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Surface characterization of glass fibers made from silicate waste: Zeta-potential and contact angle measurements

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The surface properties of three glass fibers made from silicate waste and of various commercial glass fibers have been characterized by zeta (ζ)-potential and contact angle measurements. ζ-Potential measurements indicate that the formation of the electrochemical double layer is clearly affected by the type and amount of network former and network modifier oxides in the glass structure. A high negative ζ-potential is measured for fibers containing large amounts of network former oxides. The amount and type of network modifier cations leaching from the glass and adsorbing in the electrochemical double layer causes the negative ζ-potential to decrease. pH-depending ζ-potentials show that the Brønsted acidic surface character predominates. The ratio of network former to network modifier oxides affect the course of the $\zeta = f(\text{pH})$ function and, therefore, the acidity of the fiber surfaces. Contact angles of glass fibers against water and diiodomethane have been measured in order to estimate the fiber surface tensions. All investigated glass fibers are rather hydrophobic. The surface tension of the fibers is similar to polymer. The results of the present study are relevant for the use of such glass fibers as reinforcement for polymer matrix composites. © *2004 Kluwer Academic Publishers*

1. Introduction

The increasing amount of industrial waste being produced, the simultaneous decrease of waste disposal space, as well as the problems associated with the contamination from hazardous and toxic elements are urgent issues demanding the attention of scientists and technologists. An important group of industrial waste is that of silicate residues, which include coal power station ash, fly-ash from waste incinerators, slags from the steel production, sewage sludge ash as well as several types of glass cullet [1–4].

One conventional method for the recycling and reuse of silicate residues is vitrification, i.e., the melting of the residues at high temperatures (1300–1500°C) to produce homogeneous glasses [5]. A disadvantage of vitrification is that it is an energy-intensive process involving relatively high costs. Therefore, its use can only be fully justified and commercially viable if high-quality products with optimized properties can be fabricated from the vitrified waste. These products may then find applications on their own or in combination with other conventional materials in diverse areas such as architecture, structural building and construction components, insulation or other specialized applications.

The fabrication of glass fibers from silicate waste using electronic glass cullet from television (TV) set components, e.g., cone and screen, and computer monitors residues has been considered in the past [6–8]. The

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fabricated fibers, which contain significant amounts of heavy metals (e.g., lead, barium), have been proposed as suitable reinforcement elements for polymer composites with possible applications in radiation protection panels [6–8]. It has been suggested that the procedure of transforming electronic glass cullet into fibrous products is a very attractive way of recycling such valuable and problematic glasses that can not usually (or in limited amount only) be remelted for electronic glass component manufacture due to compositional problems [9]. In preliminary work, also sewage sludge ash (KSA) from a municipal sludge incinerator plant has been used to fabricate glass fibers [10, 11].

For the further use of "recycled" glass fibers fabricated from silicate waste a detailed characterization of their surface properties, and their comparison with those of conventional glass fibers, is required. This is particularly important if the fibers are to be used as reinforcement in polymer matrix composites. In fiber reinforced polymers the fibers have to carry the load applied to the material. The matrix holds the fibers in place, protects them and also determines the materials performance at elevated temperatures and the composite's chemical resistance [12]. However, the level of 'practical' adhesion between the fibers and the surrounding polymer matrix determines the stress transfer from the matrix into the fibers and, therefore, the overall mechanical performance of the composite. Characterizing the single components of a composite material provides useful information to predict the effective properties and macroscopic performance of the composite since the overall materials behavior, including the mechanical properties, depends on the properties of the single components as well as on the interfacial compatibility between them. Additionally, knowing the surface properties of the components (fibers and matrix) enables on the one hand to tailor surface treatments for the reinforcing fibers and on the other hand to select a suitable matrix material or to modify the polymer matrix properties.

In the present investigation the surface properties of three experimental glass fibers obtained from silicate waste, including TV screen, TV cone and sewage sludge ash, are studied by means of ζ-potential and contact angle measurements. ζ-Potential measurements not only offer a possibility to estimate the state, type and amount of dissociable surface functional groups on the investigated solid surfaces but also to characterize the dispersion forces proceeding from solid surfaces [13]. It has been shown that the difference in the adsorption-free energies of the electrolyte ions, like K^+ and Cl^-, adsorbing at the solid surface corresponds to the dispersive forces occurring at the solid/electrolyte interface [14]. Furthermore, it has been stated [15] that ζ-potential measurements are an easy and reliable method to estimate adhesive properties between hot melts and solid substrates. With increasing differences between the ζ-potential plateau values ($\Delta\zeta = \zeta^{\text{adhesive}}_{\text{plateau}} - \zeta^{\text{adherend}}_{\text{plateau}}$) for both components as obtained from the pH dependence of the ζ-potential ($\zeta = f\,(\text{pH})$), the measured adhesive strength should also increase. Recent publications confirmed that ζ-potential measurements allow predicting the trend of changing adhesion between two adhesive partners [16, 17].

From the thermodynamic point of view of adhesion [18], it is necessary to know the surface tensions of the adhesive and adherend (i.e., polymer and reinforcement in case of composite materials) in order to estimate the reversible thermodynamic work of adhesion W_a, which has been found to be proportional to the measured (practical) adhesion [19]. Measuring contact angles is a useful tool to characterize solid surfaces, and these methods are easy to handle and reliable to obtain information about the outermost surface layers [20, 21].

2. Experimental

2.1. Materials

A total of three test glass fibers obtained from silicate waste including TV screen (test glass S), TV cone (test glass K) and sewage sludge ash (test glass KSA) were considered.

KSA fibers could not be drawn directly after the draining of the sludge. Sewage sludge ash was used instead for the tests. In order to improve the melting and forming process other silicate residues containing more SiO_2 and Al_2O_3 were added and mixing and charging problems had to be solved. In order to achieve an almost constant composition of the resulting fibers it was necessary to add the residuals in predetermined quantities. All corrections were made using a pot melt [10, 11].

All three test glass fibers that were made from silicate waste were drawn using a commercial bushing. This means, continuous fibers are produced by the rapid attenuation of molten glass drops exuding from nozzles located on the bottom-side of a resistance-heated channel [10, 11].

Fibers produced from sewage sludge ash (KSA) have relatively large diameters in the range of $15 \leq d_f \leq 18\ \mu m$ due to the drawing conditions and an average tensile strength of 930 MPa and a Young's-modulus of 67 GPa.

The average diameter of both recycled TV-glass fibers (test glass S and K) was $11.8\ \mu m$. The measured tensile strength values σ_f of the S test glass fibers depend on the fiber diameter and vary between $1000 \leq \sigma_f \leq 1154$ MPa for fibers having a diameter of $13\ \mu m$ and are in the range of $1200 \leq \sigma_f \leq 1870$ MPa for smaller diameter ($d_f = 10\ \mu m$) fibers. The average tensile strength for the S test glass fibers is $\sigma_f = 1480$ MPa and their Young's modulus is 52 GPa.

Considering that test glass fibers are made from waste materials, one has to bear in mind the changing compositions of the waste on a day-to-day basis. The actual compositions of the S and K test glass fibers depend on the recipe used by the manufacturer of the TV-tubes. The composition of the S and K test glass fibers can be found in the references [22, 23], respectively. In the case of the KSA test glass fibers the composition depends on the location of the municipal sewage plant and, therefore, individual glass fiber batches will differ widely in their composition depending on the actual sewage sludge ash composition used. The composition

TABLE I Chemical composition of the test glass fibers manufactured from silicate waste (see text) and some commercial glass fibers, expressed as wt%. The chemical composition was determined using energy dispersive X-ray fluorescence analysis

	Amount (%)					
Component[a]	Test glass S	Test glass K	Test glass KSA	C-glass	E-glass	S2-glass
SiO_2	58.36/59.38/58.64	56.16/56.21/56.80	32.5	60–65	53–60	65
Na_2O	9.02/4.73/4.53	4.16/4.94/4.97	0.6	7.5–12	<2	
K_2O	7.93/13.23/12.08	8.04/8.87/8.55	10.2	0–2		
MgO	0.66/0.13/<0.12	1.76/1.61/1.72	1.2	3–4	20–25	10
CaO	1.95/2.37/1.79	4.13/3.30/3.78	18.0	13–16		
SrO	7.17/7.39/8.65	0.13/0.16/0.18				
BaO	8.42/7.55/6.85	1.27/1.21/1.16				
B_2O_3				2–7	0–9	
Al_2O_3	1.97/2.03/1.97	2.65/1.32/2.42	14.1	2–6	11–15.5	25
PbO	1.44/0.87/0.86	20.69/21.97/17.81				
P_2O_5	0.43/0.29/0.36	0.02/0.02/0.02	6.4			
Sb_2O_3	0.51/0.01/1.28	0.22/<0.01/0.23				
SO_3	0.01/0.22/0.23	0.01/<0.01/<0.01				
CeO_2	0.30/0.30/0.31	0.02/0.03/0.02				
TiO_2	0.65/0.19/0.46	0.03/0.05/0.04	0.5		0–3	
ZrO_2	0.67/0.71/0.78					
MnO		0.22/0.30/0.25	0.2			
Fe_2O_3	0.24/0.40/0.32	0.22/0.30/0.25	12.7	0.3	0.05	

[a] Expressed in oxides.

of the glass fibers used in the present study was determined using energy-dispersive X-ray fluorescence analysis and it is shown in Table I.

Standard glass fibers were also investigated, including E-glass, C-glass, S2-glass and Silfa (silica) fibers. E-glass is a boro-aluminosilicate glass having a very low alkaline and a high CaO content. S2-glass fibers are high strength fibers without alkaline oxides, containing MgO and a higher percentage of both SiO_2 and Al_2O_3 as compared to E-glass. The quoted values of the tensile strength of the commercially available S2 [24] -and E [10]-glass fibers are 3700 to 4300 MPa and 3450 MPa, respectively.

2.2. Methods

2.2.1. Preparation of the glass fibers for the measurements

Prior the measurements the test glass fibers were rinsed with distilled water in order to remove the water-soluble processing finish. All commercial glass fibers were desized in a tube oven at 550°C in airflow and afterwards extracted in a Soxhlet extractor in hot methanol for 24 h.

All fibers were dried in a vacuum oven at 100°C at 1 mbar overnight in order to remove residual solvent or water.

2.2.2. Fiber surface morphology

Scanning electron microscopy (SEM) using a Hitachi S-2700 scanning electron microscope was applied to detect eventual differences in the surface morphology of all fibers. The excitation energy was 10 keV with a beam current of 0.5 nA.

2.2.3. Zeta-potential measurements

The electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method [25] was used to measure the electrokinetic or ζ-potential of glass fibers. The streaming potential is measured as function of the pressure decay (in the range of 30–150 mbar) in a fiber plug (capillary system) while the electrolyte solution (1 mM KCl) is pumped through a cylindrical cell. The streaming potential that arises due to the shear off of the diffuse part of the electrochemical double layer, is measured as a function of time, electrolyte concentration ([KCl]) and the pH at 20°C using two perforated Ag/AgCl electrodes. In order to minimize the asymmetric potential, the used electrodes are short circuited after each measurement in 0.1 mM KCl-solution.

In order to measure the time dependence of the ζ-potential the analyzer was filled with a 1 mM KCl supporting electrolyte solution. Before starting the measurements the measuring cell is connected to the analyzer, quickly rinsed with the electrolyte solution and trapped air removed.

ζ-Potentials as function of the electrolyte concentration are measured starting from 'distilled' water (Millipore, pH 5.6), after the measuring cell is rinsed several times until the conductivity in the measuring system fell below a value of 300 μS/m. First the 'water value' of the ζ-potential is determined and subsequently the KCl-concentration increased using a digital burette (Brand, Wertheim, Germany). Between each measuring step the system including the measuring cell is rinsed in both measuring directions. The KCl concentration is increased stepwise up to 0.01 M KCl.

From the $\zeta = f([\mathrm{KCl}])$ courses the maximal (or minimal) ζ-potential values $\zeta_{\max}$ and corresponding concentration values $c_{\max}$ can be extracted. Using these values the non-electrostatic components of the molar free adsorption energies or adsorption potentials for the dissolved potassium and chloride ions can be determined [25]:

$$\Phi_{-} = RT \cdot \ln c_{\max} - F \cdot \zeta_{\max} \tag{3}$$

$$\Phi_{+} = RT \cdot \ln c_{\max} + F \cdot \zeta_{\max} \tag{4}$$

where F and R are the Faraday and Gas constants, respectively, and T is temperature.

The pH-dependence of the ζ-potential is determined in a 1 mM KCl supporting electrolyte solution in order to keep the ionic strengths constant. The pH-value is varied in a range of $3 < \text{pH} < 10$ by adding drops of 0.1 M HCl or KOH. The electrolyte solution is continuously stirred and kept at constant temperature of 20°C. Further experimental details about the technique can be found in the literature [26, 27].

2.2.4. Contact angle measurements

Contact angles θ of test liquids on glass fibers where measured using the gravimetric method, the modified Wilhelmy-technique, against water and diiodomethane. Because of the very small mass change during the measurement while using a monofilament, five fibers were put parallel to each other onto an aluminum carrier. The carrier was placed attached to an ultramicroelectrobalance (MP8, Sartorius, Göttingen, Germany, accuracy = 0.1 μg) so that the ends of the fibers were located just over the test liquid surface. Weight recordings were obtained during fiber immersion/emersion cycle at a constant stage velocity of 3 μm/s. After immersing the fibers into the liquid, which took approx. 5 min, the direction was changed till the fibers were pulled out of the liquid. The immersion or emersion was realized through a reversible elevator driven by a direct current motor. The direct current was taken from a constant current source (Philips Power Supply Unit PE1507).

The contact angles θ were calculated using Wilhelmy' equation:

$$\cos\theta = \frac{\Delta m \cdot g}{\pi d \cdot \gamma_l} \tag{1}$$

where Δm is the recorded mass change during immersion or emersion of the fibers into the liquid resulting in advancing θ_a and receding θ_r contact angles, respectively. The effective fiber diameter d was determined from scanning electron micrographs. In Equation 1, g is the acceleration due to gravity and γ_l the surface tension of the test liquid used.

No buoyancy slope was observed during immersing the fibers into or withdrawing them from the test liquid due to the very small fiber diameters. To check the reproducibility all measurements were carried out at least six times using fibers from the same sample batch. All contact angle values presented are averaged values and the errors given are their standard deviations. All contact angle measurements were performed in an air-conditioned room at a constant temperature of 20°C.

Surface tensions of the investigated fibers were estimated using the geometric mean method based on the polar/dispersive approach [18]:

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

where θ is the contact angle (we used the advancing contact angle), γ the surface tension of the liquid l and solid s and γ^d and γ^p are the dispersive and polar component of the surface tension. In order to be able to estimate the surface tension of a solid, contact angles between the solid and a test liquid with known surface tension components but different polar/dispersive properties have to be measured.

3. Results and discussion

3.1. Surface morphology

As can be seen from the scanning electron micrographs (Fig. 1a–d) all test glass fibers (S, K and KSA) investigated have smooth surfaces. All fibers have, however, some particles attached to them. Fig. 1c clearly shows that the diameter of test glass fibers K is varying to a certain extent.

3.2. ζ-Potential measurements

Time-dependent ζ-potential measurements (at constant pH and supporting electrolyte concentration) can be used to characterize ageing processes of the material under investigation. The materials- and its surface properties affect ageing processes and their time scales but they also depend on the surrounding electrolyte; its pH, ionic strength and temperature, which in turn, influences the electrochemical double layer. It is known that inorganic oxides and related materials are often slow to establish equilibrium with electrolyte solutions [28]. Generally, inorganic oxides must dissolve until the solution composition is corresponding to their solubility condition [28]. The ageing in case of glass is due to leaching or dissolution of water-soluble components; pure silica shows substantial (at pH > 7) and pH-dependent solubility in water [29]. For instance alkali and alkaline earth rich glass fibers will lose up to 6.2% in weight after boiling for 3 h in water [30]. The changes induced in case of quartz glass in contact to an electrolyte solution can also be due to the formation of a swollen gel-like silica layer [31] combined with diffusion controlled dissolution and ion exchange reactions affecting the time to establish the equilibrium.

Table II contains a summary of the ζ-potential measurements of various glass fibers in 1 mM KCl solution. As can be seen in the Fig. 2a and b (exemplarily for the test glass fibers S and S2-glass fibers) the initially high negative ζ-potential of all glass fibers decreases slowly as function of time to a smaller but relatively constant plateau value. Simultaneously both the pH and the conductivity of the background electrolyte solution are considerably increasing up to 1.0 pH unit and up to 3%, respectively, reflecting the dissolution of basic components from the glass fibers (2 g glass fibers in a total volume of 1 l supporting electrolyte). The time the systems need to establish the equilibrium is quite long and clearly reflects the high chemical resistance of the investigated glasses. It can therefore be concluded that the dissolution of network modifier cations (accompanied by surface rearrangements) and their impact on the formation of the electrochemical double layer affect the measured ζ-potentials. The dissolved network modifying alkali and alkaline earth cations seem to compensate, according to their Dietzel

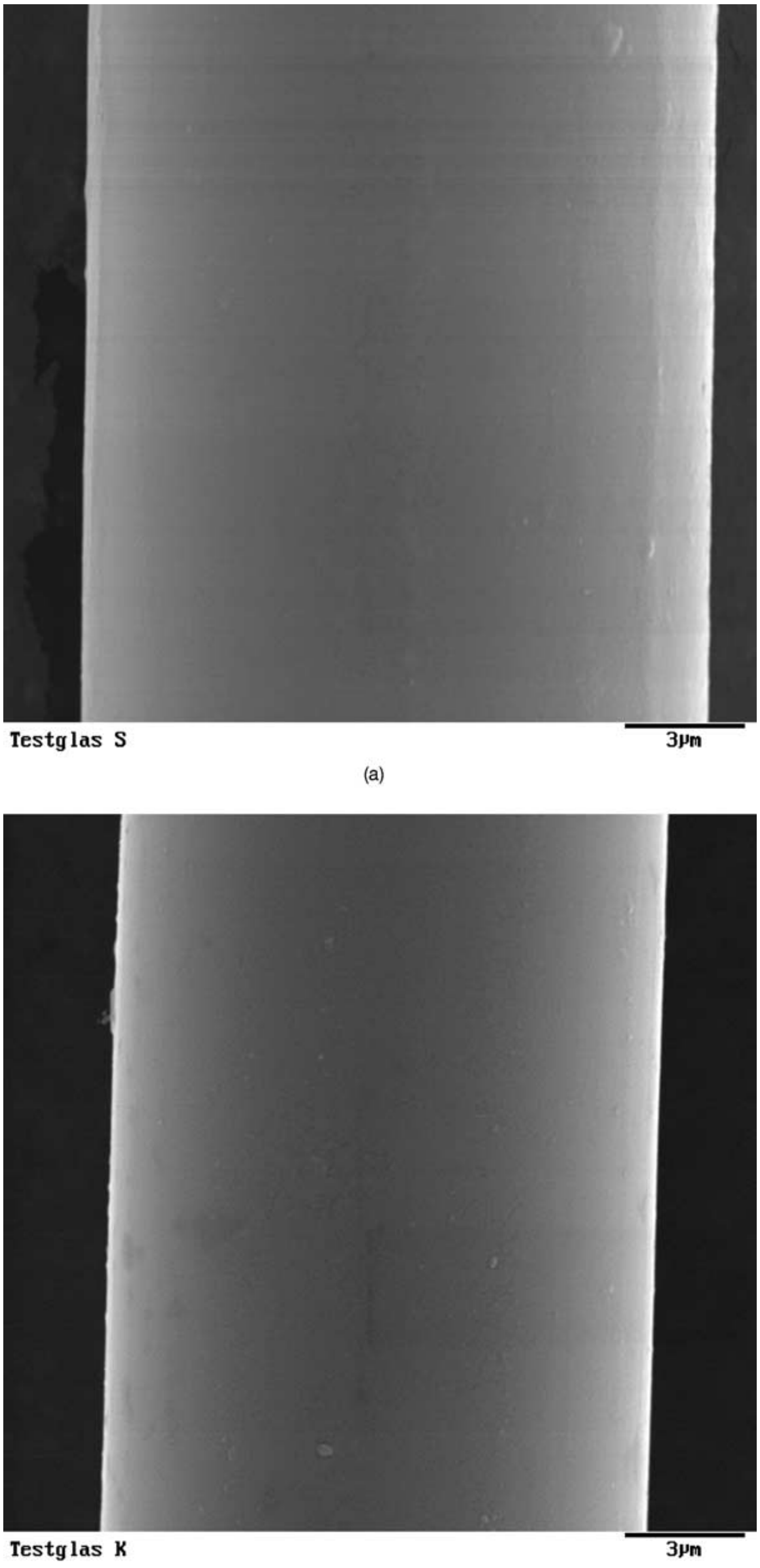
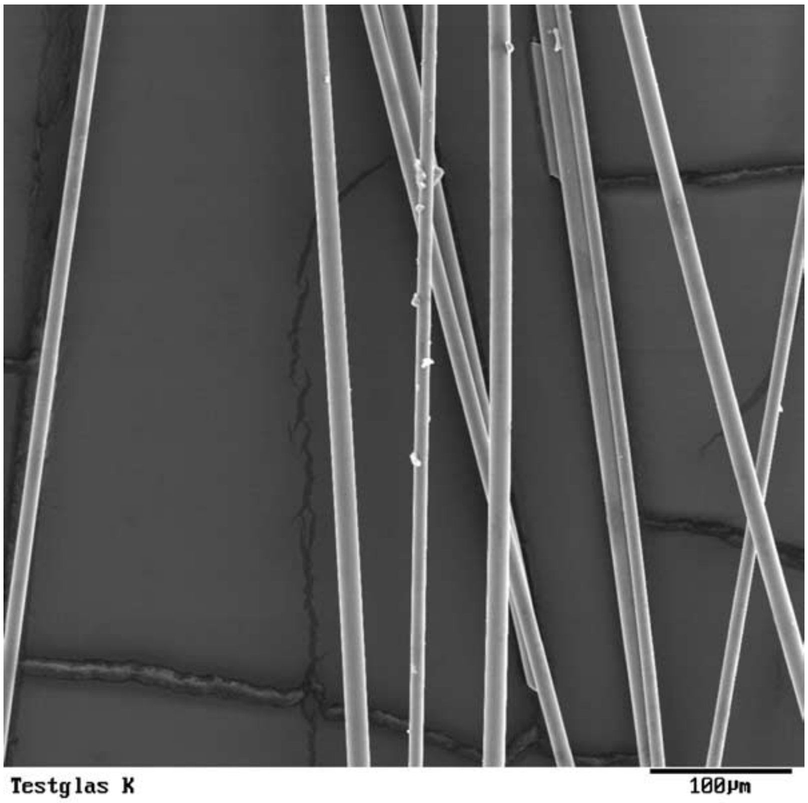
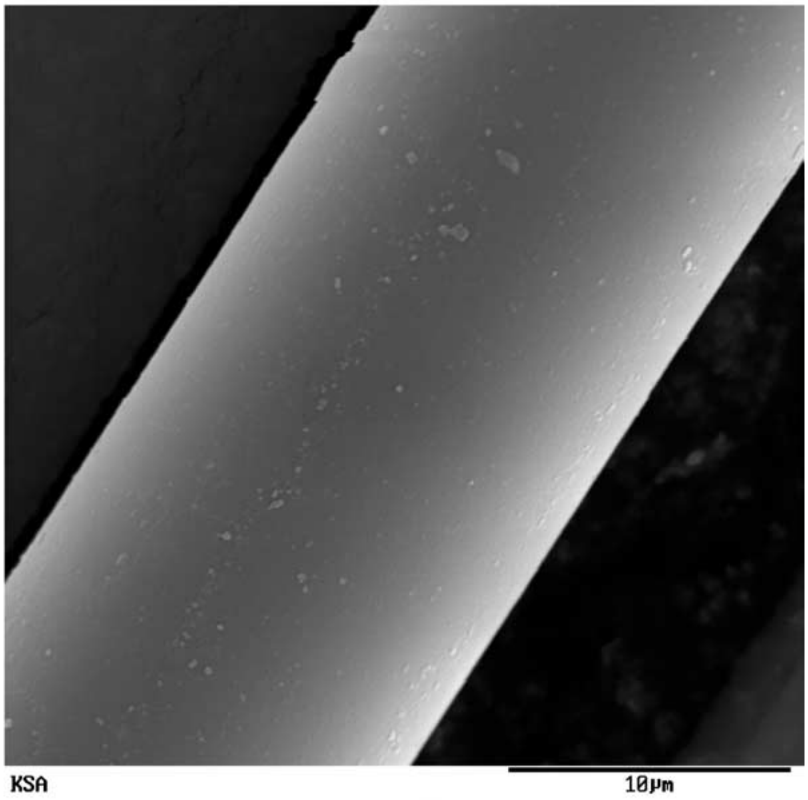


Figure 1 SEM micrographs of the investigated test glass fibers: (a) Test glass fiber S, (b) Test glass fiber K, (c) Test glass fibers K, and (d) Test glass fiber KSA. (*Continued*)

[32] field strength and their Pauling electronegativity (following almost the same trend), the initially high negative ζ-potential towards the plateau value. The finally established plateau value seems to depend on the amount and type of cations leaching from the glass, and follows the trend of increasing electronegativity and field strength [33]: $K^+ \rightarrow Na^+ \rightarrow Ba^{2+} \rightarrow Sr^{2+} \rightarrow Pb^{2+} \rightarrow Ca^{2+} \rightarrow Mg^{2+}$ (neglecting interactions between the ions). All the quantities derived from the measured ζ-potentials discussed further down below might be also influenced by the dissolution of specifically adsorbing ions that will influence the



(c)



(d)

Figure 1 (*Continued*).

ζ-potentials, iep as well as the adsorption potentials [29]. However, it was not possible to quantify these effects using the present experimental approach.

Time-dependent ζ-potential measurements were also performed in order to establish a starting point for all further ζ-potential measurements since any process that could disturb the pH- and concentration depending ζ-potential measurements should be excluded.

3.3. ζ-Potential—pH dependence

pH-depending ζ-potential measurements of solids in contact with aqueous electrolyte solutions reflect the

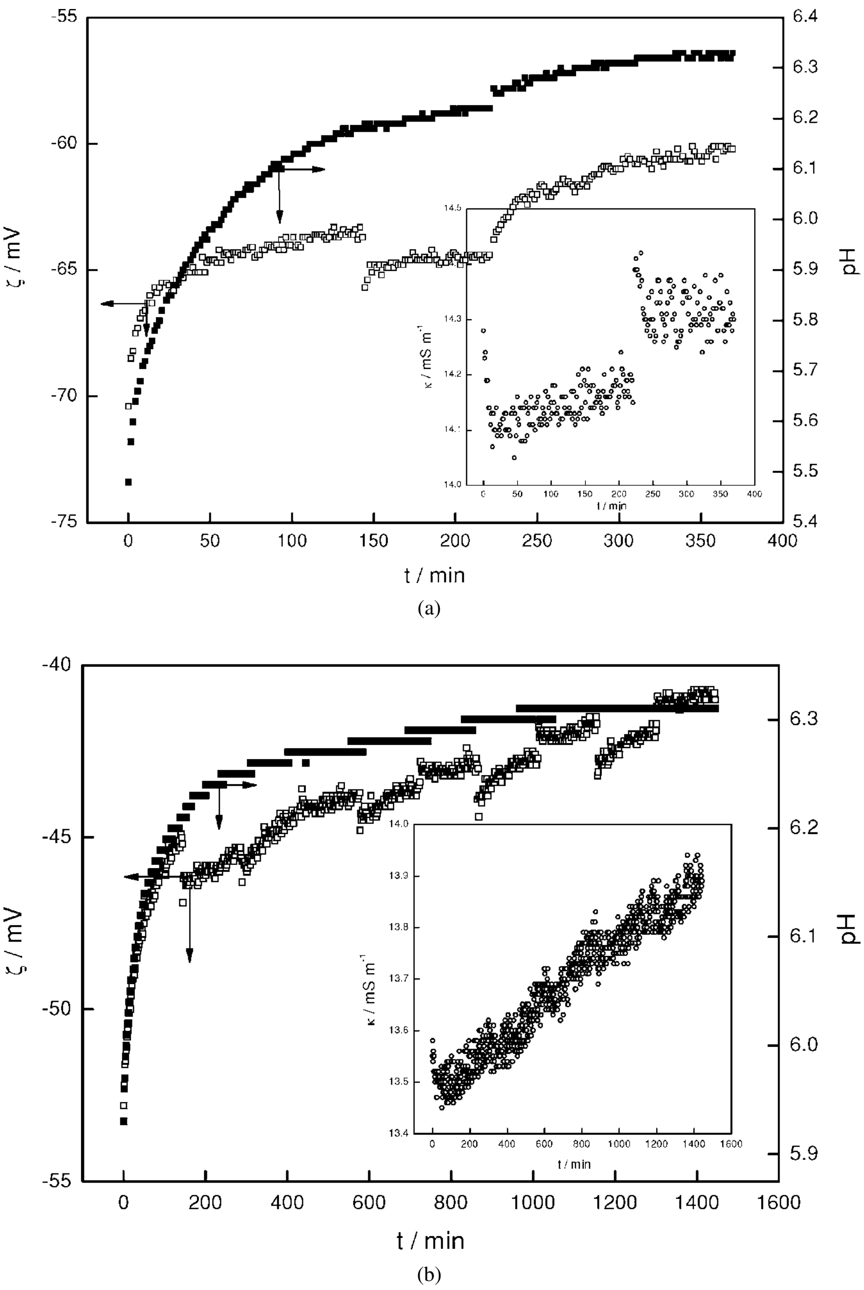
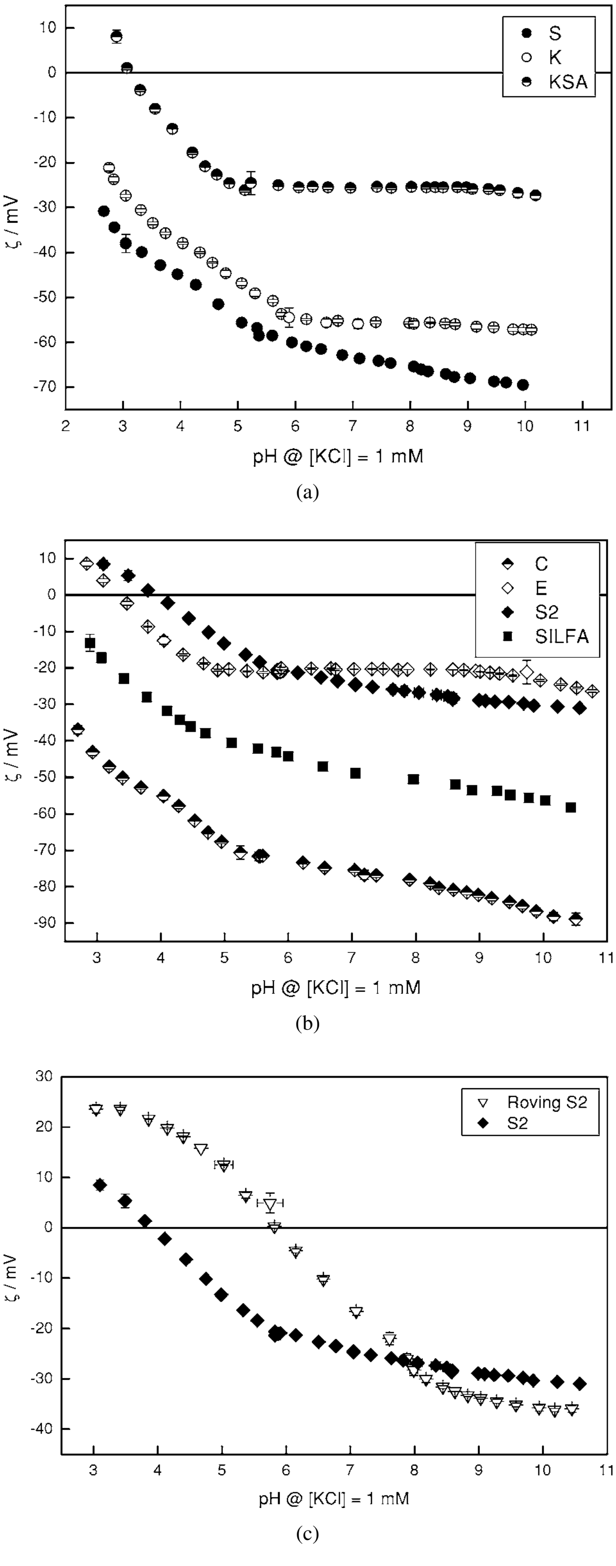


Figure 2 (a) ζ-Potential, pH and conductivity of test glass fibers as function of time in 1 mM KCl supporting electrolyte solution: (a) test glass S and (b) S2 glass fibers.

surface chemistry/nature of the investigated solid (fibers) and, therefore, can be used to characterize the Brønsted acid/base character of the solids. In case of the investigated glass fibers the protons and hydroxyl ions are potential determining ions. As can be seen in Fig. 3a and c, the $\zeta = f(\text{pH})$ courses for all investigated glass fibers, with exception of the sized S2-glass fibers, have a continuously decreasing tendency. In all

TABLE II Results of the ζ-potential measurements of glass fibers in 1 mM KCl solution: isoelectric point (iep), ζ-potential plateau value, the maximum KCl concentration ($c_{\max}$) at the maximum ζ potential value ($\zeta_{\max}$) and the adsorption potentials for chloride (Φ_-) and potassium ions (Φ_+) and their difference ($\Phi_- - \Phi_+$)

Fibers	iep	ζ_{plateau} (mV)	$c_{\max}$ (mmol l^{-1})	$\zeta_{\max}$ (mV)	Φ_- (kJ mol^{-1})	Φ_+ (kJ mol^{-1})	$\Phi_- - \Phi_+$ (kJ mol^{-1})
S	–	−65.7 ± 1.7	0.6	−56.9	−12.6	−23.6	11.0
K	–	−55.9 ± 0.3	1.0	−59.6	−11.1	−22.6	11.5
KSA	3.1	−25.5 ± 0.1	0.3	−45.1	−15.4	−24.1	8.7
C	–	−77.7 ± 1.8	1.0	−67.5	−10.3	−23.4	13.1
E	3.3	−20.7 ± 0.4	0.3	−12.4	−18.6	−21.0	2.4
S2	3.9	−25.8 ± 0.8	–	–	–	–	–
S2 (sized)	5.8	–	0.6	+2.9	−18.4	−17.8	−0.6
Silfa	–	−52.9 ± 1.7	1.0	−25.9	−20.0	−24.9	4.9



(a)

(b)

(c)

Figure 3 ζ-Potential as function of pH for (a) S, K and KSA test glass, (b) fibers C, E, S2 standard glass fibers and (c) sized and desized S2 standard glass fibers.

cases there is a more or less well-established plateau in the basic pH range ($6 < \text{pH} < 10$). Lowering the pH further, increasing the proton concentration, causes the repression of the dissociation and/or protonation of the surface hydroxyl groups and, therefore, leads to a reduction of the negative ζ-potential, which results in a zero ζ-potential, the iep value. Again in all cases the iep is or would be in the acidic low pH range. Such a behavior points to the existence of acidic surface functions on all glass fibers. In the basic pH range, all acidic surface groups are fully dissociated creating a net negative surface charge. In case of glass fibers containing a high amount of network former oxides (e.g., SiO_2, P_2O_5, Al_2O_3 and B_2O_3—the later two in coordination number 4), see Table I, the iep is not experimentally accessible, but the iep (if there is any [29]) should be around pH 2 [34–36]. Such low iep values are not measurable since the required low pH values would lead to very high ionic strengths which cause the compression of the electrochemical double layer and, therefore, the ζ-potential to approach zero. Low iep values point to the fact that the existing surface groups have a low affinity to protons [34].

Comparing the pH depending ζ-potentials of the test glass fibers fabricated from TV-screen (S) or TV-cone (K) glass and from sewage sludge ash (KSA) the following trend can be seen (Fig. 3a); the test glass fibers containing the highest amount of sodium oxide and a relatively low amount of calcium oxide display the highest negative ζ-potential. The test glass fibers K contain a relative large amount of PbO (20%), which does not seem to affect the measured ζ-potentials. Such a behavior is not surprising considering the similarity of the ion radii of Pb^{2+}, Sr^{2+} and (with some restrictions) Ba^{2+}. In case of the KSA test glass fibers the smallest negative ζ-potential and an iep = 3.1 was measured, which still clearly indicates the predominating acidic surface character of the fibers and the low affinity to protons. From the above-mentioned it might be concluded that the PbO component must be completely encapsulated within the glass network.

For comparison some commercial standard glass fibers having different chemical compositions have also been investigated. Fig. 3b shows the ζ-potential-pH courses $\zeta = f(\text{pH})$ for desized C, E, S2 glass and Silfa silica fibers. The graph confirms the above mentioned fact, that the $\zeta = f(\text{pH})$ course is mainly affected by the amounts of the network former (SiO_2 and Al_2O_3) and the network modifiers (i.e., Na_2O) present in the fibers. The C-glass fibers have the highest negative ζ-potential plateau values of around −80 mV and the iep is situated in the low pH range, that can not be assessed by ζ-potential measurements. In contrast to S2- and E-glass fibers, C-glass contains a high amount of Na_2O. The E and S2 glass fibers have less negative ζ_{plateau} values and iep's of 3.3 and 3.9, respectively. The measured $\zeta = f(\text{pH})$ course for the E-glass fibers agrees quite well with published data [37]. The E-glass fibers contain less SiO_2 as the S2-glass fibers and also significantly lower amounts of Al_2O_3, which should cause a more negative ζ-potential as compared to S2-glass. However, the effect is compensated by the high CaO content in E-glass that causes the negative ζ-potential to decrease (compare to KSA glass). Again, all the fibers contain acidic surface functionalities and a low affinity to protons. A pure silica glass (Silfa) fiber (SiO_2 content >99%) was also investigated and the results are shown in Fig. 3b. Again, the $\zeta = f(\text{pH})$ course and the not-measurable iep reflect the dominate acidic surface character of the glass. The measured ζ-potential courses are (surprisingly) relatively similar to those measured for C, S and K glass fibers even though these fibers contain larger amounts of basic components. The results for the Silfa fibers agree quite well with published data for native pure silica [26].

In one case, for S2 glass fibers, we have studied the effect of a commercial fiber sizing on the measured ζ-potentials. As can be seen form Fig. 3c the measured $\zeta = f(\text{pH})$ course has changed: the course has now a sigmoid shape and the iep is shifted by almost 2 pH units to higher pH values as compared to the desized S2 fibers. Such a behavior is probably due to an aminosilane sizing. At low pH values the amino groups will be protonated. Increasing the pH causes deprotonation and OH^- will adsorb causing a net negative surface charge in the high pH range.

From the measured $\zeta = f(\text{pH})$ courses it becomes quite obvious that the surface properties of glass fibers are mainly influenced by the fiber glass composition; i.e. amount and type of network former and network modifier oxides. The network former oxides P^{5+}, B^{3+}, Si^{4+} and Al^{3+} (but only if present in coordination number 4), characterized by their high Pauling's electronegativity, and their content in the glass fibers as compared to the network modifiers Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+ and K^+, cause the high negative ζ-potential of the fibers. This explanation holds for the Silfa fibers (Fig. 3b), however, for other fibers, like the C-glass (Fig. 3b), it appears contradictory. The ζ-potential will be modified by the leaching behavior of the alkali and alkaline earth oxides from the glasses into the electrolyte, which affects the formation of the electrochemical double layer according to their field strength and electronegativity. As described above, the ζ-potential is affected by the network modifiers leaching from the glass, however, K^+ and Na^+ will only marginally affect the formation of the electrochemical double layer, which also explains why the K-, S- and C-glass fibers (containing a high amount of alkali ions) exhibit high negative ζ-potential plateau values (ζ_{plateau}) similar to the Silfa fibers. The C-glass fibers have the highest negative ζ-potential, which could be due to the high electronegative character of B^{3+}. The glasses containing large amounts of the small 2-valent network modifier cations Mg^{2+} and Ca^{2+}, which strongly absorb in the electrochemical double layer and, therefore, cause the negative ζ-potential to decrease significantly. Such a behavior can be observed for the KSA-, E and S2-glass fibers, for which iep > 3. The network modifying Pb^{2+}, Ba^{2+} and Sr^{2+} ions have comparable electronegativities and so we observe that the ζ-potential courses for the S- and K-fibers are quite similar. The KSA fibers contain a noticeable amount of P_2O_5, so a high negative ζ-potential would be expected, but the fibers also have a significant Fe_2O_3 content. The Fe^{2+}/Fe^{3+} ratio is unknown, but the Fe-ions will certainly have a strong impact on the formation of the electrochemical double layer and since Fe^{2+} has similar properties as Mg^{2+} the ζ-potential is found to be less negative compared to the silica fibers.

As reported in the literature [15, 38], pH dependent ζ-potential measurements should also give indications about the trend in which adhesion between the adhesive and the substrate will change, i.e., the larger the difference of the measured ζ-potentials for the matrix (e.g., a polymer) and the reinforcement ($\Delta\zeta_{\text{plateau}}$ at given pH and ionic strength) the 'better' should be the adhesion behavior between them.

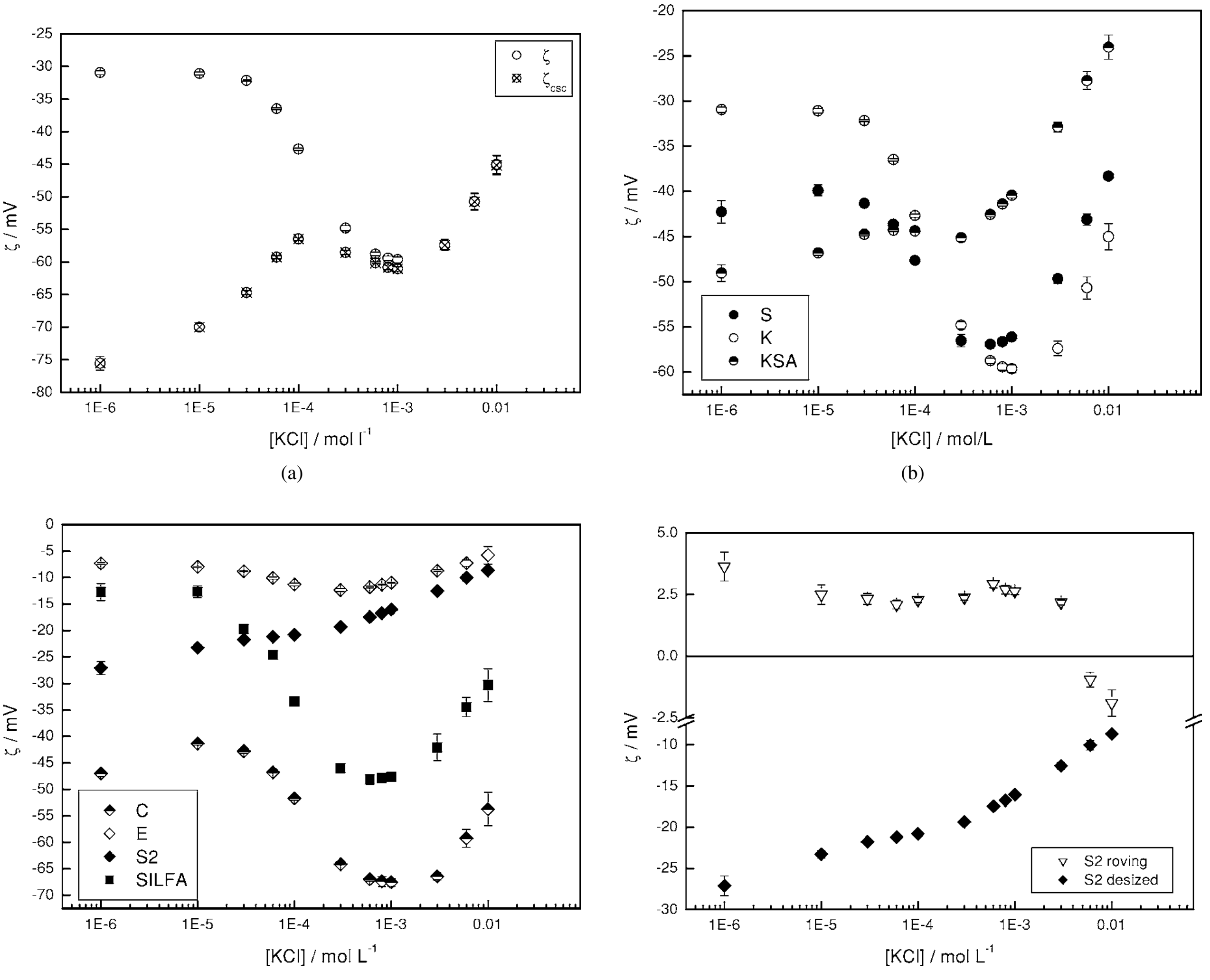
3.4. ζ-Potential measurement as function of [KCl]

It is known that the formation of the electrochemical double layer depends strongly on the surface character (hydrophilicity/hydrophobicity) and the adsorption of dissolved ions, which competes with water adsorption [39]. Thus, less adsorption of anions takes place at hydrophilic surfaces; consequently they exhibit a smaller ζ-potential compared to hydrophobic surfaces. Measuring the concentration dependence of the ζ-potential in KCl solutions should also reflect the dispersion forces occurring at the solid surfaces [13].

The concentration dependence of the ζ-potential of glass fibers was measured with increasing KCl concentration. First the ζ-potential value was measured in distilled water (Milipore). As can be seen in Fig. 4a–e the ζ-potentials as function of the electrolyte concentration follow more or less a parabolic trend with exception of the S2 glass fibers (Fig. 4d). The ζ-potential stays initially constant and then decreases (more negative) with increasing KCl concentration. Increasing the ionic strength further beyond $\zeta_{\max}$ causes the ζ-potential to decrease due to the compression of the electrochemical double layer. As expected the $\zeta = f([\text{KCl}])$ functions for the various glass fibers are different (Fig. 4b–e), reflecting the interactions of the fiber surfaces with the dissolved ions. The sized S2 fibers have a positive ζ-potential over a wide concentration range, going through a small maximum (Fig. 4d). However, beyond the maximum value the ζ-potentials decrease and a ζ-potential reversal occurs at about 4 mM KCl at constant pH $\approx 5.5 \pm 0.1$. In case of the unsized S2 glass fibers, the ζ-potential is just increasing, starting from the "water"-value, with increasing salt concentration. No pronounced minimum in the $\zeta = f([\text{KCl}])$ course can be detected. Such a behavior is characteristic for an indifferent "adsorption" behavior of the dissolved K^+ and Cl^- ions.

As exemplarily shown in Fig. 4a, correcting for the surface conductivity of the glass fiber "plug" during the ζ-potential measurement indicates the significant influence of the surface conductivity at low ionic strength. The differences however vanish for higher ionic strengths. Typically, the contribution of the surface conductivity to the measured ζ-potentials becomes insignificantly small at salt concentrations of around 1 mM [40]. Therefore, the uncorrected ζ-potential values were considered here for further discussion.

As can be seen from the tabulated values of the adsorption potentials for chloride and potassium ions in Table II, in almost all cases (except for the sized S2-fibers) cations adsorb more strongly at the glass/electrolyte interphase, even though the glass surfaces have a low affinity to protons. It has been reported



(a) (b) (c) (d)

Figure 4 (a) ζ-Potential and ζ-potential corrected with respect to the surface conductivity as function of KCl concentration of K. (b) ζ-Potential as function of KCl electrolyte concentration of S, K and KSA test glass fibers. (c) ζ-Potential as function of KCl electrolyte concentration of C, E, S2 standard glass and SILFA silica glass fibers. (d) ζ-Potential as function of KCl electrolyte concentration of sized and unsized S2 glass fibers.

that the difference in the adsorption free energies ($\Phi_- - \Phi_+$) is characteristic for the dispersion interactions occurring at the solid/electrolyte interface [13]. Therefore, the dispersion interactions should be greater in case of unsized glass fibers whereas a sizing causes the dispersive interactions occurring at the modified solid interface to decrease.

3.5. Contact angle measurements and fiber surface tensions

Contact angle measurements are a powerful tool to characterize solids with respect to their wettability and their surface tension. Furthermore, contact angles tend to be very sensitive to probe only the very "outermost" surface layers (about 0.5 nm).

Silicate glasses are considered to display high-energy surfaces and, therefore, one would expect that water (and all the other test liquids) would spread on their surfaces. However, high-energy surfaces will absorb readily everything, including every low-energy compound available from a normal environment (including water vapor and organic contaminants) causing the surface energy to decrease rapidly, thus turning them into 'low-energy' surfaces [18]. It is therefore not unexpected that the fibers have only intermediate contact angles, tending to be more hydrophobic, i.e., the water contact angle is closer to 90°, as can be seen from the results shown in Table III. Only the test glass fibers S (and K) and the standard C glass fibers are more hydrophilic, i.e., their water contact angle is much lower.

The advancing contact angles θ_a should be characteristic for the low-energy parts of the investigated surface whereas the receding angles θ_r reflect the high-energy portion of the surface [18]. The contact angle hysteresis

TABLE III Water and DIM contact angles measured on glass fibers and their contact angle hysteresis $\Delta\theta$

Fibers	$\theta_a^{H_2O}$ (°)	$\theta_r^{H_2O}$ (°)	$\Delta\theta^{H_2O}$ (°)	θ_a^{DIM} (°)	θ_r^{DIM} (°)	$\Delta\theta^{DIM}$ (°)
S	45 ± 5	42 ± 4	3	64 ± 4	52 ± 6	12
K	52 ± 4	45 ± 5	7	64 ± 2	41 ± 5	23
KSA	71 ± 3	49 ± 2	22	53 ± 1	38 ± 6	15
C	44 ± 2	29 ± 4	15	51 ± 3	42 ± 1	9
E	84 ± 4	44 ± 4	40	69 ± 5	44 ± 2	25
S2	62 ± 4	36 ± 8	26	39 ± 3	36 ± 2	3
Silfa	65 ± 2	43 ± 2	22	45 ± 4	33 ± 4	12

$\Delta\theta$, defined as the difference between θ_a and θ_r, therefore, can be assumed to be a measure of the surface heterogeneity. The glass fiber surfaces are by no means homogeneous suggesting that the surface composition of the fibers might vary locally, since the difference between advancing and receding contact angles is quite large.

As mentioned above, ion adsorption at the solid/electrolyte interface is competing with the adsorption of water. Therefore, it should be expected that the ζ-potential in KCl solutions should be increasing (decreasing negative ζ-potential) with increasing hydrophilicity. In contrast to polymer surfaces for which a linear dependence of the water contact angle (or cosine of the contact angle) and the maximum ζ-potential (ζ_{max}) measured in KCl electrolyte solutions was reported [39, 41, 42], such a dependence could not be found for the investigated glass fibers. This behavior is not surprising, since the prolonged contact to water "modifies" the glass surfaces much more (see above) than is the case for organic polymers. Contact angle measurements, therefore, reflect the fiber surface properties and the interactions at the fiber surfaces in the "dry" state due to the relative short time of the test (the longest the studied glass fibers were in contact with the test liquids was approx. 10 min), whereas ζ-potential measurements mirror the properties in the "wet" state.

3.6. Determination of solid surface tensions

The values of the solid surface tensions to be estimated from contact angle measurements are quite sensitive to the measured contact angles against the test liquids and, therefore, to their accuracy. It was quite difficult to determine the contact angles between the glass fibers having varying fiber diameters (see also Fig. 1b) and the test liquids accurately. The mean contact angle data listed in Table III scatter over a large range therefore having large standard deviations. The fiber surface tensions are calculated from the contact angle values and, therefore, their components are also largely affected by the accuracy of the contact angles (as can be seen also in Table III). The glass fiber surface tensions were calculated (estimated) using the '*old*' (but simpler) dispersive/polar approach [18], even though it has been proven that the polar interactions of permanent dipoles are negligibly small [43, 44]. Table IV summarizes the 'estimated' surface tensions of the glass fibers. With respect to the surface tension values, which should be considered as an estimate, it can be stated that irrespectively what approach was used in order to calculate the surface tensions (acid/base or dispersive/polar), the actual values will be in the same order of magnitude [45, 46].

TABLE IV Glass fiber surface tension γ and its dispersive γ^d and polar γ^p component and the surface polarity, the polar fraction of the fiber surface tension X^p calculated from the measured water and DIM advancing contact angles using the geometric mean method

Fibers	γ^d (mN m^{-1})	γ^p (mN m^{-1})	γ (mN m^{-1})	$X^p = \gamma^p/\gamma$
S	15.3 ± 2.2	37.8 ± 5.0	53.1 ± 7.2	0.71
K	16.2 ± 1.2	31.4 ± 3.8	47.6 ± 5.0	0.66
KSA	26.0 ± 0.9	11.7 ± 2.0	37.7 ± 2.9	0.31
C	22.1 ± 1.7	32.4 ± 2.1	54.5 ± 3.7	0.59
E	18.9 ± 3.1	7.8 ± 2.6	26.7 ± 5.8	0.29
S2	32.0 ± 1.8	14.4 ± 2.9	46.4 ± 4.7	0.31
Silfa	30.5 ± 1.2	13.3 ± 1.4	43.8 ± 2.7	0.30

For 'high-energy' surfaces the determined solid surface tension values are quite low, comparable to that of polymers ($\gamma < 45$ mN/m). However, it is still remarkable that the estimated solid surface tension of (almost all) glass fibers stored in a normal laboratory atmosphere is relatively high. Even though the water contact angles are quite high (but also the contact angles against DIM) it is still the polar component γ^p that is the predominating component. Comparing the fiber surface polarity X^P with the Na_2O and the CaO/MgO content in the glass fibers we find a good correlation; an increasing Na_2O content causes X^P to increase and an increasing amount of CaO and MgO will diminish the polarity. It seems that an increasing amount of Fe_2O_3 acts in the same direction.

4. Conclusions

The surface properties of three experimental glass fibers obtained from silicate waste and various commercial glass fibers have been characterized by ζ-potential and contact angle measurements.

Time-dependent ζ-potential measurements showed that for the investigated glass fibers it takes between 5 to 16 h until the equilibrium at the fiber/electrolyte interface is established. During this time significant portions of basic metal oxides from the glass fibers dissolve in the electrolyte affecting the pH and the conductivity of the supporting electrolyte solution. The high negative starting values of ζ-potential of all glass fibers decrease slowly as function of time to a smaller but relatively constant plateau value. The long times the systems need to equilibrate reflects the good chemical resistance of the investigated test glasses. It can be concluded that the dissolution of network modifier cations and their influence on the formation of the electrochemical double layer clearly affect the measured ζ-potentials. The leaching/dissolution and subsequent adsorption of network modifying alkali and alkaline earth cations seems to decrease (according to their field strength and their electronegativity) the initially high negative ζ-potential towards the plateau value. The finally established plateau value depends on the amount and type of cations leached from the glass.

As shown by the measured pH-depending ζ-potentials, the overall course of the $\zeta = f$ (pH) functions as well as the position of the iep, the Brønsted acidic surface character predominates for all glass fibers except for the sized S2 fibers. The $\zeta = f$ (pH) functions are mainly dominated by the ratio of the network former to network modifier oxides, especially by the amount of Na_2O and CaO, MgO, Fe_2O_3. They clearly affect the course of the $\zeta = f$ (pH) function and, therefore, the acidity of the fiber surfaces. Applied glass fiber coatings or sizings clearly determine the surface properties of the fibers, as shown for the sized S2-fibers. The sizing, probably containing amino functionalities, causes an amphoteric character as indicated by the sigmoidal shape of $\zeta = f\,(\text{pH})$ and the shift of the iep towards higher pH.

The ζ-potentials measured as function of the supporting electrolyte (KCl) concentration ($\zeta = f\,([\text{KCl}])$) follow for almost all investigated glass fibers the predicted parabolic curve for 1:1 electrolytes. The dispersion interactions for the different unsized glass fibers should be greater than that for sized fibers; the sizing causes the dispersive interactions occurring at the modified solid interface to decrease.

Contact angles of glass fibers against water and diiodomethane have been measured in order to estimate the fiber surface tensions. All investigated glass fibers are rather hydrophobic, that is, their contact angles are closer to 90° since glass, a high-energy surface, tends to adsorb moisture and other contaminants in normal atmospheres. Therefore, the surface tension of the fibers is similar to that of polymer surfaces.

ζ-Potential and contact angle measurements complement each other and allow to estimate the forces and interactions which might also influence the adhesive behavior between reinforcing fibers and a surrounding polymer matrix. It can be anticipated that the glass fibers prepared from silicate waste will be able to be used without further sizings or surface treatments as reinforcement in most polymers (at least thermoplastics), since good wetting properties between the fibers and polymer melts are expected. Furthermore, the difference in ζ-potential plateau values ($\Delta\zeta$) between the fibers and thermoplastic polymers (see for example [46]) will be high, which could indicate a good level of adhesion between the components [15, 17].

References

1. R. GUTMAN, *Glastech. Ber. Glass Sci. Technol.* **69** (1996) 285.
2. A. R. BOCCACCINI and R. D. RAWLINGS, *Mater. World* **10** (2002) 16.
3. D. HÜLSENBERG, Glastechnologien für Recyclingaufgaben, in "Abhandlungen der Sächsischen Akademie der Wissenschaften" (Technikwissenschaftliche Klasse, Band 1, Heft 1, Verlag S. Hirzel, Leipzig, 1998) p. 1.
4. A. KARAMANOV, G. TAGLIERI and M. PELINO, *J. Amer. Ceram. Soc.* **82** (1999) 3012.
5. C. C. CHAPMAN, *Ceram. Trans.* **23** (1991) 223.
6. B. HAMANN, D. HÜLSENBERG and T. LEUTBECHER, *Glastech. Ber. Glass Sci. Technol.* **68** (1995) 183.
7. R. CLASEN, I. KRAVTCHENKO and G. ONDRACEK, Fibre Preparation from TV Glass for Fibre Reinforced Recycled Products, in "Environmental Aspects in Materials Research," edited by H. Warlimont (DGM, Oberursel, 1995) p. 301.
8. I. KRAVTCHENKO, V. GOROBINSKAYA and J. BOSSERT, *Mater. Eng.* **10** (1999) 193.
9. J. M. HERMANS, J. G. J. PEELEN and R. BEI, *Ceram. Bull.* **80** (2001) 51.
10. D. HÜLSENBERG, B. HAMANN, E. KUHN, G. HUNGENBACH, J. BRÜNNERT and S. HEUSING, *Glas-Ingenieur* **6** (1996) 53.
11. B. HAMANN, E. KUHN and D. HÜLSENBERG, Einsatz von Klärschlammasche zur Herstellung glasähnlicher Werkstoffe, in Proceedings of the ATV Klärschlammtage (Würzburg, 1999) Vol. 4.
12. F. L. MATTHEWS and R. D. RAWLINGS, "Composite Materials: Engineering and Science" (Chapman and Hall, London, 1994) p. 168.
13. E. UCHIDA and Y. IKADA, Zeta-Potential of Polymer Surfaces, in "Encyclopedia of Surface and Colloid Science" edited by A. Hubbard (Marcel Dekker, New York, 2002) p. 5657.
14. H.-J. JACOBASCH, K. GRUNDKE, P. UHLMANN, F. SIMON and E. MÄDER, *Comp. Interf.* **4** (1996) 293.
15. R. HÄßLER and H.-J. JACOBASCH, *Kleben & Dichten, Adhäsion* **38** (1994) 36.
16. A. BISMARCK, D. RICHTER, C. WUERTZ and J. SPRINGER, *Coll. Surf.* A **159** (1999) 341.
17. C. CAMPAGNE, E. DEVAUX, A. PERWUELZ and C. CAZÉ, *Polymer* **43** (2002) 6669.
18. S. WU, in "Polymer Interface and Adhesion" (Marcel Dekker, New York, 1982).
19. M. NARDIN and J. SCHULTZ, *Comp. Interf.* **1** (1993) 177.
20. Y. GU, "Contact angle Measurement Techniques for Determination of Wettability," in "Encyclopedia of Surface and Colloid Science," edited by A. Hubbard (Marcel Dekker, New York, 2002) p. 1213.
21. A. BISMARCK and J. SPRINGER, Influence of Plasma Treatments on the Wettability of Material Surfaces, in "Encyclopedia of Surface and Colloid Science" edited by A. Hubbard (Marcel Dekker, New York, 2002) p. 2471.
22. Prüfbericht Labor Fresenius vom 28.05.1996.
23. Prüfbericht Labor Fresenius vom 27.10.1994.
24. Advanced Glassfiber Yarns, Product Information "High Temperature 933 S-2 Glass Roving" 2000.
25. H.-J. JACOBASCH, F. SIMON, C. WERNER and C. BELLMANN, *Technisches Messen* **63** (1996) 439.
26. R. TAHHAN, "Elektrokinetische und oberflächenenergetische Untersuchungen an Silizium und Kohlenstoff" (Wissenschaft & Technik Verlag, Berlin, 1997).
27. A. BISMARCK, M. E. KUMRU and J. SPRINGER, *J. Coll. Interf. Sci.* **210** (1999) 60.
28. R. J. HUNTER, "Zeta Potential in Colloid Science, Principles and Applications" (Academic Press, London, 1988).
29. M. KOSMULSKI, Electric Charge Density of Silica, Alumina, and Related Surfaces, in "Encyclopedia of Surface and Colloid Science," edited by A. Hubbard (Marcel Dekker, New York, 2002).
30. "Basalt: The material for the 21st Century" Link in: http://basalt-alf.narod.ru/ accessed on: 20.10.2002.
31. M. P. SIDOROVA and D. A. FRIEDRICHSBERG, *Acta Polymerica* **31** (1980) 522.
32. A. DIETZEL, *Z. Elektrochem.* **48** (1942) 9.
33. W. HINZ, "Silikate, Einführung in Theorie und Praxis" (VEB Verlag für Bauwesen, Berlin, 1963).
34. J. JEDNACAK and V. PRAVDIC, *J. Coll. Interf. Sci.* **1** (1974) 17.
35. J. LYKLEMA, *Mol. Phys.* **100** (2002) 3177.
36. "Zeta Potential and Stability" link in: http://www.bic.com/ztheory1.htm accessed on: 20.10.2002.
37. A. K. BLEDZKI, J. LIESER, G. WACKER and H. FRENZEL, *Comp. Interf.* **5** (1997) 41.
38. H.-T. CHIU and J.-H. WANG, *Polym. Comp.* **19** (1998) 347.
39. N. KUEHN, H.-J. JACOBASCH and K. LUNKENHEIMER, *Acta Polym.* **37** (1986) 394.
40. R. A VAN WAGENEN and J. D. ANDRADE, *J. Coll. Interf. Sci.* **76** (1980) 305.
41. N. KUEHN, Elektrokinetische Erscheinungen im Offsetdruck, in "Symposium Proceedings Elektrokinetische Erscheinungen '85 (Institut für Technologie der Polymere, Dresden, 1985).
42. H.-J. JACOBASCH, K. GRUNDKE, S. SCHNEIDER and F. SIMON, *J. Adhesion* **48** (1995) 57.
43. C. DELLA VOLPE and S. SIBONI, Acid-base Behavior of (Polymer) Surfaces: Theory, in "Encyclopedia of Surface and Colloid Science," edited by A. Hubbard (Marcel Dekker, New York, 2002) p. 17.
44. M. MORRA, "Acid-base Behavior of Polymer Surfaces," in Encyclopedia of Surface and Colloid Science, edited by A. Hubbard (Marcel Dekker, New York, 2002) p. 74.
45. N. T. CORREIA, J. J. MOURA RAMOS, B. J. V. SARAMAGO and J. C. G. CALADO, *J. Coll. Interf. Sci.* **189** (1997) 361.
46. A. BISMARCK, M. E. KUMRU and J. SPRINGER, *J. Coll. Interf. Sci.* **217** (1999) 377.

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