviour of joined carbon fibre yarn, three different tests were developed where special prepared carbon fibres were required. The fibres were cut in a certain length and assembled at the end by a ferrule. To prepare the peel test as well as the shear test, the yarns need to be joined parallel, as presented in Fig. 2 (a) and (b). For the transverse tensile test, the yarns were glued in orthogonal direction (Fig. 2 (c)). The joining of samples was done by a P-jet CT nozzle system (Liquidyn, Germany) and with a custom-made sample holder. For constant conditions during gluing an even contact force of 10 N was used. The Griltex®CE 21

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hotmelt adhesive was applied with this system. The measuring of the maximum force of detachment took place at a tensile testing machine Z2.5 with a nominal load of 2.5 kg. The experimental set-up was realised according to Fig. 2.

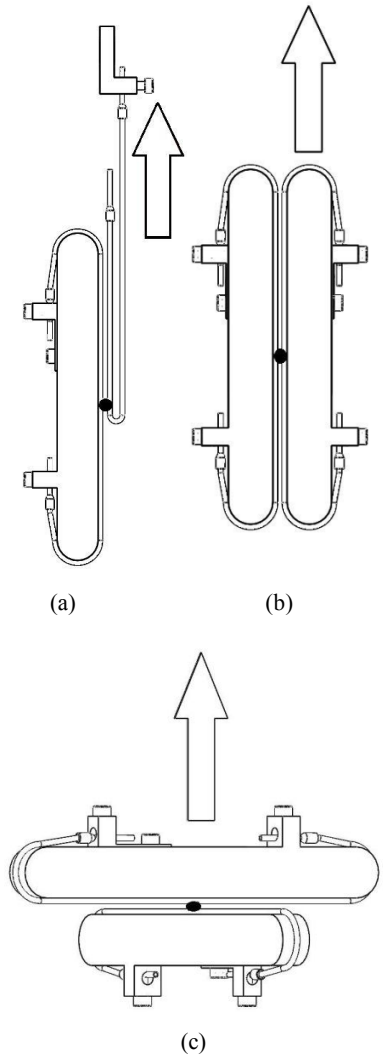


Fig. 2 Experimental set-up for measuring the maximum force of detachment: A, peel test; B, shear test; C, transverse tensile test

IV. Results and Discussion

A. SEM Images

After the oxy-fluorination process, typical and representative peculiarities of carbon fibres are getting more obvious. Before the treatment, the surface of both fibre types looks smooth and with slight grooving (Figs. 3, 5). These striations are mainly caused by the stretching of PAN-precursor during the production process of the carbon fibres themselves. This effect was also described in Krekel et al. [12]. Compared to the oxy-fluorinated samples, the references of both fibre types look filled. This is probably a result of the sizing. It is epoxy sizing for the HTS 45 E23 and polyurethane sizing for the HTS 40 F13 fibre. For oxy-fluorinated fibres, the striations are increasingly discernible (Figs. 4, 6). But the effect is stronger for the HTS 40 F13 (Fig. 6). It can be assumed that the sizing gets reduced by the treatment. Additionally, also micro-roughness did increase by the oxy-fluorination treatment for both fibre types. Due to the higher specific surface, the mechanic adhesion will be supported during the gluing of carbon fibres. According to the literature, a higher micro-roughness maintain a better physical adhesion [13].

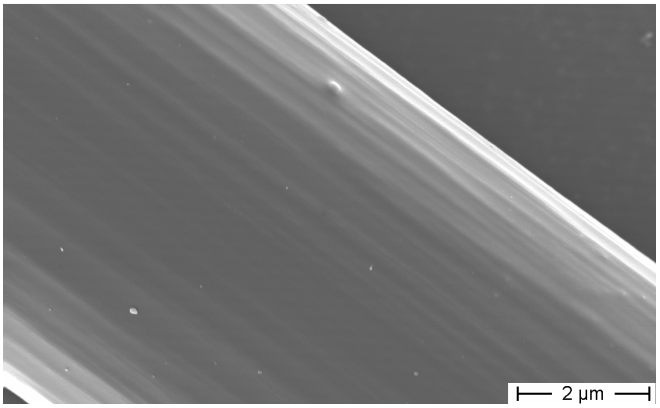


Fig. 3 SEM image of HTS 45 E23 carbon fibre, reference

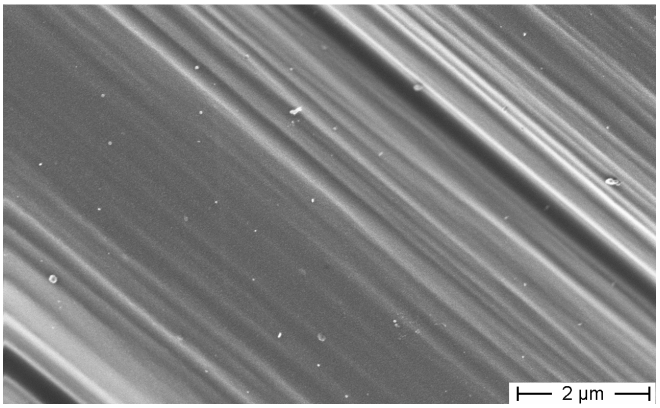


Fig. 4 SEM image of HTS 45 E23 carbon fibre, oxy-fluorinated

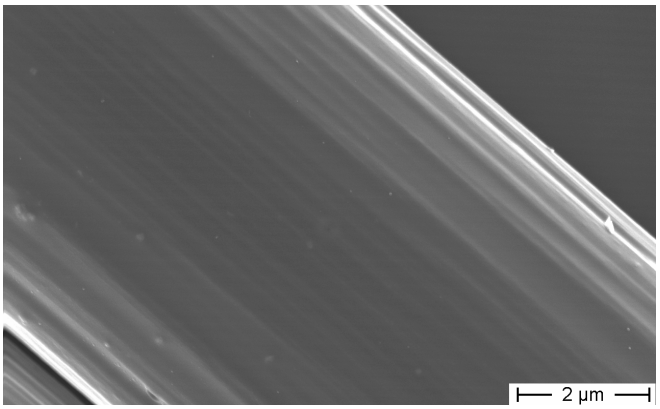


Fig. 5 SEM image of HTS 40 F13 carbon fibre, reference

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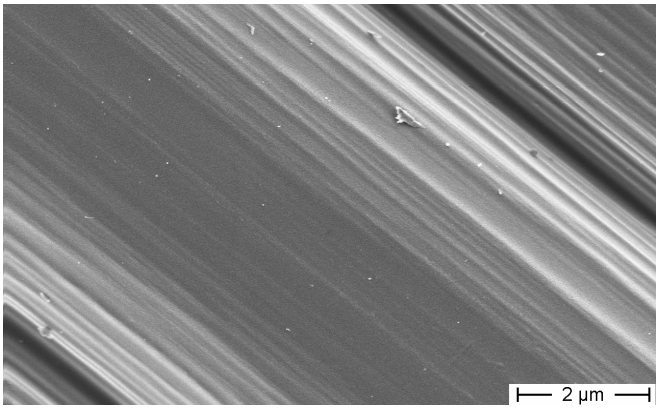


Fig. 6 SEM image of HTS 40 F13 carbon fibre, oxy-fluorinated

B. XPS

For the XPS-study, desized and oxy-fluorinated carbon fibres were compared to reference samples. The samples differ also in the type of sizing. HTS 40 F13 exhibits a polyurethane sizing and HTS 45 E23 is sized with epoxy. The composition of the surface of the HTS 40F13 is primarily defined by 74.1 atomic percentage (at.%) carbon Cs1, 2.6 at.% N1s and 23.3 at.% Os1. Whereby, the fraction of carbon is defined by 12.5 at % sp²-hybridized. In general, the sizing a used to initialize a better handling of the roving and also to prepare the carbon fibre surface for the matrix to receive a better adhesion by functional groups. The carbon fibre with polyurethane sizing exhibits numerical ratio of carbon to oxygen of 0.31 compared to the desized sample with 0.14 (Fig. 7). Therefore, the polyurethane sizing induces hydroxyl groups (at 286.7 eV). The nitrogen content stays nearly constant for the reference and desized sample with 2.6 at.% and 2.7 at.%. The reference carbon fibre with epoxy sizing demonstrates a numerical ratio of carbon to oxygen of 0.26 compared to the desized sample with a ratio of 0.17. The responding surface functional groups are hydroxyl groups and ether groups.

Both types of carbon fibres exhibit in surface bound nitrogen after the desizing process. For the HTS 45 E23 the nitrogen content is 3.0 at% and for HTS 40 F13 it is 2.7 at %, which is an increase from the reference to desized sample.

After the oxy-fluorination, the Fluor is bound at the HTS 45 E23 as –C-F-H groups up to 95 at.% and at HTS 40 F13 up to 83 at.%. The remaining Fluor is bound as –C-O-F-H groups. Furthermore, the numerical ratio of carbon to oxygen increases up to 0.45 for HTS 40 F13 and up to 0.36 for HTS 45 E32. According to this, functional groups, i.e. –COOH and more –C-O- bound oxygen, confirm these findings. The nitrogen content decreases from 2.6 at.% down to 1.8 at.% for the polyurethane sized sample. For the carbon fibre HTS 45 E23, novel –COOH were introduced by the oxy-fluorination process.

C. Wettability Tests

Wettability indicates the grade of interaction between a liquid and a surface and gives information about the formed contact surface. On the one hand, the surface energy of carbon fibres was determined to characterise the efficiency of oxy-fluorination. In this case, the references exhibit a lower total surface energy compared to the modified fibres (Table I). After the oxy-fluorination treatment, it is noticeable that the polar surface energy increases for each fibre type: From 9.7 mN/m to 18.4 mN/m for the HTS 40 F13 and from 6.5 mN/m to 14.9 mN/m for the HTS 45 E23. This have to be seen in relation to the further introduced functional groups which were determined by XPS-measurements.

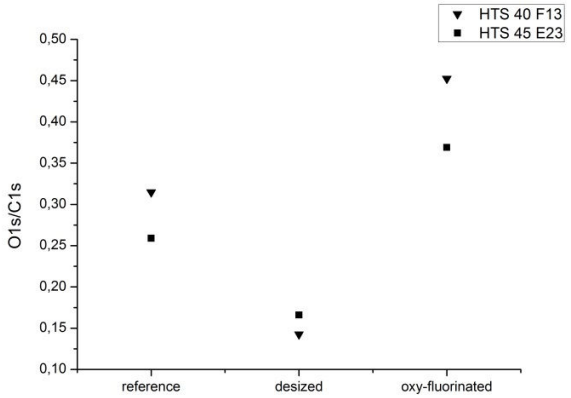


Fig. 7 Numerical ratio of Oxygen [in at.%] to Carbon [in at.%] from oxy-fluorinated samples

TABLE I
SURFACE ENERGIES OF REFERENCE FIBRES, OXY-FLUORINATED FIBRES AND THE USED HOTMELT ADHESIVE GRILTEX® CE 21

	Υ_{total} [mN/m]	Υ_{polar} [mN/m]	$\Upsilon_{disperse}$ [mN/m]
HTS 40 F13, reference	43.3	9.7	33.6
HTS 40 F13, oxy-fluorinated	57.5	18.4	39.1
HTS 45 E23, reference	39.9	6.5	33.4
HTS 45 E23, oxy-fluorinated	53.2	14.9	38.3
Griltex® CE 21	37.3	6.6	30.7

In the case, two to be joined adherends have to exhibit similar surface energies, a good adhesion is realised. According to Table I, the wettability between the carbon fibres and the used adhesive (Griltex® CE 21) fits for the references but is theoretically improved for the oxy-fluorinated samples by the higher surface energy. Mainly the polar part of surface energy increases which leads to the assumption that a better adhesion is expected due to more functional groups on the surface.

D. Tensile Tests

Comparing oxy-fluorinated carbon fibres with references reveals no significant change in stiffness. According to Table II, the Young's modulus is around 190 GPa for both fibre types. In contrast to this, maximum tensile force and stress are increased significantly by oxy-fluorination.

The reference samples of HTS 40 F13 and HTS 45 E23 are different in sizing and the tensile strength. Epoxy sizing offers an increased tensile strength by factor 1.15 compared to polyurethane sizing. This effect is probably introduced by the different surface sealing by sizing which reduces the crack rose and the crack initiation. The further treatment by oxy-fluorination increases tensile strength even more. Tensile

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strength of HTS 40 F13 rises from 1155 MPa by 27% to 1473 MPa. For HTS 45 E23 a gain in strength of 18% is observed.

After the oxy-fluorination, the greater increase in strength for the fiber with lower strength is not surprising, since the increase in strength of the fibre type with the higher strength is in itself unexpected. In general, the main effect of oxy-fluorination at the fibres themselves is not fully understood in this moment, but the following theory has to be taken in account. The constant Young's modulus leads to the assumption that the reversible deformability is driven by the same bond type of carbon before and after the treatment. Due to the treatment, the increase of tensile load and tensile strength is probably caused by two effects: Firstly, the healing of defects and secondly, the introduction of a new bond type of carbon in the fibre as proved by the constant Young's modulus. It has to be examined, if the higher strength is also recognisable in carbon fibre plastics. This will be interesting for further investigations.

TABLE II
RESULTS OF TENSILE TEST WITH Z100

	E_{mod} [GPa]	F_{max} [N]	σ_M [MPa]
HTS 40 F13, reference	188	528	1155.41
HTS 40 F13, oxy-fluorinated	189	673	1472.63
HTS 45 E23, reference	193	609	1331.6
HTS 45 E23, oxy-fluorinated	189	718	1569.73

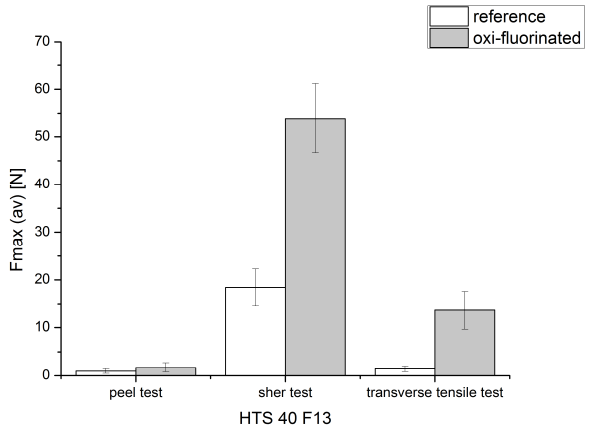


Fig. 8 Maximum force of detachment via peel test, shear test and transverse tensile test of glued (Griltex® CE 21) carbon fibres yarns of HTS 40 F13

E. Maximum Force for Detachment

In regard to the results of the measured forces, there is a strong dependence to the newly developed detachments setups. For the two types of fibers seen in the untreated as well as oxy-fluorinated each state the same ratio of the maximum force for detachment in the various tests.

In Fig. 8 (HTS 40 F13) and Fig. 9 (HTS 45 E23), the lowest forces are present for the peel test and the highest for the shear test. The used tests represent a variety of functional load types for the general use of fibres and yarns. The detachment geometry causes mainly tensile forces compared to the transverse tensile test and the shear test where the bending load has more influence to the fibre and the adhesive bond. In short, this explains the high detachment force for the peel test in general.

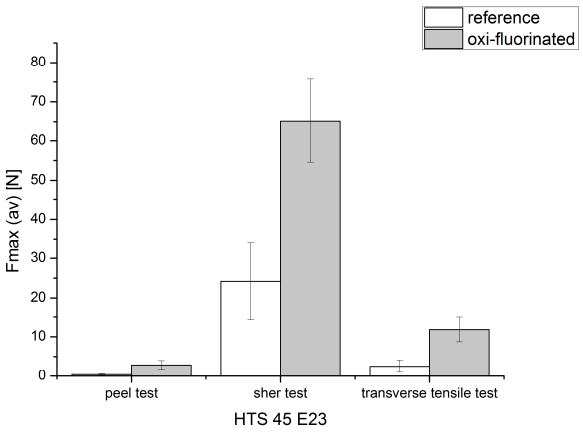


Fig. 9 Maximum force of detachment via peel test, shear test and transverse tensile test of glued (Griltex® CE 21) carbon fibres yarns of HTS 45 E23 with epoxy sizing

The comparison of the HTS 40 F13 before and after the treatment, there is shown an increased resistance to detachment for all cases and testing geometries. However, it is not clear whether the increase of the maximum force of detachment of the fiber is attributed to the increase of tensile strength or confirmed by XPS with the increase in the binding sites which improves the adhesion. The better adherence of the hotmelt Griltex® CE 21 can be introduced by the higher micro-roughness as well as by the increase of the polar part of the surface energy of carbon fibres (tensiometry tests) respective by the novel functional groups shown in results. The improved adherence of the adhesive to the fibre is shown as best in the shear test, because the main load is correlated to the direction of fibre. The apparent increase in the detachment force here by a factor of 2.9 (HTS40F13) and 2.7-fold (HTS45E23) reveals the high potential of the fiber modification by oxy-fluorination. Comparing the treated and the untreated fibres, there are differences according to the amount of maximum detachment force for the peel test and the transverse tensile test. This leads to a high variability of the factor of the increase of force. According to this, the HTS 40 f13 exhibits a factor of 1.8 and the HTS 45 E23 a factor of 8.1 for the increase of maximum detachment force during the peel test. For the transverse tensile test, the increase of the maximum force of detachment reveal a factor of 9.3 for the HTS 40 F13 and a factor of 4.7 for the HTS 45 E23 after the oxy-fluorination. According to the peel and the transverse tensile test, the deviations of the measured forces in relation to the fibre type exhibit a higher dependence to the testing geometries and further parameters compared to the shear test set up. The enormous increase of the maximum detachment force demonstrates the usefulness of the oxy-fluorination to improve bonding forces.

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V. Conclusion

This work aims the understanding of the novel way manufacturing NCF by the use of hotmelt adhesive as binding system. According to this, new testing methods were developed to evaluate the bonding strength between high-performance fibres such as carbon fibres. It is essential to determine the peel strength, the shear strength and the transverse load strength to mimic loads to bear by the novel binding system as they may occur in production and application of NCF. Therefore, the developed investigation setups revealed good reproducibility and practicability.

The oxy-fluorination was introduced as a surface modification method to improve the adherence of carbon fibres. Furthermore, the oxy-fluorination exhibits a high potential to change the intrinsic structure of carbon fibres leading to significant increase of tensile strength.

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