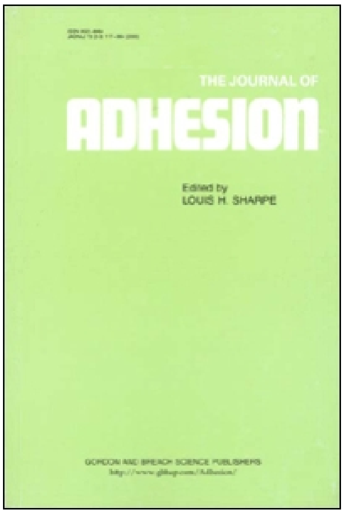

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion: Comparison Between Physico-chemical Expected and Measured Adhesion of Oxygen-plasma-treated Carbon Fibers and Polycarbonate

A. Bismarck[a]; D. Richter[a]; C. Wuertz[a]; M. E. Kumru[a]; B. Song[a]; J. Springer
[a] Technische Universität Berlin, Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie, Berlin, Germany

To cite this Article Bismarck, A. , Richter, D. , Wuertz, C. , Kumru, M. E. , Song, B. and Springer, J.(2000) 'Adhesion: Comparison Between Physico-chemical Expected and Measured Adhesion of Oxygen-plasma-treated Carbon Fibers and Polycarbonate', The Journal of Adhesion, 73: 1, 19 — 42

To link to this Article: DOI: 10.1080/00218460008029295

URL: http://dx.doi.org/10.1080/00218460008029295

J. Adhesion, 2000, Vol. 73, pp. 19-42
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Adhesion: Comparison Between Physico-chemical Expected and Measured Adhesion of Oxygen-plasma-treated Carbon Fibers and Polycarbonate

A. BISMARCK, D. RICHTER, C. WUERTZ, M. E. KUMRU,
B. SONG and J. SPRINGER*

*Technische Universität Berlin, Institut für Technische
Chemie, Fachgebiet Makromolekulare Chemie, Sekr. TC6,
Straße des 17. Juni 135, D-10623 Berlin, Germany*

(Received 3 May 1999; In final form 27 January 2000)

The adhesive interaction between oxygen-plasma-treated, polyacrylonitrile-based, high-tensile-strength carbon fibers and a polycarbonate matrix has been studied. Several models have been used to predict the impact of the plasma treatment process on the strength of adhesion between both jointing partners. These approaches have been the thermodynamic work of adhesion which was calculated from the solid surface tensions, based on the results of contact angle measurements *versus* test liquids, the contact angle which was directly obtained *via* polycarbonate melt droplets on single carbon fibers and the zeta (ζ)-potential data provided by streaming potential measurements. The results have been compared with the interfacial shear strength determined from the single-fiber fragmentation test. Additionally, the single-fiber tensile strength of the oxygen-plasma-treated carbon fibers was determined.

We confirmed that any physico-chemical method on its own fails to describe exactly the measured adhesion. However, for the investigated system, the conscientious interpretation of the data obtained from wetting measurements, in conjunction with the thermodynamic approach, is sufficient to predict the success of a modification technique which has been applied to one component in order to improve adhesion.

Keywords: Oxygen-plasma-treatment; contact angle; work of adhesion; interfacial shear strength; zeta-potential; carbon fiber; polycarbonate

---

*Corresponding author. Tel.: ++49 30 314 22262, Fax: ++49 30 314 79237, e-mail: spri0534@mailszrz.zrz.tu-berlin.de

INTRODUCTION

Thermoplastic polymers find an increasing interest due to their chemical properties (*e.g.*, recyclability, durability, good chemical resistance, compliance with modern requirements in safety at work) as well as their mechanical properties (*e.g.*, high failure elongations, improved impact resistance) [1, 2]. Thus, thermoplastic matrices give effect to the excellent properties of carbon fiber reinforcement. Research had been addressed to a number of thermoplastic polymers [3 – 5], such as polycarbonate (PC), polyphenylensulfide (PPS), polyetheretherketone (PEEK) and polysulfone (PSU). Normally, thermoplastic mass-produced polymer-matrices (*e.g.*, polypropylene (PP), polyethylene (PE) and polystyrene (PS)) as well as engineering-polymer-matrices (PC, polyamide (PA), *etc.*) do not have, or have fewer, chemically reactive sites. Thus, other kinds of "specific" interactions than the formation of chemical bonds are necessary to achieve the desired adhesive strength between the jointing partners. Typically, these interactions are of the acid-base type (including hydrogen bonding) [4, 6]. In addition to specific interactions, mechanical interlocking might contribute to the adhesion [7].

Yuan *et al.* [3] showed that an oxygen plasma treatment of carbon fibers decreases the fiber tensile strength but increases the interfacial shear strength between those fibers and PPS. Bascom and Chen [4] studied the influence of carbon fiber modification in various plasmas on the surface composition as measured by X-ray photoelectron spectroscopy (XPS). They applied the single-fiber fragmentation (SFF) test to investigate the changes in adhesion between the modified fibers and a PC, as well as a PSU, matrix and they found that a treatment of the fibers in oxygen plasma (OP) significantly improved the adhesion to both matrices. Although the modification increases the oxygen content of the fiber surface dramatically, the authors concluded that the chemical state of the surface oxygen was not related to the improvement in adhesion. Bourgeois and Davidson [4] also treated carbon fibers in OP and investigated the changes in the fiber surface chemistry by XPS and contact angle measurements and compared the results with the measured adhesion to various thermoplastic matrices. OP-treatment of carbon fibers exhibited much better interaction to all investigated matrices. It was concluded that the increase in adhesion of the modified fibers (compared with untreated fibers) was caused by mechanical interlocking (the plasma treatment roughened the fiber surface) as well as by specific molecular interaction between oxygen-containing surface groups on the fiber (introduced by plasma treatment) and the matrix material.

The aim of our study is the identification of those interactions which mainly control the adhesion in a composite consisting of OP-treated carbon fibers and polycarbonate. We intend to correlate data obtained by thermodynamic and electrokinetic approaches with the measured adhesive strength of the investigated systems estimated by a micromechanical test. We apply experimental techniques such as contact angle measurements performed directly between the adhesive partners themselves and for each component *versus* test liquids, ζ-potential measurements and the single-fiber fragmentation test (SFF). We investigate the possibility of estimating the impact of the modification on the ability of the fibers to undergo adhesive interactions only on the basis of the results obtained from the physico-chemical methods.

THEORY

Theoretical Approach to Predict Adhesion *Via* Thermodynamics of Wetting

A basic requirement of adhesion in composites is an intimate contact between the reinforcement and the matrix, as well as the formation of a cohesively strong solid by the matrix material [8]. Thus, from the thermodynamic point of view, adhesion should improve with better wettability between the "liquid" matrix and the reinforcement. This is indicated by a lower contact angle observed by wetting measurements between the jointing partners.

Taking the thermodynamic theory of adhesion into consideration, the wetting of the solid by the liquid matrix is improved when the surface tensions of both the reinforcing material, γ_s, and the liquid matrix, γ_l (*i.e.*, the polymer melt), are almost equal and the interfacial tension, γ_{ls}, is negligible. In order to establish intimate contact between the reinforcement and the "liquid" matrix material, the liquid matrix should not be too viscous, and there should be a thermodynamic driving force which effects good wettability [9]. This driving force can be expressed by the thermodynamic work of adhesion, W_a, which is the energy required to separate reversibly two phases coexisting in an equilibrium state. W_a is the sum of all the interaction energies between the two phases. It should be possible to calculate W_a by the harmonic mean equation introduced by Wu [10] based on the dispersive-polar approach, which is applicable to low-energy materials

$$W_a^h = 4 \cdot \left(\frac{\gamma_l^d \cdot \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p \cdot \gamma_s^p}{\gamma_l^p + \gamma_s^p} \right) \tag{1}$$

and the geometric mean equation [10], preferably used to describe interactions between low-energy and high-energy materials,

$$W_a^g = 2 \cdot \left(\sqrt{\gamma_l^d \cdot \gamma_s^d} + \sqrt{\gamma_l^p \cdot \gamma_s^p} \right) \tag{2}$$

by using the solid surface tension of adherend and adhesive (*i.e.*, plasma-modified carbon fibers and the PC) estimated at room temperature. Reflecting these equations, the work of adhesion is proportional to the surface tension of both adhesion partners.

According to Griffith and Wu [10], the fracture energy identifies the surface free energy of newly-created surfaces and is a fundamental measure of the quality of an adhesive joint. Since the fracture energy is the sum of thermodynamic work and plastic work,[1] only at zero rate is the work of adhesion directly proportional to the fracture energy. That means in the absence of viscoelastic effects and, thus, in the case of thermodynamic reversibility of the separation process.

For the adhesion of liquids which do not completely spread on the solid surface (*e.g.*, a polymer melt), the Young-Dupré equation should be valid

$$W_a = \gamma_l \cdot (1 + \cos\theta). \tag{3}$$

Assuming that the surface tension of the polymer melt remains constant at a given temperature, W_a should be directly proportional to $(1 + \cos\theta)$.

---

[1] Nomenclature according to Wu [10].

Since a reversible formation of a surface is difficult, an indirect method must be used to estimate the surface tension of a solid polymer (as PC). In this study, we applied the harmonic mean method [10], which is based on a combination of Eqs. (1) and (3). However, there are some important critics on the suitability of this empirical approach. Fowkes *et al.* [11] disputed the possibility to obtain correct values for the solid surface tension in principle. Sauer *et al.* [12] reported an agreement of theoretically- and practically-obtained results under certain restrictions. The basic requirement which should be fulfilled is the predominance of dispersive interactions contributing to surface tension. On the other hand, (modified) carbon fibers are known to mainly interact *via* polar forces.

Theoretical Approach to Predict Adhesion *Via* Electrokinetics

Another approach to estimate interactions which might contribute to adhesion was proposed by Häßler and Jacobasch [13]. The assumption is that ζ-potential measurements can be used to characterize the interactions between adhesive and adherend if they are mainly caused by acid-base interactions. It was shown that ζ-potential measurements could be used to assess the adhesive properties of hot melts on polymeric or wood-veneered surfaces. The higher the difference between ζ_{plateau}-values ($\Delta\zeta_{\mathrm{plateau}}$) (taken from pH-dependent ζ-potential measurements) of the matrix and the adhesive, the higher the adhesive strength between them. Generally speaking, improved adhesion should be found with an increased difference between the ζ_{plateau}-values of both materials. Furthermore, Jacobasch reported [14] that the ζ_{max}-values (taken from KCl-concentration-dependent ζ-potential measurements) of glass fibers correlate with the adhesive properties to unsaturated polyester resins. It was reported that the difference of the adsorption potentials $\Phi_{-} - \Phi_{+}$ ($\Phi_{\pm}$ is the non-electrostatic adsorption free energy of the ions) of Cl^{-} (Φ_{-}) and K^{+} (Φ_{+}) ions correlates with the adhesion force caused by van der Waals interactions [15]. The decrease of the adhesion by adsorbed layers can be elucidated by ζ-potential measurements [16, 17], since adsorption processes of ions (rated to the absorption potentials $\Phi_{\pm}$) will affect ζ_{max}.

Practical Approach to Rate Adhesion *Via* Single-Fiber Fragmentation Test (SFF)

A practical approach for the investigation of fiber/matrix adhesion in a single-fiber composite (SFC) is given by the single-fiber fragmentation test, which is – applying the approximation of the simple Kelly-Tyson model [18] – used to determine the interfacial shear strength, τ_{IFSS}. Applying tensile stress to the composite, the same deformation is experienced by the matrix and the fiber. Due to different values of elastic moduli between fiber and matrix, an interfacial shear stress is induced by the relative displacement between fiber and matrix. If the tensile strain in the fiber exceeds the fracture strain of the fiber the latter fails at its weakest point. A precondition is a higher rupture strain of the matrix compared with that of the fiber. Afterwards, the fractured ends of the fiber will not carry any load and a new stress profile will be generated perpendicularly along the fragment and away from the rupture, provided that the fiber/matrix interface did not fail. When the load increases, the fiber continues to break into shorter fragments until the pieces become too short to fracture again by the induced stress. This state is referred as the "saturation state". The estimation of fiber/matrix adhesion using this model is based on the assumption that the length of the fiber fragments and, therefore, their quantity in the entire sample depends on the quality of the interfacial bonding. A "good" interface transfers higher tensile stress to the embedded fiber and causes shorter fragments than a "poor" interface.

The constant-shear model proposed by Kelly and Tyson [18] assumes a linear elastic/plastic (*i.e.*, viscoelastic) behavior of the matrix. Thus, it should be applicable to thermoplastics. The model defines the interfacial shear strength

$$\tau_{\mathrm{IFSS}} = \frac{\sigma_{fu} \cdot d_f}{2 \cdot l_c}, \tag{4}$$

where d_f is the average fiber diameter and σ_{fu} is the ultimate single-fiber tensile strength at the critical fragment length, l_c. Statistical considerations on the distribution of the measured fragment lengths yield the critical fragment length and – according to the entire fiber geometry – the critical aspect ratio, l_c/d_f.

Bascom and Chen [4] reduced the discussion to terms of l_c/d_f without applying Eq. (4) to get τ_{IFSS}. Since both the interfacial shear strength and the specific tensile strength of the single fiber are important factors to determine the tensile properties of the entire composite, this appears to be a critical simplification. Various chemical treatments of carbon fiber surfaces do not always cause an alternation in the fiber diameter but, nevertheless, they might significantly influence the mechanical properties of the fibers [6, 19]. A shorter critical fragment length may be caused by better fiber/matrix adhesion or by smaller fracture strain of the fiber, and both can be influenced by the fiber treatment.

EXPERIMENTAL

Materials

We choose PC Macrofol® DE 1-1 (Bayer AG, Leverkusen, Germany) as the matrix material in order to obtain data comparable with those reported by Bascom and Chen [4]. The molecular mass was estimated using static light scattering (SLS) in tetrahydrofurane (THF) to be $M_w = 39300$ g/mol. The glass transition temperature ($T_g = 150°\mathrm{C}$) and the melting temperature ($T_m = 230°\mathrm{C}$) of PC were determined by differential scanning calorimetry (DSC).

As the reinforcing material, polyacylonitrile (PAN) based, unsized and untreated high tenacity (HT) carbon fibers, C320.00A (Sigri SGL Carbon, Meitingen, Germany), were used. Supplier information reports a single-fiber tensile strength of 3000–3500 MPa, an elastic-modulus of 230 GPa and a maximum elongation of 1.3%. The fibers were treated in low-pressure oxygen plasma. The process of modification and the influence on chemical, physico-chemical and morphological fiber surface properties have been reported [20].

Contact Angle Measurements

Contact angle measurements are a useful tool to characterize solid surfaces, since they are sensitive to (chemical as well as morphological) changes in the outermost surface layers within nm depth [21]. They offer the possibility of chemical and thermodynamic characterization of solid surfaces, whereas elemental analytical methods (*e.g.*, ESCA) give only chemical information [22].

The advancing and receding contact angles of the investigated carbon fibers have been measured applying the modified Wilhelmy-technique [20], whereas the contact angles of the test liquids (water and diiodomethane) on PC have been determined using the sessile drop method [23].

Until now, only a very few methods are available to study directly the wetting behavior of fibers and polymer melts or other viscous fluids. First of all, there is the modified Wilhelmy-technique [12, 24] providing the wetting tension ($\gamma_l \cdot \cos\theta$) from which, if the surface tension of the polymer melt is known, the contact angle can be calculated. Secondly, there are some direct methods, detecting the contact angle by analyzing the drop shape [25–27].

The majority of reported contact angles obtained for polymer melts on fibers have been measured using the modified Wilhelmy-technique, which offers the possibility to study wetting kinetics [12, 28]. The latter should not be underestimated since the high melt viscosity of polymers (besides the difficulties of polymer oxidation, degradation or crosslinking) affects its interaction with the fiber. Thus, not only surface tension effects have to be considered but also hydrodynamic effects [12, 29]. Two factors influence the rate of equilibration and the extent of the equilibrium of the fiber menisci [12]. Firstly, with thin fibers the height of the meniscus is proportional to the fiber diameter [28]. Thus, the meniscus equilibrates more rapidly. Secondly, the process of equilibration is accompanied by a change in the amount of impurities, which concentrate in the small volume fracture of the moving, equilibrating contact layer.

For drop-on-fiber-systems (*e.g.*, PC-melt on carbon fiber), a reliable and convenient contact angle determination method had been developed, extending the concept of the common (K, L)-method [25, 26], where K is the dimensionless maximum drop height and L is the dimensionless maximum drop length referred to the fiber diameter, r, to the generalized (K, L_y)-method [27], where L_y is the dimensionless drop length taken at a distance, y, from the fiber middle axis. Therewith we established a basis for investigations on the possibility to predict adhesion by simply applying the Young-Dupré Eq. (3).

The PC was fixed onto the carbon fiber by pulling the latter through a highly concentrated PC/THF solution. The solvent was evaporated at elevated temperatures. Afterwards, the droplets were formed under argon atmosphere by raising the temperature in a hot stage (TH 600 Linkam Scientific Instruments Ltd., UK) at a rate of 5 K/min up to 285°C. The solid polymer on the fiber surface was melted by increasing the temperature and, therefore, the polymer melt forms droplets out of a retracting movement. Due to this particular preparation method of single droplets, we can only measure receding contact angles. To ensure equilibration, the droplets were tempered at 285°C over 15 min.[2] Afterwards, the contact angles were determined as a function of decreasing temperature ($dT/dt = -1°\mathrm{C/min}$). Although we could only measure receding contact angles, one composite preparation technique should be reflected well. The polymer-powder impregnation technique starts with the wetting of the fiber roving by aqueous polymer powder dispersion and continues with a heating process [30]. Thus, the obtained contact angle values might refer to the wetting properties of the fibers during the melting process and give some further information, which is important for this application. The droplet images were recorded (top view) using a light microscope (BHS POL Olympus, Type PM-10 ADS, Hamburg, Germany) connected with a CCD-camera (DXC-101, Sony, Japan). Every contact angle value presented here was the average of at least 15 single measured values.

Zeta (ζ)-potential Measurements

To measure the electrokinetic properties of the modified carbon fibers [23] and the PC [20], the electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method was used. The streaming potential for carbon fibers was obtained at 20°C ± 1°C as a function of the applied pressure (30 – 150 mbar) using

---

[2] However, on fibers with small diameters the equilibration took a few seconds (poly (dimethylsiloxane) [22] with a viscosity of 500 P at 20°C on 8.1 µm diameter glass fibers less than 30 s and on 155 µm diameter fibers less than 200 s [12]) and up to several minutes (polypropylene melt on approx. 60 µm glass fibers at temperatures above $T >$ 160°C less than 5 min [24]).

a fiber/powder measuring cell. The latter contains the fiber bundle (capillary system) through which the electrolyte solution is pumped. The commercial plate/foil-measuring cell was used to obtain the electrokinetic potential of the PC. In this case the electrolyte stream is realized between two equal polymer foils, which are distanced by a PTFE-foil with a defined channel geometry (70 mm × 10 mm × 0.5 mm). The streaming potential, which arises from shearing off the diffuse part of the electrochemical double layer, was measured using two Ag/AgCl electrodes. More detail about this technique is reported in the literature [14, 31].

In order to measure the ζ-potential as a function of the KCl-electrolyte concentration, the analyzer was filled with de-ionized water (Millipore, pH 4.6–5.1) and the measuring cell was rinsed several times to drive the conductivity of the medium down below 300 μS/m. Firstly, the water value of the ζ-potential was measured and, subsequently, the KCl-concentration was raised using a digital burette (Brand, Wertheim, Germany). The entire system (including the measuring cell) was rinsed before each new measurement cycle was activated. The ζ-potential obtained from concentration-dependent measurements was corrected in surface conductance according to the method of Fairbrother and Mastin [32].

By determining the pH-dependence of the ζ-potential, it is possible to estimate the acidic and/or basic character of the investigated solid surfaces. In order to keep the ionic strength constant (1 mM KCl), we have altered the pH value at intervals of $\mathrm{pH} = 3$ to $\mathrm{pH} = 10$ by adding a 0.1 M HCl or a 0.1 M KOH solution. If the sample carries any acidic functional surface groups, the negative ζ-potential increases with pH due to advanced dissociation of these groups. Complete dissociation causes the ζ-potential to remain constant with increasing pH (neglecting any further adsorption phenomena). If basic functional groups are present at the investigated surface, the obtained curves show an inverse behavior. If the dissociation of surface groups is the predominant formation mechanism in the electric double layer, the pH-value where the ζ-potential is zero, the isoelectric point (i.e.p), can be considered as a measure of acidity or basicity of a solid surface. An i.e.p. at low pH-values indicates an acidic surface character. In contrast, the solid surface contains basic surface groups if an i.e.p.-value in the alkaline range is present [33].

Single-Fiber Tensile Test

The influence of the applied fiber surface treatment on the fiber tensile strength was determined by the single-fiber tensile test. Single fibers were separated from the roving and each end glued onto a small piece of paper for better handling. The distance between the papers, the "free length", was 3 mm. The samples were fixed and tested by a microtensile testing device [34] (Einzelfaserzugmodul Raith HTS/FTM) at a speed of 0.5 µm/s. At least 20 single samples were tested. The ultimate strain, σ_{fu}, was calculated from the ratio of the maximum force, $F_{\max}$, and the fiber area

$$\sigma_{fu} = \frac{4 \cdot F_{\max}}{\pi \cdot d^2}. \tag{5}$$

Single-Fiber Fragmentation-Test

Unfortunately, it was not possible to prepare single-fiber composites using the polymer melt impregnation technique, because of the very different thermal expansion coefficients of the carbon fibers and the PC. Using this preparation method, the residual thermal stress caused prefracturing of the embedded carbon fibers. Therefore, sample specimens were prepared in a two-step process. At first, single-fibers were tightened on a 100 µm thick aluminum mould. The polymer was dissolved in dichloromethane and the highly concentrated solution was poured into a film applicator. In the second step, wet films with a defined thickness of 300 µm were cast, covering the fibers completely. The films were dried for 24 h in the air and afterwards for 3 h at 60°C and 1 mbar. The preparation was finished by cutting dumbbell shaped specimens out of the model composites, which kept within the uniaxially-centered embedded fiber running along the bigger side of the shape.

The SFF was performed with a custom-built tensile loading machine [35] at a constant tensile speed of 0.12 mm/min. Simultaneously, tensile strength and tensile length were recorded. The entire SFF was monitored *via* polarized light macroscopy.

Pre-tests were done to ensure that the "state of saturation" could be reached and it was found out that a strain rate of about 5% satisfied this requirement. In order to optimize the identification process of the single-fiber fragments, the test was continued to a strain rate of about 33%.

For easy examination of the single fragment lengths, the stretched SFF sample was digitized in conjunction with a reference scale (objective micrometer). The resulting bitmaps were analyzed using a standard drawing application. Ten samples of each species were investigated (yielding a total of 150 fragments) in order to obtain a representative fragment length distribution.

RESULTS

Expected Adhesion – Wetting Behavior of the Single Components

Table I contains the advancing and receding contact angles of the untreated and OP-treated carbon fibers and PC measured against water and diiodomethane.

Reflecting the wetting behavior of the carbon fibers, an increase in polar interaction forces with plasma treatment time can be noticed, while the contact angles, which were obtained *versus* the non-polar test liquid (diiodomethane), remain constant for all OP-treated fibers. Thus, the plasma treatment presumably causes a step-by-step generation of oxygen-containing polar surface groups. Furthermore, an interaction of the treated carbon fibers *versus* the polar test liquid (water) is much more intensive. Since the wetting behavior of the untreated fiber is in the opposite direction, the treatment must have caused a drastic change in the chemical and physico-chemical surface

TABLE I Averaged advancing and receding water (*W*) and diiodomethane (DIM) contact angles of the untreated and plasma-treated carbon fibers and PC*

OP-treatment [*min*]	$\bar{\theta}_{a,W}$ [°]	$\bar{\theta}_{r,W}$ [°]	$\bar{\theta}_{a,DIM}$ [°]	$\bar{\theta}_{r,DIM}$ [°]
0	82.5 ± 2.9	56.3 ± 3.1	49.5 ± 3.2	47.7 ± 1.9
1	56.2 ± 4.3	38.6 ± 5.9	60.1 ± 0.1	58.5 ± 0.5
5	52.7 ± 1.4	34.9 ± 5.0	62.5 ± 1.4	61.1 ± 0.8
10	46.7 ± 3.5	30.7 ± 8.2	60.5 ± 1.8	58.9 ± 1.7
20	39.5 ± 3.5	32.2 ± 3.8	61.6 ± 2.6	59.4 ± 1.3
PC*	89.1 ± 1.6	–	23.2 ± 1.8	–

*Note: The contact angles measured on the PC-foil are "static" contact angles. They were measured directly after a drop of the test liquid has been placed onto the polymer surface. Thus, the values correspond to advancing contact angles.

properties. Considering the wetting behavior of the PC, the interaction *versus* the non-polar test liquid seems to be preferred.

Thus, taking the basic requirement of adhesion – that is, an intimate contact between the jointing partners – into account, the interactions between PC and untreated carbon fiber should provide better adhesion (mainly caused by dispersion forces) than those between PC and the treated carbon fiber.

Expected Adhesion – Direct Wetting Behavior Between Polymer Melt and Carbon Fiber

Table IIa gives the results for the contact angles obtained by direct wetting of the carbon fibers with polymer melt as a function of temperature and OP-treatment time. Each value was measured using both the (K, L)- and (K, L_y)-methods.

The high temperature and the high viscosity of the polymer melt decisively affected the contact angle measurement. Thus, the error-range of each single contact angle value obtained from direct wetting is much broader than those of the values provided by measuring the contact angles of test liquids. Nevertheless, a difference in the wetting behavior of the untreated and the treated carbon fibers can be observed, though the values do not change consistently with OP-treatment time. In any case, the treatment decreased the wettability by the PC-melt. Applying Eq. (3) to θ_m, the values of $(1+\cos\theta_m)$ are proportional to W_a (see Tab. IIb) and, hence, the adhesive interaction should be weakened by the OP-treatment.

Within the applied temperature range (245°C–285°C), there seems to be no or only slight influence on the direct wetting behavior of the PC on the modified carbon fibers with varying temperature. The changes in θ_m can not ambiguously refer to the environmental

TABLE IIa Contact angles of a PC-melt on single carbon fibers at different temperatures determined using the K, L- and K, L_y-method

OP-treatment	$T=245$ [°C]		$T=265$ [°C]		$T=285$ [°C]	
[*min*]	θ_m (KL) [°]	θ_m (KL_y) [°]	θ_m (KL) [°]	θ_m (KL_y) [°]	θ_m (KL) [°]	θ_m (KL_y) [°]
0	8.8 ± 3.3	13.2 ± 4.0	9.1 ± 4.1	8.8 ± 3.9	10.0 ± 2.6	11.0 ± 4.9
1	12.1 ± 3.9	15.0 ± 4.3	15.3 ± 3.8	15.3 ± 4.8	14.9 ± 1.6	17.5 ± 3.3
5	13.2 ± 4.0	16.6 ± 3.3	14.2 ± 2.2	15.9 ± 3.7	15.3 ± 2.4	16.5 ± 4.5
10	12.9 ± 4.4	21.3 ± 4.4	20.0 ± 4.4	21.1 ± 3.7	13.9 ± 4.7	17.7 ± 4.5
20	19.9 ± 3.9	18.5 ± 3.9	17.6 ± 3.9	18.5 ± 4.7	18.1 ± 4.7	17.4 ± 4.6

TABLE IIb $x = (1 + \cos\theta_m)$ based on contact angles, θ_m, from Table IIa

OP-treatment	$T = 245$ [°*C*]		$T = 265$ [°*C*]		$T = 285$ [°*C*]	
[*min*]	x (*KL*)	x (KL_y)	x (*KL*)	x (KL_y)	x (*KL*)	x (KL_y)
0	1.99 ± 0.06	1.97 ± 0.07	1.99 ± 0.07	1.99 ± 0.07	1.98 ± 0.05	1.98 ± 0.09
1	1.98 ± 0.07	1.97 ± 0.07	1.96 ± 0.07	1.96 ± 0.08	1.97 ± 0.03	1.95 ± 0.06
5	1.97 ± 0.07	1.96 ± 0.06	1.97 ± 0.04	1.96 ± 0.06	1.96 ± 0.04	1.96 ± 0.08
10	1.97 ± 0.08	1.93 ± 0.08	1.94 ± 0.08	1.93 ± 0.06	1.97 ± 0.08	1.95 ± 0.08
20	1.94 ± 0.07	1.95 ± 0.07	1.95 ± 0.07	1.95 ± 0.08	1.95 ± 0.08	1.95 ± 0.08

conditions since the error range of each averaged value interferes with the temperature effect. However, this is in good agreement with the observations about the size of $-(d\theta/dT)$, which should be quite small and centered at about 0.05°/°C [10]. Temperature-dependent contact angles are a function of the relative magnitude of the surface entropy $(d\gamma/dT)$ of the adjacent phases [10].

Expected Adhesion – Surface Tension and Work of Adhesion

Since the measured (advancing and receding) contact angles are very sensitive to changes in the surface composition and, thus, to the surface chemistry, the calculated surface tension (as well as the work of adhesion values) should be sensitive to changes in the surface composition.

Table III summarizes the results for the calculated surface tension values. The polarity, X^p, is defined as the ratio of the polar surface tension component to the overall surface tension and, thus, it allows a quick rating of the respective surface properties. The solid surface tension of PC was calculated from the measured water and diiodomethane "static" advancing contact angles (at 20°C) [23], using the

TABLE III Solid surface tensions of modified carbon fibers [18] and polycarbonate [17]

OP-treatment [*min*]	γ [*mN*/*m*]	γ^p [*mN*/*m*]	γ^d [*mN*/*m*]	X^p
0	37.5 ± 2.3	10.0 ± 1.6	27.5 ± 1.7	0.27
1	47.4 ± 2.9	27.7 ± 2.9	19.7 ± 0.2	0.58
5	49.4 ± 1.2	30.8 ± 1.1	18.6 ± 0.6	0.62
10	53.4 ± 2.6	34.2 ± 2.4	19.2 ± 0.8	0.64
20	57.9 ± 3.3	39.4 ± 3.2	18.5 ± 0.5	0.68
PC	47.4 ± 1.4	4.2 ± 0.7	43.2 ± 1.3	0.09

harmonic mean method. The same mathematical algorithm was applied to obtain the values of the solid surface tension of the carbon fibers.

As expected, the particular parts of the overall surface tension (reflecting the dispersive and polar contributions) are in good agreement with the values obtained for the single contact angles. Obviously, the polarity characteristics of the untreated fiber surface drastically changes with the OP-treatment. Whereas the contribution to the overall surface tension of the untreated fiber mainly lies with the non-polar interactions, the situation inverts with the treatment of the fibers. The overall surface tension of PC is ruled by the non-polar contributions.

Considering W_a^g, the adhesive strength should not vary at all (see Tab. IV). Yet, evaluating the surface tensions determined for carbon fibers and PC (see Tab. III), both materials should be considered as low-energy materials. Thus, the geometric mean approach should not be valid, as described above. Referring to the W_a^h-values after extended treatment, the same trend can be observed; no changes in the strength of adhesion should be detected (see Tab. IV). But, obviously, there is a big gap between the system containing the untreated carbon fiber (SUF) and the systems containing the OP-treated carbon fibers (STF) in any thermodynamic values. In some cases (W_a^h, γ^d) the values of the STFs remain constant but are entirely shifted to smaller values compared with the original value of the SUF. In the case of γ^p the SUF starts at a distinctly lower value, which increases rapidly to the value of the 1 min STF followed by a steady increase to bigger values. Thus, it suggests itself to consider the SUF as a physically and chemically differing system. Any changes that had been made to the fiber during the treatment affected the principal properties of the untreated fiber and generated a different type of surface.

TABLE IV Work of adhesion between carbon fibers and PC

OP-treatment [*min*]	W_a^h [*mN/m*]	W_a^g [*mN/m*]
0	79.1 ± 3.1	81.9 ± 2.8
1	68.8 ± 2.1	80.0 ± 2.2
5	66.7 ± 2.4	79.4 ± 2.2
10	68.0 ± 2.6	81.5 ± 2.5
20	66.9 ± 2.4	82.2 ± 2.5

Summarizing the results based on the fracture energy model, there should be no change in the adhesion between OP-treated fibers and PC with prolonged OP-treatment time. The system containing the untreated carbon fiber should indicate a much better adhesive interaction to PC compared with all the PC/OP-treated carbon fiber combinations.

Expected Adhesion – Electrokinetic Effects

Table V gives the results for the measured difference between ζ_{plateau} (at pH ≥ 7) of both jointing partners (see also Fig. 1). $\Delta\zeta_{\text{plateau}}$ steadily increases with OP-treatment time, running through a plateau

TABLE V ζ_{plateau} of modified carbon fibers [18] and PC [17]

OP-treatment [*min*]	$\Delta\zeta_{plateau}$ [*mV*]	ζ_{max} [*mV*]	$\Phi_- - \Phi_+$ [*kJ/mol*]
0	-22.0 ± 1.8	-28.4 ± 0.2	-5.4 ± 0.2
1	-12.0 ± 1.9	-35.5 ± 1.3	-6.8 ± 0.6
5	-21.7 ± 2.2	-44.8 ± 0.1	-8.6 ± 0.2
10	-22.5 ± 1.6	-39.1 ± 0.5	-7.6 ± 0.3
20	-29.7 ± 3.3	-31.4 ± 0.2	-6.1 ± 0.9

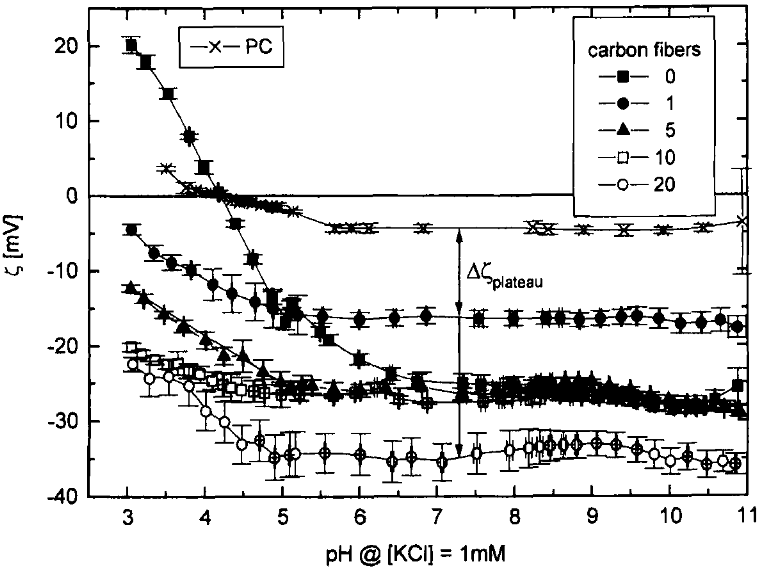

FIGURE 1 ζ-Potential as a function of pH at c(KCl) = 10^{-3} mol/L of untreated and oxygen-plasma-treated carbon fibers as well as polycarbonate. The arrows illustrate the estimation of $\Delta\zeta_{\text{plateau}}$.

state between 5 min and 10 min treatment time. Again, there is a gap between the SUF and all the STFs. Thus, according to Jacobasch [13] – and presuming the presence of acid-base-interactions – at the beginning of the OP-treatment, the adhesive interactions should be diminished and with prolonged treatment, improved again.

Assuming that the same functional groups are present on the surface of the treated carbon fibers, the change in the value of ζ_{plateau} indicates a step-by-step increase in the quantity of acidic surface groups with treatment time. Although ζ_{plateau} of the 5-min-treated and the 10-min-treated carbon fibers has the same value, another effect can be observed. The decay of the negative ζ-potential in the acidic range is much slower for the 10-min-treated carbon fiber. This behavior indicates a higher pK-value of the surface groups, quantifying their proton affinity (adsorption or chemisorption). Prolonged OP-treatment increases ζ_{plateau} again and the decay reaches its original strength.

$\zeta_{\max}$ – according to Jacobasch reflecting the van-der-Waals forces which are available for interactions on the surface – does not show any consistent trend. However, the difference, $\Phi_- - \Phi_+$, as a measure of the dispersive forces, which act at the surface of the untreated carbon fiber, improved with plasma treatment. Therefore, a prolonged treatment should cause the van-der-Waals-forces to reach a near-maximum at 5 min and then to be diminished again.

Single-Fiber Tensile Strengths and Single-Fiber Fragmentation Test

Table VI gives the results from the micromechanical tests. The values obtained for the single-fiber tensile strength, σ_{fu}, and the fiber

TABLE VI Fiber diameter, d_f, single-fiber tensile strength, σ_{fu}, mean fragment length, l, standard deviation of fragment distribution, s, critical fiber fragment length, $l_c = 4/3 \cdot l$ and interfacial shear strength, τ_{IFSS}, of original and OP-treated carbon fibers

OP-treatment	0 *min*	1 *min*	5 *min*	10 *min*	20 *min*
d_f [µm]	8.0	7.0	7.5	7.5	7.5
σ_{fu} [MPa]	3060 ± 480	3040 ± 390	3190 ± 570	3010 ± 480	3060 ± 530
l [10^{-3} m]*	0.83 ± 0.04	1.17 ± 0.07	0.88 ± 0.04	0.75 ± 0.04	0.88 ± 0.03
s [10^{-3} m]	0.25	0.53	0.33	0.38	0.32
l_c [10^{-3} m]	1.11 ± 0.05	1.56 ± 0.09	1.18 ± 0.05	1.00 ± 0.05	1.17 ± 0.03
l_c/d_f	138	223	156	133	156
τ_{IFSS} [MPa]	11.1 ± 1.2	6.8 ± 0.5	10.1 ± 1.4	11.3 ± 1.2	9.8 ± 1.4

d_f [µm] 8.0 7.0 7.5 7.5 7.5

diameter, d_f, indicate that the oxygen plasma treatment did not significantly damage the fibers (see also SEM-micrographs in [20]). This is in good agreement with the results of Bogoeva-Gaceva *et al.* [36]. Thus, the critical aspect ratio, l_c/d_f, can be approximately used as an inverse measure of the adhesion.

The fragment length distribution generated from the data of the untreated fiber shows a symmetric and close ($s = 0.25$) shape. Thus, the interface should have a quite homogeneous character [35]. Since the model of Kelly and Tyson provides no real characteristic value for the material, the mean fragment length of this distribution serves as the reference point for further considerations.

At the beginning, OP-treatment causes a broadening of the distribution ($s = 0.53$) and gives the latter a clearly asymmetric shape. The mean fragment length becomes much bigger. Those occurrences indicate a distinct worsening of the adhesive interactions by OP-treatment. After prolonging the treatment, the distributions entirely shift to smaller fragment lengths; they become closer and much more symmetrically shaped.

Applying these results to Eq. (5), τ_{IFSS} has been calculated. Thus, the ability of the untreated fiber to incur adhesive interactions with the PC seems to be worsened by OP-treatment. However, prolonged OP-treatment improves the adhesion, but not beyond the original strength.

DISCUSSION

Bascom and Chen [4] detected a remarkable decrease in the critical aspect ratio, l_c/d_f, obtained by single-fiber fragmentation tests with freshly OP-treated Hercules AS1 and AS4 fibers embedded within a PC-matrix. In contrast, the critical aspect ratio increased for those modified fibres which had been stored after treatment for one week before the composite was prepared. We assume that the improved adhesion is caused by the presence of free radicals on the graphitic surface. Right after plasma treatment, the surface can be considered as a high-energy surface due to the partial removal of adsorbed layers. Since this effect vanishes with storage time, the use of the pre-stored fibers worsened the adhesive interactions.

Combining all the results, we found that the values of W_a^h are in good agreement with the ones obtained for γ^d, θ_m and $(1+\cos\theta_m)$. That is, the values of W_a arising from two different sources (the harmonic mean model and the direct-wetting-method in combination with the Young-Dupré-equation) lead to equivalent predictions of the behavior of the system. Thus, for the given system the thermodynamic approach is self-consistent.

The particular parts of the overall surface tension – each addressing either the polar or the non-polar (dispersive) forces – reflect the values of the contact angles obtained by the wetting measurements *versus* test liquids. Generally, the surface tension component, γ^d, and the work of adhesion reflect the dispersive interactions. In contrast, the polar interactions do not significantly affect the values of W_a^h. However, the latter is in no way expected, because the OP-treatment drastically changes the ability of the carbon fiber to interact *via* polar surface forces and, so, the course of the overall surface tension is mainly predetermined by the contribution of its polar part, γ^p. This is confirmed by the drastic increase of the surface polarity, X^p, which is caused by the OP-treatment.

Otherwise, this result seems quite reasonable, since the contact angle values obtained from wetting measurements *versus* test liquids clearly point out that the PC dislikes polar interactions, but has an affinity to dispersive interactions. Fowkes assumed [37, 38] that surface interactions are only possible between forces of the same kind. As already described, the treated carbon fibers mainly interact *via* polar forces. Thus, an adhesive interaction is not promoted. This is exactly what the values of W_a^h predict.

But there is a discrepancy in the result obtained from the micromechanical – and therefore more practical – approach to describe adhesion. The drop of the adhesive strength at the beginning of the treatment is in good agreement with the predictions of both the fracture-energy-model with its zero-state-approximation and the direct wetting measurements according to the Young-Dupré approach. However, both models fail to describe the improvement of the adhesive interactions, which arise after a prolonged treatment. Only the simple interpretation of the test-liquid-measured contact angles and the consideration of the particular contributing parts of the overall surface tension correspond with the data obtained from the SFF.

There are several possibilities to explain the deviation of predicted and micromechanically-estimated adhesive strength:

Firstly, the different sample preparation processes might cause it. Whereas the polymer drops for the direct contact angle measurements were formed by melt coating, the single fiber composites were produced *via* solvent coating. The different mobility of low molecular weight (polymer) molecules in solution and in the melt may cause a system-dependent variance in the amount of those molecules which can diffuse to the interface. However, although dichloromethane is very volatile, the polymer solution is very concentrated (and, hence, highly viscous). Therefore, the time taken for diffusion into the interphase is expected to be long in comparison with the time taken for the solution to become a swollen gel or glass-like polymer. Otherwise, even during the direct-wetting measurements the low molecular weight species have the possibility to diffuse into the interphase. Nevertheless, the main argument against this impurity-effect is the fact that the results of the direct-wetting measurements are in good agreement with the calculated W_a^h-values obtained from the contact angle values measured using the test liquids (neither a polymer melt nor a polymer solution is involved). Furthermore, only in the case of the SFF sample preparation is there an additional molecular component (dichloromethane) present during equilibration of the interphase. But even those measurements, which are based on this process, clearly show an increase in the adhesive forces. It seems not reasonable to consider dichloromethane as an agent promoting polar interactions.

Secondly, on the assumption that the same kinds of forces cause the adhesion between the treated fibers and PC and only their proportions change with the treatment time, and further assuming that the failure modes during the fragmentation process do not vary within the different systems containing the treated carbon fibers, then the strength of the polar forces involved in adhesive interactions seems to be underestimated by the thermodynamic approach. This thesis is supported by the results of the ζ-potential measurements. The ζ_{plateau}-values indicate a rising activity of polar interactions. Nevertheless, though the drop of $\Delta\zeta_{\text{plateau}}$ and its increase at the beginning of the treatment is in good agreement with the results obtained by SFF, the drastic growth in $\Delta\zeta_{\text{plateau}}$ with extended treatment time does not fit them. The values obtained for ζ_{max}

give no further information. They do not correspond to the results of the wetting measurements using the test liquids, since the interaction between the dissolved ions (K^+ and Cl^-) and the surface specifically depends on the presence, as well as the type, of dissociable surface groups [20]. Thus, the simple $\Delta\zeta_{\mathrm{plateau}}$- and ζ_{max}-models according to Jacobasch seem to overestimate the polar interactions and do not allow unambiguous separation of polar and dispersive forces.

Thirdly, the fracture-energy-model, as a part of the thermodynamic approach as it is used here to predict adhesion, includes two decisive restrictions. Accordingly, only in the case of zero-rate is the work of adhesion equal to the fracture energy and, thus, to the quality of an adhesive joint since, in this case, the plastic work does not contribute to the total fracture energy. Nevertheless, reflecting a process at non-zero-rate, for a given adhesive on a series of differently-modified adherends (here reinforcing fibers), the plastic contribution should be nearly constant and, so, the fracture energy can be considered as directly proportional to the work of adhesion [10]. The second assumption is the exclusive occurrence of adhesive fracture. If cohesive and adhesive fractures coexist, the overall fracture energy is given by a linear combination of the single modes (as adhesive fracture energy) [10]. Whereas the first assumption addresses the adhesive failure mode itself, the second restriction questions the ability to correlate the thermodynamic approach with the micromechanical description and the macroscopic behavior of composites. However, both simplifications stand in contradiction to the results of the SFF-test. The interfacial shear strength, τ_{IFSS}, refers to the capability of the interphase to transfer load from the surrounding polymer matrix into the reinforcing fiber. The process of load transfer must be considered as a quite complex mechanism based on a concurrence of several material properties of the bulk phases as well as the interphase. Thus, cohesive as well as adhesive interactions (and even phenomena like plastic yielding of the polymer matrix) are included in the overall result obtained by the single-fiber fragmentation test. That is why the interfacial shear strength, τ_{IFSS}, cannot be considered as a characteristic material value and gives only an idea of the adhesive interactions within the interphase.

CONCLUSION

Contact angle measurements well reflect those surface properties addressed by the wetting model. For the investigated systems, the thermodynamic approach is self-consistent, though it is not able to describe completely the real situation. It fails mainly in the assessment of polar interactions (by their underestimation).

ζ-potential measurements are sensitive to changes in the chemical surface properties. However, the values obtained are the measured net effect of a complex concurrence of several interaction mechanisms on a solid surface. If two systems are comparable, in the sense of kind(s) of interactions, then some simple rules of thumb might be applicable to predict the relative strength of adhesion. But in coexistence of different interaction forces, which are equal in weight, those principles do not reflect the real situation. We found that ζ-potential measurements fail in the assessment of polar interac tions (by their overestimation) and are not able to describe separately the non-polar interactions.

Oxygen-plasma treatment of carbon fibers causes a worsening in their ability to interact *via* dispersive forces but improves their capability to support polar interactions. Thus, this treatment method is not applicable to improve the adhesion between carbon fibers and those thermoplastics which do not have, or have few, polar functional groups.

Evidently, any physico-chemical method must fail to describe exactly the adhesion phenomena. However, the simple interpretation of the data obtained from contact angle measurements, in accordance with some basic considerations (wetting model), can be applied to predict the tendency of the changes in adhesive strength dependent on any modification of one of the jointing partners. This approach is valid for a composite consisting of a thermoplastic matrix polymer (if chemical interactions can be excluded) and modified carbon fibers, as shown for other investigated systems [6, 39].

Acknowledgements

Special thanks to Dipl.-Ing. Thomas Lampke, TU Chemnitz, Lehrstuhl für Verbundwerkstoffe, for immediate help with the single-fiber tensile strength tests, Dipl.-Ing. Egon Moos, Institut für Verbundwerkstoffe (IVW) Kaiserslautern, for the polycarbonate, and Dipl.-Ing. Jörg Nissen, ZELMI, TU-Berlin, for the fiber diameters. We would also like to thank Dr. Chris J. Bottrill, Surfactant Science Group, The University of Hull, for improving our English.

Financial support from NATO-project No. HTECH.LG 960084, the Fonds der Chemischen Industrie and the Berliner Verband für Polymerforschung (BVP) e.V. is gratefully acknowledged. One of the authors (D.R.) would like to thank the Graduiertenkolleg "Polymerwerkstoffe" for financial support.

References

[1] Sprenger, K.-H., "*Aufbau und Eigenschaften von themoplastischen Hochleistungs-Faserverbundwerkstoffe*", In: *Faserverbundwerkstoffe mit thermoplastischer Matrix; Hochleistungswerkstoffe für rationelle Verarbeitung*, Zempf, H.-P. Ed. (expert verlag, Renningen-Malmsheim, 1997).

[2] Kempe, G., "Duroplastische und Thermoplastische Faserverbundwerkstoffe – Vorteile – Eigenschaften – Verarbeitung und Anwendungsgebiete beider Werkstoffgruppen", In: *Faserverbundwerkstoffe mit thermoplastischer Matrix; Hochleistungswerkstoffe für rationelle Verarbeitung*, Zempf, H.-P. Ed. (expert verlag, Renningen-Malmsheim, 1997).

[3] Yuan, L. Y., Shyu, S. S. and Lai, J. Y., *J. Appl. Polym. Sci.* **42**, 2525 (1991).

[4] Bascom, W. D. and Chen, W.-J., *J. Adhesion* **34**, 99 (1991).

[5] Bourgeois, P. and Davidson, T., *J. Adhesion* **45**, 73 (1994).

[6] Bismarck, A., Richter, D., Wuertz, C. and Springer, J., *Colloids Surf. A* **159**, 341 (1999).

[7] Ismail, I. K. and Vangsness, M. D., *Carbon* **26**, 749 (1988).

[8] Comyn, J., *Adhesion Science* (RSC paperbacks, Cambridge, 1997).

[9] Hull, D. and Clyne, T. W., *An Introduction to Composite Materials* (Cambridge University Press, Cambridge, 1996), 2nd edn.

[10] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker, New York, 1982).

[11] Fowkes, F. M., Riddle, F. L. Jr., Pastore, W. E. and Weber, A. A., *Colloids Surf.* **43**, 367 (1990).

[12] Sauer, B. B. and Diapaolo, N. V., *J. Colloid Interface Sci.* **144**, 527 (1991).

[13] Häßler, R. and Jacobasch, H.-J., *kleben und dichten, Adhäsion* **38**, 36 (1994).

[14] Jacobasch, H.-J., Oberflächenchemie faserbildender Polymerer (Akademie Verlag, Berlin, 1984).

[15] Jacobasch, H.-J., Grundke, K., Schneider, S. and Simon, F., *J. Adhesion* **48**, 57 (1995).

[16] Jacobasch, H.-J., *Angew. Makromol. Chem.* **128**, 47 (1984).

[17] Jacobasch, H.-J., Simon, F. and Weidenhammer, P., *Colloid Polym. Sci.* **276**, 434 (1998).

[18] Kelly, A. and Tyson, W. R., *J. Mech. Phys. Solids* **13**, 329 (1965).

[19] Bismarck, A., Pfeifer, G. and Springer, J., *J. Adhesion Sci. Technol.*, **14**, 661 (2000).

[20] Bismarck, A., Kumru, M. E. and Springer, J., *J. Colloid Interface Sci.* **210**, 60 (1999).

[21] Uyama, Y., Inoue, H., Ito, K., Kuhida, A. and Ikada, Y., *J. Colloid Interface Sci.* **141**, 275 (1991).

[22] Sauer, B. B. and Carney, T. E., *Langmuir* **6**, 1002 (1990).
[23] Bismarck, A., Kumru, M. E. and Springer, J., *J. Colloid Interface Sci.* **217**, 377 (1999).
[24] Grundke, K., Uhlmann, P., Gietzelt, T., Redlich, B. and Jacobasch, H.-J., *Colloids Surfaces A* **116**, 93 (1996).
[25] Yamaki, J. and Katayama, Y., *J. Appl. Polym. Sci.* **19**, 2897 (1975).
[26] Carroll, B. J., *J. Colloid Interface Sci.* **57**, 488 (1976).
[27] Song, B., Bismarck, A., Tahhan, R. and Springer, J., *J. Colloid Interface Sci.* **197**, 68 (1998).
[28] Sauer, B. B. and Kampert, W. G., *J. Colloid Interface Sci.* **199**, 28 (1998).
[29] Giannotta, G., Morra, M., Occhiello, E., Garbassi, F., Nicolais, L. and D'Amore, A., *J. Colloid Interface Sci.* **148**, 571 (1992).
[30] Vodermayer, A., "*Herstellung von unidirektional kohlefaserverstärkte Thermoplasten durch Polymerpulverimprägnierung mittels einer wäßrigen Dispersion*", *Doctoral Thesis*, TU-Berlin, D83, 1992.
[31] Tahhan, R., *Doctoral-Thesis*, TU Berlin, 1997.
[32] Fairbrother, F. and Mastin, H., *J. Chem. Soc.* **125**, 2319 (1924).
[33] Mäder, E., Grundke, K., Jacobasch, H.-J. and Wachinger, G., *Composites* **25**, 739 (1994).
[34] Krönert, W. and Raith, A., *Chemiefasern/Textilindustrie* **92**, 40 (1990).
[35] Richter, D., *Diploma-Thesis*, TU Berlin, 1998.
[36] Bogoeva-Gaceva, G., Mäder, E., Häussler, L. and Dekanski, A., *Composites Part A* **28A**, 445 (1997).
[37] Fowkes, F. M., *J. Phys. Chem.* **66**, 382 (1962).
[38] Fowkes, F. M., *J. Phys. Chem.* **67**, 2538 (1963).
[39] Bismarck, A., Kumru, M. E., Song, B., Springer, J., Moos, E. and Karger-Kocsis, J., *Composites A* **30**, 1351 (1999).