Colloid Polym Sci 276:1110–1116 (1998)

ORIGINAL CONTRIBUTION

A. Bismarck
M. Pfaffernoschke
M. Selimović
J. Springer

Electrokinetic and contact angle measurements of grafted carbon fibers

Part III: Grafting of 2-(*N*,*N*-dimethylamino)ethyl methacrylate

Received: 9 June 1998
Accepted: 13 August 1998

A. Bismarck · M. Pfaffernoschke
M. Selimović · Prof. Dr. J. Springer (✉)
Institut für Technische Chemie
Fachgebiet Makromolekulare Chemie,
Sekr. TC 6
Straße des 17. Juni 135
D-10623 Berlin
e-mail: spri0534@mailszrz.zrz.tu-berlin.de

Abstract The grafting method that has successfully been applied to methacrylic acid and liquid crystalline monomers was expanded to prepare amphoteric carbon fiber surfaces using 2-(*N*,*N*-dimethylamino)ethyl methacrylate as monomer. The obtained carbon fiber surfaces were characterized by contact angle and ζ-potential measurements. The expected basic behavior was not observed, instead an amphoteric character of the modified carbon fiber surface was found. The fiber surfaces display a basic character in the acidic pH-range, while they are acidic in the alkaline part of the pH-scale.

An important influence is derived from the amount of initiator used to graft the monomers onto the fibers. The smaller the initiator concentration used during polymerization, the larger the amount of amino functionalities introduced to the carbon fiber surface.

The wetting behavior versus water depends on the overall conformation of the immobilized polymer. During immersion into water the polymer acts hydrophobic, while during emersion, a hydrophilic character is observed, probably derived from conformational changes and swelling during the contact angle measurements in water.

Key words Grafting reaction – carbon fiber – amphoteric surface – contact angle – zeta-potential

Introduction

Carbon fibers are used in various applications as reinforcing component in a number of different matrices. To improve the fiber/matrix adhesion it is necessary to increase the surface polarity of usually nonpolar and hydrophobic carbon fibers [1]. Normally sizing and different oxidizing methods are applied to modify carbon fiber surfaces (i.e. boiling in oxidizing acids, plasma modifications and electrochemical oxidations) [2, 3]. Furthermore, it is possible to achieve good stress transfer by mechanical interlocking between covalently bonded polymer on the carbon fiber surface and the matrix [4]. Koschinski et al. [5] described grafting of carbon fibers with polyphenylene sulfide (PPS) by "in situ" polycondensation. A high adhesion between grafted fibers in a PPS-matrix resulted. Polymethylmethacrylate was grafted onto carbon fiber surfaces by electron beam irradiation of methylmethacrylate soaked carbon fibers [6]. Tschobokawa et al. [7] modified thin carbon films through the introduction of azo-, acylperchlorate- or carboxyl surface groups. In a second reaction step these groups were grafted with vinyl- or epoxy monomers by radical, cationic- or anionic-initiated polymerization.

As described in earlier publications, it is possible to graft various methacrylic monomers onto carbon fiber surfaces conducting free radical polymerization in the presence of suitable modified carbon fibers [8]. Grafting of water soluble polymers onto carbon fiber surfaces causes significant changes of the surface properties. An increased hydrophobic character was found. For methacrylic acid a quasi-micelle-like structure was proposed which minimizes the surface free-energy, where the hydrophilic carboxyl groups are organized inside the micelle, thus forming a hydrophobic shell. When water insoluble, such as liquid crystalline monomers were used, an analogous tendency was found, derived from the hydrophobic character of the liquid crystals.

The surface properties of carbon fibers are extremely important to achieve high-performance carbon fiber composites. Since thermoplastic engineering (e.g. polyamide, polycarbonate) and high-performance (e.g. polyetherimide, polyetheretherketone) materials encompass acidic groups [9] due to the industrial processing, it appears highly desirable to improve the adhesion between carbon fibers and such matrices by suitable acid and base interactions. According to Häßler and Jacobasch [10] adhesion should improve with an increasing difference between the ζ_{plateau} values, obtained by $\zeta = f(\text{pH})$ of adherent and adhesive. It was shown that the adhesive strength between a polyamide 12 and carbon fibers containing basic surface oxides improved due to acid–base interactions. Therefore thermochemically modified carbon fiber surfaces with basic character (H-carbon fibers) add to the adhesive behavior between carbon fibers and the matrix polymer, and improve the properties of the obtained composite material [11].

Zhang et al. [12] grafted 2-(*N*,*N*-dimethylamino)ethyl methacrylate onto polyethylene-terephthatlate (PET) and cellulose surfaces and studied the influence of different surface charges on adhesion in water, but no correlation between the zeta (ζ)-potentials of the surfaces and their adhesive strength was found. An amphoteric surface character of carbon fibers should combine attractive forces between reinforcing fibers and the surrounding polymer matrix, like acid and base interactions or possible hydrogen bonds [13].

Experimental part

Materials

In this study we used untreated and uncoated (high tenacity (HT)) polyacrylontirile (PAN)-based carbon fibers C320.00A supplied by SGL Sigri Carbon Group, Meitingen, Germany. To guarantee as good as possible wetting of the fiber surfaces by the monomer used for the grafting procedure, the surface polarity needs to be optimized as far as the surface tensions are concerned (condition for good wetting: $\gamma_s > \gamma_l$, where γ_l is the surface tension of used liquid and γ_s of the fiber (s = solid)). If no or bad wetting of the carbon fiber surface occurs, then no or little grafting will take place. Therefore, it is necessary to treat carbon fibers for 10 min in an oxygen plasma (sample name "OP") to introduce oxygen-containing surface groups to the carbon fiber surface prior to grafting. Otherwise, no grafting will occur as already shown [8]. The OP fibers were removed from the plasma reactor, stored under air and then transferred to the reaction vessel, where the grafting took place by polymerizing the monomer in the presence of OP carbon fibers in bulk. 2-(*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) was purchased from Polysciences Inc. (Eppelheim, Germany) and used without further purification. The grafting procedure was performed using 1, 5 and 10 mol% initiator (AIBN). Detailed experimental procedures of plasma treatment and grafting are described in other publications [8, 14]. After the grafting procedure was finished, unreacted monomer and non-covalently bonded polymer were removed by extraction of the carbon fibers with water for 7 days.

SEM investigations

In order to show possible changes in the surface morphology, all treated fibers were analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 (Nissei Sangyo GmbH, Rathingen, D) scanning electron microscope. The grafted carbon fibers were sputtered with gold prior to investigation to avoid artifacts caused by electrical charges.

Zeta (ζ)-potential measurements

To determine the ζ-potentials of all investigated carbon fibers we used the electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria), based on the streaming potential method [15]. The streaming potential is measured as a function of the pressure decay in a fiber bundle (capillary system) while the electrolyte solution (KCl) is pumped through it. More details about this experimental technique are described in the literature [16–19].

The reproducibility of electrokinetic measurements depends strongly on the sample quality. This means that every measurement of the concentration- or pH-dependence needs a well-defined starting point. To remove all soluble components from the carbon fiber surface and to equilibrate the system, the ζ-potential of the fibers was measured as a function of time in 10^{-3} mol/l KCl. It is possible to acquire information about the degree of interaction between the solid surface and the ions in the electrolyte solution from the concentration dependence of the ζ-potential, based on specific or electrostatic interactions.

For most fiber materials the ζ-potential values show – corresponding to the Stern theory [20] – a parabolic curve like trend, which is caused by the adsorption properties of the solid for potential determining ions as well as by specifically adsorbed ions. This parabolic trend is characterized by two extreme parameters, the maximal ζ-potential $\zeta_{\max}$ and the maximal concentration value $c_{\max}$. The Stern theory makes no assumptions regarding the nature of charge carriers close to the phase border. Therefore the theory should be valid for solids, provided the surface potential is determined through dissociation of surface groups or through the adsorption of ions. The molar adsorption free-energies Φ_{K^+} for potassium and Φ_{Cl^-} for chloride ions by a solid surface can be calculated from $c_{\max}$ at $\zeta_{\max}$ using a combination of the following equations:

$$2RT \ln c_{\max} = \Phi_- + \Phi_+ \tag{1}$$

and

$$\Phi_- - \Phi_+ = 2F\zeta_{\max} \, . \tag{2}$$

(R: gas constant, F: Faraday constant)
The difference in the adsorption free-energies of inert electrolyte ions should correspond with the dispersion forces spread by the solid surfaces.

Since the ζ-potential as a property of the electrochemical double layer cannot depend on the geometry of the investigated capillar bundle, like a fiber bundle, it is necessary to characterize the pore geometry as well as possible. The method to correct the surface conductance (CSC) according to Fairbrother and Mastin [21] enables one to characterize the pore geometry by measuring the electrical conductivity and resistance in the fiber bundle with the electrolyte solution under use, and then by changing the electrolyte again to a 0.1 M KCl solution after the measurement.

ζ-potential values of the investigated carbon fibers were determined in 10^{-3} mol/l KCl electrolyte solutions at various pH values. The presence of acidic or basic dissociable surface functional groups can be estimated from the pH dependence of the ζ-potential. If the investigated solid contains acidic surface groups, the negative ζ-potential will enlarge with increasing pH due to the increased dissociation of those groups. If basic functions are present at the surface, the amount of positively charged groups increases with diminishing pH. The complete dissociation of surface groups causes a plateau area in the ζ-potential–pH plot. The isoelectric point (i.e.p.) is another measure of the acidity or basicity of a solid surface, if the dissociation of surface groups is the predominant mechanism for the formation of the electric double layer. The solid surface has an acidic character if the value of i.e.p. is low. If the i.e.p. value is situated in the alkaline range, the solid surface contains basic surface groups [22].

Measuring the ζ-pH dependence for hydrophobic, nonpolar solids will result in a plot without plateaus due to the absence of dissociable surface functionalities. The increase in negative and positive ζ-potential with increasing or decreasing pH is caused by the enlarged adsorption of hydroxyl ions or protons.

Contact angle measurements

To determine the solid surface tension of the investigated fiber materials contact angle measurements were carried out on single carbon fibers using the modified Wilhelmy technique. Details of the experimental procedure can be found in literature [14].

Advancing θ_a and receding θ_r contact angles were calculated by the Wilhelmy equation from the obtained mass changes Δm, which were measured during the immersion and emersion cycle of the fibers into the test liquid

$$\cos\theta = \frac{\Delta m \cdot g}{\pi \cdot d \cdot \gamma_l} \, , \tag{3}$$

where g is the acceleration of gravity, d the fiber diameter and γ_l the surface tension of the used test liquid.

According to Fowkes [23] the surface tension should be considered as a sum of independent terms, representing a particular intermolecular force. The surface tension can be divided into a polar term and a dispersive term [24].

$$\gamma = \gamma^p + \gamma^d \, . \tag{4}$$

We used the harmonic mean method introduced by Wu [25] to calculate the solid surface tension. The harmonic mean equation should be valid for interactions between low-energy materials. To solve these equations, contact angles between the investigated solid and a pair of liquids have to be determined. Wu suggested water and diiodomethane. The surface tensions of both liquids are known (surface tension of water $\gamma = 72.8$ mN/m, polar component of the surface tension $\gamma^p = 50.7$ mN/m, dispersive component of the surface tension $\gamma^d = 22.1$ mN/m and polarity $X^p = \gamma^p/\gamma = 0.7$ and of diiodomethane $\gamma = 50.8$ mN/m, $\gamma^p = 6.7$ mN/m and $\gamma^d = 44.1$ mN/m, $X^p = 0.13$). The surface polarity is defined [25] by the following equation:

$$X^p = \frac{\gamma_s^d}{\gamma_s} \, . \tag{5}$$

Results and discussion

SEM

The fiber surface morphology was determined by SEM investigations. As described, the grafting was carried out in the presence of carbon fibers treated for 10 min in oxygen plasma. The fiber shows for PAN-based fibers typical striations parallel to the fiber axis. It seems that the plasma treatment does not cause any disruption of the fiber surface. Only for the sample prepared with 1 mol% initiator significant amounts of the polymer are observable on the fiber surface. The grafted polymer appears to have reacted with carbon from the outer striation levels, causing these to look macroscopically gnawed. We assume that most of the visible surface is covered by grafted polymer. All other fibers only display very few and small, scattered, ball-like polymer structures on the fiber surface. The higher the amount of initiator, the lower the number of visible polymer on the fiber surface.

ζ-potential measurements

Grafting DMAEMA onto carbon fiber surfaces changes the surface properties of the carbon fibers completely. The first ζ-potential measurement focused on the time dependence. Over a period of 26 h, no change in the ζ-potential value was detected. This means, that the grafted fibers do not swell in the electrolyte.

Depending on the amount of initiator used, the ζ_{max} at c_{max} value experiences a sign reversal. The positive ζ-potential decreases with increasing amount of initiator (Fig. 1). The immobilized DMAEMA exhibits cationic charges, when dissolved in water. The smaller the initiator content, the longer the polymer-chains grafted onto the carbon fiber surface, which derives from the common free radical polymerization kinetics. From the ζ-c-function it is evident that cations present in the electrolyte will be preferably adsorbed by the polymer-grafted surface. With increasing amount of initiator the number of adsorbed cations decreases, i.e. the positive ζ-potential diminishes. The correction in surface conductance does not influence the general course, but shifts the ζ-potential values to higher values.

The adsorption free-energies (absorption potentials) for anions Φ_- and cations Φ_+ (Table 1) from ζ_{max} and c_{max} are calculated by using Eqs (1) and (2). Φ_+ decreases with increasing amount of initiator and approaches the Φ_+ value of the ungrafted, plasma treated carbon fiber (OP). Φ_- drops to a nearly constant value ($\Phi_- \sim -12$ kJ/mol) with decreasing initiator content.

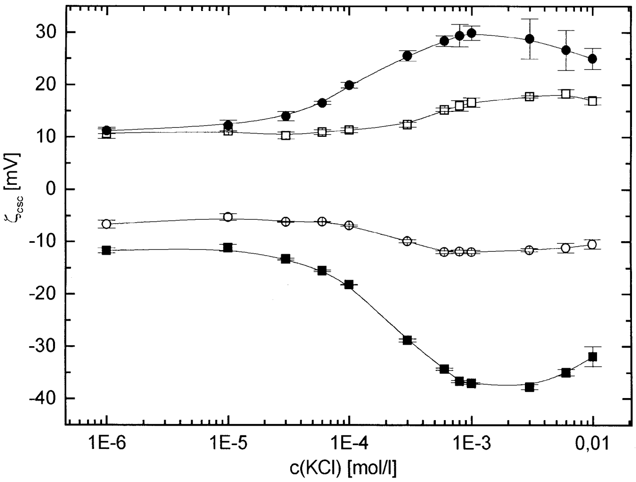

Fig. 1 ζ-c-function. ■ OP, ● DMAEMA grafted with 1 mol% AIBN, □ DMAEMA grafted with 5 mol% AIBN, ○ DMAEMA grafted with 10 mol% AIBN

The pH-dependence of the ζ-potential (Fig. 2) displays a typical acidic trend for OP which includes a negative sign of the ζ-potential and a not measurable acidic i.e.p. value (extrapolated to i.e. $p \sim 2.0$). All grafted fibers exhibit a sigmoidal $\zeta = f(\mathrm{pH})$ curve which indicates an amphoteric surface character. The plateau values in the alkaline range correspond to the plateau value of OP. As the initiator content increases, the i.e.p. decreases. This leads to the assumption that the sample prepared with 1 mol% initiator contains the largest amount of immobilized polymer, which is inverse to the behavior of the methacrylic acid grafted carbon fibers [8]. For the methacrylic acid grafted carbon fibers, an increase of the initiator content causes an increase of the i.e.p. values. The OP carbon fiber surface is very acidic and the higher the degree of covering of the surface with polymethacrylic acid the lower the i.e.p., because the free acid fiber surface decreases.

The basicity of the DMAEMA-grafted fibers depends on the number of polymer chains immobilized on the surface. This corresponds to the number of protonable amino groups.

Our observations correspond well with ζ-potential measurements made by van Wagenen et al. [26]. They found that the incorporation of DMEMA or salts of DMEMA into neutral polymers or polymer networks reduces the negative ζ-potential up to a sign inversion of the ζ-potential. A higher incorporated amount of DMEMA leads to positive ζ-potential values for the investigated system.

The pure and onto carbon fibers adsorbed poly-2-(*N*,*N*-dimethylamino)ethyl methacrylate cannot be characterized via ζ-potential measurements using the

Table 1 ζ_{max}, c_{max} values, adsorption free-energies Φ_- for chloride and Φ_+ for potassium and i.e.p. values

Carbon fiber	ζ_{max} (csc) [mV]	c_{max} [mol/l]	Φ_- [kJ/mol]	Φ_+ [kJ/mol]	i.e.p.
OP	-37.73 ± 0.50	0.003	-17.94 ± 0.19	-10.66 ± 0.10	2.0[a]
1 mol% AIBN	29.87 ± 0.30	0.003	-11.42 ± 0.45	-17.19 ± 0.18	8.2
5 mol% AIBN	18.35 ± 0.79	0.006	-10.83 ± 0.27	-14.37 ± 0.12	7.2
10 mol% AIBN	-11.93 ± 1.38	0.003	-15.45 ± 0.14	-13.15 ± 0.08	5.4

[a] Extrapolated.

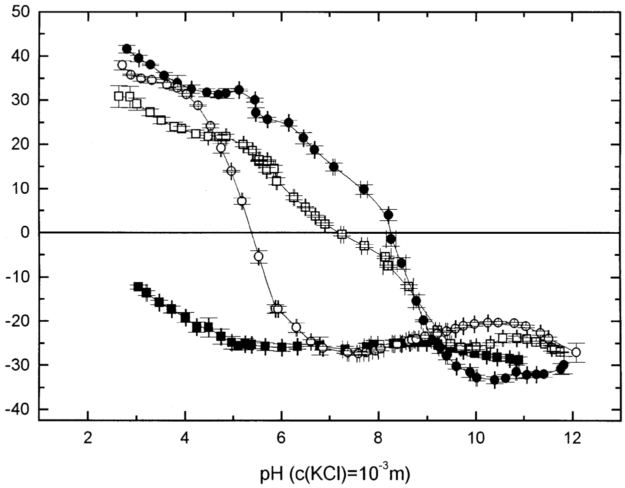

Fig. 2 ζ-pH-plot. ■ OP, ● DMAEMA grafted with 1 mol% AIBN, □ DMAEMA grafted with 5 mol% AIBN, ○ DMAEMA grafted with 10 mol% AIBN

streaming potential method in aqueous solutions, due to its water solubility.

Contact angle measurements

Contact angles (Fig. 3a) measured versus water during immersion θ_a increase with decreasing initiator content, while the value of the sample grafted with 10 mol% AIBN is lower than that of OP. Whereas the receding contact angles θ_r remain constant. We assume that this behaviour is caused by the overall structure of the dry polymer. The hydrophobic polymer backbone, composed of methyl and methylene groups determines the wetting behavior during immersion, while the wetting behavior during emersion is a function of the untied, swollen polymer. θ_r resembles a combination of the hydrophobic backbone and the hydrophilic amino groups. This means that the wettability in the receding mode is mainly influenced by the interactions between water and the amino groups. If regular free radical polymerization kinetics are valid when carbon fibers are present, using small amounts of initiator should result in few but long polymer chains, which are able to form entanglements. Shorter polymer chains, derived from polymerizations with larger amounts of AIBN (i.e. 10 mol%), which are not able to form those many entanglements, display a more hydrophilic character during immersion and θ_a is influenced mainly by the polymeric amino groups as well as acidic fiber surface groups. This corresponds well with our observations on methacrylic acid-grafted

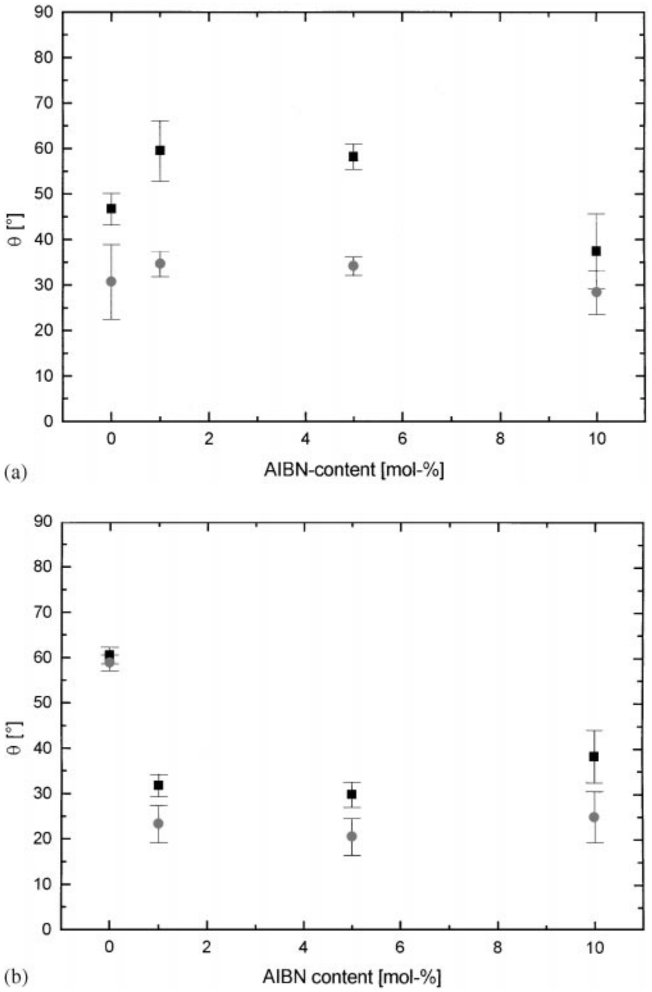

Fig. 3 (a) Contact angle measured versus water. (b) Contact angle measured versus diiodomethane. ■ θ_a, ● θ_r

Table 2 Surface tension and surface polarities of grafted carbon fibers

Carbon fiber	γ^p [mN/m]	γ^d [mN/m]	γ [mN/m]	X^p
OP	34.2 ± 2.5	19.2 ± 0.8	53.4 ± 2.6	0.64
1 mol% AIBN	20.1 ± 3.8	31.8 ± 1.2	51.9 ± 4.0	0.39
5 mol% AIBN	20.6 ± 1.0	32.6 ± 1.0	53.2 ± 1.4	0.39
10 mol% AIBN	34.0 ± 4.8	27.8 ± 2.2	61.8 ± 5.3	0.55

carbon fibers [8]. By grafting the water soluble methacrylic acid onto the carbon fiber surface, a strong dependence between amount of initiator used and the hydrophobic surface character was found. The longer the polymer chains as observed through SEM, the higher the surface hydrophobicity.

The wetting behavior versus water is influenced by the structure of the grafted polymer, while the ζ-potential is only determined by the number of dissociable groups. The more polymer is immobilized onto the carbon fiber surface, the larger the amount of cationic charge carriers causing a high i.e.p. value. This is the case for the sample, prepared with 1 mol% initiator.

The wettability versus the nonpolar liquid diiodomethane (Fig. 3b) for DMAEMA-grafted carbon fibers is improved compared to the OP fiber, i.e. smaller contact angles were obtained. With increasing initiator content θ_a enlarges again, due to a higher percentage of uncovered free fiber surface.

Since the surface tension γ (Table 2) is calculated from the θ_a values determined versus water and diiodomethane it also resembles the same trend that was described for the contact angles. The fiber surface tension γ remains almost constant, because the polar component γ^p diminishes for 1 and 5 mol% initiator while the dispersive component γ^d enlarges. For 10 mol% γ^p increases again, while γ^d decreases for the above-mentioned reasons.

Conclusions

The grafting behavior observed for methacrylic acid and liquid crystalline monomers has also been observed using DMAEMA as grafting reagent. However, grafting DMAEMA using different initiator concentrations onto oxidized carbon fibers gives the possibility to prepare amphoteric surfaces, with different values of either basic or acidic characteristics. Additionally, the physico-chemical properties of the modified carbon fiber surface can be influenced by the amount of the grafted polymer chains. The wetting behavior is determined by the structure and number of the polymer. The smaller the initiator concentration, the more polymer is grafted to the fiber surface, the higher is the contact angle versus water and the smaller the contact angle determined against diiodomethane. However, the ζ-potential depends only on the number of amino groups in the polymer chain as well as the acidic surface functional groups on the carbon fiber. The smaller the initiator content the higher is the isoelectric point, i.e. the higher is the basic surface character of the grafted carbon fibers.

Electrokinetic (ζ-potential) measurements provide information about the surface state of carbon fiber materials, but experimental measurements and interpretation of the obtained data are influenced by a complex combination of several parameters. The pH value of the electrolyte solution during the ζ-potential measurement influences the sign as well as the value of the measurable ζ-potential. Considering the above-mentioned causes, a direct comparison of our measured ζ-potentials with ζ-potentials described in the literature is still problematic.

Acknowledgements Special thanks to Dipl.-Ing. J Nissen (Zentraleinrichtung Elektronenmikroskopie der TU Berlin, ZELMI) for recording the SEMs.

References

1. Michaeli W, Wegener M (1989) Einführung in die Technologie der Faserverbundwerkstoffe. Carl Hanser Verlag, München
2. Fitzer E, Jäger H (1985) Z Werkstofftech 16:215; 16:232
3. Yuan LJ, Shyu SS, Lai JY (1991) J Appl Polym Sci 42:2525
4. LeBonheur V, Stupp SI (1994) Chem Mater 6:1880
5. Koschinski I, Reichert KH (1988) Makromol Chem, Rapid Commun 9:291
6. Oya A, Kimura M, Sugo T, Katakai A, Abe Y, Iizuka T, Makiyama N, Linares A, Salinas C (1984) Carbon 32:107
7. Tsubokawa N, Ueno H (1995) J Appl Polym Sci 58:1221

8. Bismarck A, Pfaffernoschke M, Springer J (1998) accepted at J Appl Polym Sci
9. Kumru ME (1997) Diploma thesis, TU-Berlin
10. Häßler R, Jacobasch H-J (1994) Adhäsion 38:36
11. Bismarck A, Richter D, Wuertz C, Springer J (14–17 April 1998) Contribution to Int Symp on Electrokinetic Phenomena '98, Salzburg, Austria
12. Zhang J, Uchida E, Suzuki K, Uyama Y, Ikada Y (1996) J Coll Interf Sci 178:371
13. Bismarck A, Richter D, Wuertz C, Springer J (1998) Colloids Surf A (submitted)
14. Bismarck A, Kumru ME, Springer J (1998) J Coll Interf Sci (submitted)
15. Schurz J, Jorde Ch, Ribitsch V, Jacobasch H-J, Körber H, Hanke R (1986) GIT Fachz Lab 2:98
16. Jacobasch H-J, Schurz J (1987) Österr Chemie Z 7-8:164
17. Grundke K, Boerner M, Jacobasch H-J (1991) Colloids Surf 58:47
18. Tahhan R (1997) Doctoral thesis, TU-Berlin, D83
19. Bismarck A, Kumru ME, Springer J (1998) Composites Part A (submitted)
20. Stern O (1924) Z Elektrochem 30:508
21. Fairbrother F, Mastin H (1924) J Chem Soc 125:2319
22. Mäder E, Grundke K, Jacobasch H-J, Wachinger G (1994) Composites 25:739
23. Fowkes FM (1962) J Phys Chem 66:382
24. Fowkes FM (1987) J Adhes Sci Technol 1:7
25. Wu S (1982) Polymer Interface and Adhesion. Marcel Dekker, New York
26. van Wagenen RA, Coleman DL, King RN, Triolo P, Brostrom L, Smith LM, Gregonis DE, Andrade JD (1981) J Coll Interf Sci 84:155