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Physical characterization of E-glass fibres treated with alkylphenylpoly(oxyethylene)alcohol – fibres conditioned in solutions of different pH

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The adsorption of alkylphenylpoly(oxyethylene)alcohol on E-glass fibres was characterized by X-ray photoelectron spectroscopy, by the Wilhelmy plate method and by streaming-potential measurements. In this study, the glass fibres were conditioned in solutions of different pH. The acid resistance of the E-glass fibres was studied by treating the material with H_2SO_4. During the acid treatment the surface composition, namely the Si/Al-ratio, was changed, presumably because the aluminium ions were leached out of the glass structure. The alkaline resistance was studied by treating the material with NaOH. The Si/Al-ratio was unaffected by these moderate alkaline solutions. The effect of the surface conditioning in solutions of different pH seemed to be greatest for the acidic solutions giving rise to an increased adsorption of the surfactant on the glass-fibre surface.

1. Introduction

The extensive use of glass fibres as a reinforcement in polymer composites has caused considerable interest in the chemical reactions between the different components of the composite materials. Since surface-active molecules adsorbed on the surface may be used to introduce favourable adhesion properties to the composite materials, knowledge of the surface interactions and the modified properties are vital for understanding a large number of reactions and processes.

In this study, we investigated the influence of surface conditioning at different pH levels and its subsequent influence on the adsorption of a non-ionic surfactant: alkylphenylpoly(oxyethylene)alcohol. The methods used to characterize the change in surface properties were measurements of the wetting force against water and surface-charge determinations. The wetting behaviour was studied with the Wilhelmy plate method giving information for example, on the contact angles and the spreading wetting. The surface charge of the fibre was investigated by recording the streaming potential of the glass fibres. X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) was used to provide semiquantitative information on the surface composition of the glass fibres and on the amount of surfactant adsorbed. The Si/Al ratio of the glass fibre provided adequate information on changes in the surface composition.

2. Experimental procedure

2.1. Materials

The glass fibres (supplied by Ahlstrom Glassfibre Ltd) were drawn from E-glass. The average composition of the E-glass used was 55% SiO_2, 14.5% ($Al_2O_3 + Fe_2O_3$), 21.5% CaO, 0.5% MgO, 1.0% ($Na_2O + K_2O$) and other materials, for example B_2O_3. The manufacturing process has been described in detail in the literature [1]. The E-glass fibres were drawn to a thickness of about 11 μm and they were cut to a length of 8 mm. Although the original length of the fibres was 8 mm, some breakage during the surface treatment produced slightly shorter lengths on average. The density of the E-glass fibres was 2.50 kg dm^{-3} or 2.50 g cm^{-3}.

To studying the effect of alkali on the untreated glass fibres, the fibres were immersed in a dilute sodium-hydroxide solution of pH 9 at 25 °C for different periods of time. The effects of acid on the glass-fibre surface were studied by immersing the glass fibres in a dilute solution of the sulphuric acid of pH 2 at 25 °C for different periods of time. The treatment times for glass fibres in solutions of different pH were 5, 30 and 60 min. The dispersion was stirred during the treatment period. After the filtration of the supernatant the fibres were dried in a vacuum oven at about 50 °C for at least 36 h.

The surfactant was applied to the dried glass fibres which were treated for 5 min in solutions of pH = 2

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and pH = 9. As a reference, the natural glass fibres were immersed in deionized water (pH = 5.5) for 5 min and then dried in a vacuum oven at 50 °C.

The dried pH-treated glass fibres were dispersed in deionized water for 10 min. After being washed with deionized water, the glass fibres were treated for 5 min in a solution of 0.1–1.0% (w/w) alkylphenylpoly(oxyethylene)alcohol at 25 ± 2 °C. The dispersion was stirred during the treatment period. After the filtration of the supernatant, the fibres were dried in a vacuum oven at about 50 °C for at least 36 h. The surfactant alkylphenylpoly(oxyethylene)alcohol is a non-ionic surfactant supplied by Berol Nobel AB in Sweden. According to the supplier, the purity (determined as a percentage of the active groups) was 100%. However, a distribution of ethoxy groups ranging from 2–6, with a maximum at four, was estimated by chromatography mass (GC/MS) spectrometry. The surfactant had a semihydrophobic character exemplified by its limited solubility of 5% in water. The surfactant was used as received.

The wetting liquid used in this study was deionized water with a pH of 5.5–5.8 and a surface tension of 72.0 $\mathrm{mN\,m^{-1}}$ at 25 °C. The conductivity of the deionized water was $5.56 \times 10^{-8}\ \mathrm{S\,cm^{-1}}$ at 25 °C.

2.2. The ESCA (XPS) system

A Perkin–Elmer ESCA system (model PHI 5400) was used in all measurements. The photoelectrons, generated by X-ray photons with an energy of 1253.6 eV (MgK_α) from a spot ~ 1 mm diameter were analysed in a spherical-capacitor energy analyser [2].

The measurements were performed in CAE (constant analyser energy) mode. The base pressure in the spectrometer was 9.3×10^{-8} Pa and the pressure during the measurement was typically 1.3×10^{-7} Pa.

The glass fibres were placed under a molybdenum mask on the sample holder in the same direction, as perfectly as possible, and oriented parallel to the line of the incident beam and the energy analyser to minimize the effects of shadows.

The influence of the acid and alkali conditioning on the E-glass fibres was investigated by means of the atomic concentrations of silicon and aluminum. These signals originate from about the same depth (with binding energies of 103 and 74 eV, respectively) and are therefore comparable to each other.

2.3. The streaming-potential system

The measuring chamber of the streaming-potential apparatus, built in our University Department, consists of a tube with an electrode at each end. The glass fibres were packed between the two electrodes to form a plug with a porosity of 0.92 [3, 4].

In order to avoid air bubbles in the fibre plug during the measurements the measuring chamber was evacuated before each measurement. The electrolyte was an aqueous solution of 1.2×10^{-5} M KCl with a conductivity of $2.7 \times 10^{-6}\ \mathrm{S\,cm^{-1}}$. The electrolyte was forced to stream through the plug at a constant flow rate of $75\ \mathrm{cm^3\,min^{-1}}$ by using compressed air. The differences in potential and pressure were registered during the measurement.

From the potential difference, E_s, the zeta potential, ζ, was calculated using the Helmholtz–Smoluchowski equation [5]

$$\zeta = \frac{E_s \eta k_0}{\varepsilon_r \varepsilon_0 \Delta p} \tag{1}$$

2.4. The Wilhelmy balance method

The Wilhelmy balance method has been described more in detail in the literature [4, 6, 7]. This method was used for measuring the wetting forces between fibres and liquids with known surface tensions. These parameters can be used in turn to calculate the contact angle and the spreading coefficient.

The apparatus used in this study was a digital electrobalance with an accuracy of 10 μg (0.1 μN), constructed in our University Department. A single glass fibre was attached to the electrobalance and immersed in the liquid to a depth of 3–5 mm by moving the reservoir up and down with an elevator. The velocity of the elevator was 4.4 $\mathrm{mm\,min^{-1}}$. The wetting force developed was continuously monitored on a plotter.

According to Miller *et al.* [8], the wetting force reaches a maximum value, $F_w(m)$, when the contact angle passes through the zero value during the final pull-out of the fibre from the solution. From measurement of the initial and the final wetting forces, the advancing and receding contact angles can be directly obtained from the following relationships

$$\cos \Theta_a = F_w(a)/F_w(m) \tag{2a}$$

and

$$\cos \Theta_r = F_w(r)/F_w(m) \tag{2b}$$

3. Results and discussion

3.1. ESCA

In a previous study [4] we reported the surface composition of the untreated glass fibres (pH = 5.5) investigated by ESCA at different take-off angles and compared it to the composition determined from the nominal weights of materials used in the manufacture of glass. Since information obtained at large take-off angles does not reflect the outermost surface properties of the glass and the information obtained at very low angles is especially influenced by the undulations of fibres and the surface contamination. The take-off angle used in this study was chosen to be 30°.

According to the previous results [4] the top layer mainly consists of the surface contamination (C1s) of the untreated E-glass fibres. The results also showed that no clear layer structure exists in the glass fibres, as expected, since the glass structure is supposed to be amorphous. The Al/Si atomic concentration ratio seems, consequently, to be relatively constant as a function of the analysing depth.

The effect of alkali and acid conditioning on the atomic concentrations of silicon and aluminium is shown in Fig. 1.

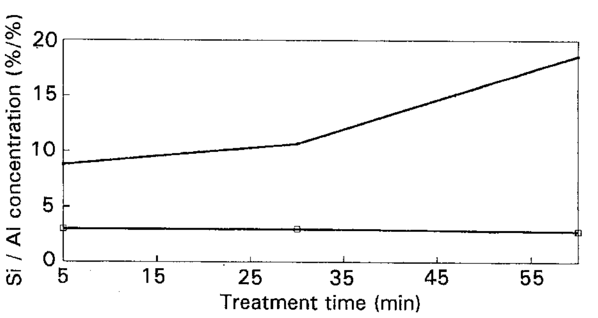

Figure 1 The effect of alkali and acid treatments on Al/Si atomic concentration ratios of the E-glass-fibre surface: (-■-) pH = 2, and (-□-) pH = 9.

TABLE I The relative ESCA atomic concentrations of E-glass fibres treated with alkylphenylpoly(oxyethylene)alcohol in solutions of different concentrations (with a take-off angle of 30°)

pH	Concentration (%)	C_1[a]	C_2[a]	O	Si	Al	Ca
2	0.1	50.2	13.3	27.0	8.9	0.6	–
	0.2	49.1	14.3	27.6	8.2	0.9	–
	1.0	40.0	18.7	31.4	9.0	0.9	–
5.5	0.1	46.2	9.0	32.1	9.5	3.2	–
	0.2	55.3	13.5	24.3	5.3	1.7	–
	1.0	54.9	14.4	24.2	4.9	1.5	–
9	0.1	46.6	16.8	26.6	7.9	1.4	0.8
	0.2	51.1	15.9	24.2	6.1	1.9	0.8
	1.0	47.3	18.0	26.5	6.0	1.6	0.6

[a] C_1 (–C=C– + –CH_2–) surfactant + contamination and C_2(–C–O–) from the surfactant.

Conditioning in a solution of pH = 2 seems clearly to have affected the Si/Al ratio on the surface, whereas conditioning in a solution of pH = 9 seems to have left the surface composition unaltered. According to Ramachandran *et al.* [9] non-siliceous (aluminium in this case) ions are leached out from the glass structure due to ion exchange during the acid treatment.

The acidic conditioning of the glass fibres has also a profound influence on the mechanical properties. The treatment in a solution of pH = 2 produced glass fibres that were highly brittle and fragile.

The influence of a subsequent treatment of E-glass fibres with a non-ionic surfactant, alkylphenylpoly(oxyethylene)alcohol is shown in Table 1.

In the analysis of the results, the ratio between C_2 and C_1 was chosen to describe the amount of surfactant adsorbed on the fibre surface. The higher the ratio is the higher is the level of surfactant on the surface. The ratio C_2/C_1 is given in Fig. 2 as a function of surfactant added to the E-glass fibres.

On the basis of the results shown in Table I and Fig. 2, it may be concluded that the surface coverage at high concentrations of surfactant is at its highest for E-glass fibres conditioned in a solution of pH = 2 and subsequently treated with the surfactant. The amount of surfactant adsorbed at low concentrations is lowest for natural glass fibres and increases again in glass fibres conditioned in acidic and alkaline solutions where the reactivity of glass (SiO_2) is known to increase [10].

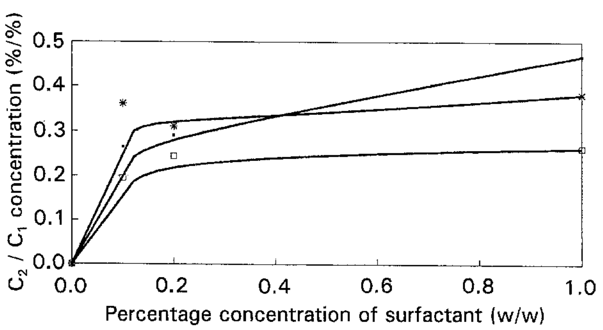

Figure 2 The ratio C_2/C_1 in E-glass fibres treated with surfactant solutions of increasing concentration: (-■-) pH = 2, (-□-) pH = 5.5, and (-∗-) pH = 9.

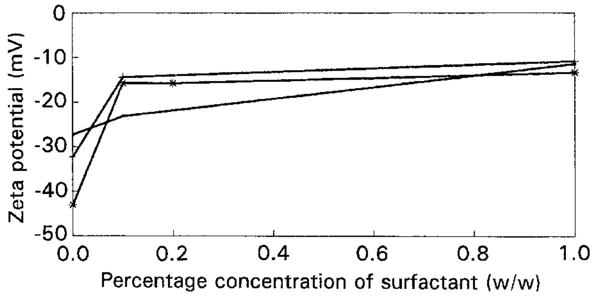

Figure 3 The zeta potentials of E-glass fibres conditioned in solutions of different pH and subsequently treated with alkylphenylpoly(oxyethylene)alcohol solutions of increasing concentration: (-■-) pH = 2, (-+-) pH = 5.5, and (-∗-) pH = 9.

3.2. Zeta potential

The influence of the surface modification on the surface charge is shown in Fig. 3. The zeta potential of untreated glass fibres (dispersed in deionized water) was measured as -32 ± 2 mV.

The sequence of the surface charge follows the expected trend, as a function of the pH of the conditioning liquid, being most positive at pH = 2 [10, 11]. The most negative surface charge was detected for fibres conditioned at a solution of pH = 9, indicating that considerable hydrolysis of the surface occurs in alkaline solutions.

According to the adsorption model of Clunie and Ingram described in [12], non-ionic surfactants displace water from the adsorbent surface at low concentrations, giving rise eventually to a monolayer of surfactant molecules oriented with their long axes parallel to the surface. At higher concentrations, the interactions between adsorbed molecules lead to close packing and to a further steep rise in adsorption. A patchwise multilayer adsorption may be favoured over monolayer adsorption. As the measured surface charge (that is, the zeta potential) is supposed to be strongly dependent on the orientation of the adsorbed molecules, the results from zeta potential measurements can only be interpreted qualitatively. The results suggest that the zeta potential measurements have a linear correlation only to the first plateau of the adsorption isotherms corresponding to the three adsorption sequences suggested by Clunie and Ingram.

Moreover, in agreement with the results of a previous study [4], the increased adsorption of the surfactant is shown to shield the aniocity of the fibres. Since the surfactant used is non-ionic, the electrostatic conditions near the surface may be assumed to remain roughly constant. Moreover, at concentrations exceeding 0.1%, hardly any additional adsorption is observed for fibres conditioned at pH = 5.5 and at pH = 9 while more surfactant is adsorbed at higher concentrations in fibres having acidic conditioning. The final charge found after the surface modification is almost equal for those solutions which are rich in surfactant indicating that the larger number of reactive sites produced during the acidic/alkaline conditioning are all consumed by surfactant adsorption.

3.3. Wilhelmy balance method

The effect of surface charging on the wettability of the E-glass fibres through conditioning for 5 min in solutions of different pH is shown in Table II.

The influence of the conditioning time on E-glass fibres in solutions of different pH is reported as a change of the advancing spreading coefficient in Fig. 4. The spreading coefficient ($S = W_a - W_k = \gamma_{H_2O}(\cos\theta - 1)$) represents the resulting tendency of the liquid to wet (spread on) the fibre surface. In order to get maximum effects and to illustrate the influence of the surface treatment (hydrophobization of the surface), the advancing properties provide the appropriate indicators for the process.

In line with the increased number of reactive sites indicated in Fig. 1, giving rise to a higher surface charge (Fig. 3), the wetting is particularly efficient for fibres conditioned at pH = 2. Since no components are leached out at pH = 9 no change in surface composition was observed (Fig. 1), although enhanced-production of surface hydroxyl groups is known to occur, resulting in a more negative surface charge (Fig. 3) and a subsequently lower wettability (Fig. 4).

TABLE II The wetting characteristics of E-glass fibres conditioned for 5 min in solutions of different pH

Characteristic	pH = 2	pH = 9
$F_w(a)$ (10^{-5} N)	0.26	0.22
$F_w(r)$ (10^{-5} N)	0.32	0.29
$F_w(m)$ (10^{-5} N)	0.34	0.31
Θ_a	40	45
Θ_r	20	21

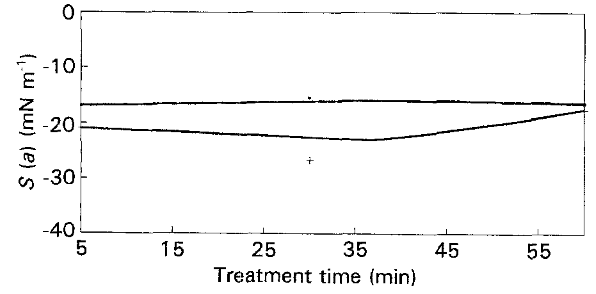

Figure 4 The advancing spreading coefficients of E-glass fibres in solutions of different pH: (-■-) pH = 2, and (-|-) pH = 9.

Compared with the changes found in the surface composition at pH = 2 the variation of the wetting parameters with time is small.

The effect of the adsorption of the surfactant on the conditioned E-glass fibres (5 min) is shown in Table III. In agreement with the previous observations, the acid and alkaline conditioning of the fibres provided a larger number of adsorption sites for the surfactant (Figs 1 and 3) and showed that patchwise multilayer adsorption may be favoured over monolayer adsorption [12].

However, as indicated by the relatively large surface charge (Fig. 3) and small contact angle ($\Theta < 90°$), even at high surfactant concentrations, the adsorption is incomplete. As shown in Table III and Fig. 5, the surfactant treatment is found to most effectively decrease the wetting of E-glass fibres conditioned at pH = 2; the wetting is more effective at pH = 9 and pH = 5.5.

The spreading coefficients of E-glass fibres conditioned in aqueous solutions of different pH (5 min) and subsequently treated with surfactant solutions of increasing concentration are shown in Fig. 5.

It thus seems that adsorption to specific sites on the glass fibre surface is sufficient to produce the macroscopic hydrophobicity. This is in agreement with previous observations that the contact angle between water and glass in increased considerably even by an adsorbed monolayer of greasy material such as a fatty acid [5].

TABLE III The wetting characteristics for glass fibres, pre-conditioned (5 min) and subsequently treated with surfactant solutions (5 min) of increasing concentration

pH	Concentration (%)	$F_w(a)$	$F_w(r)$	$F_w(m)$	Θ_a	Θ_r
5.5	0.1	0.26	0.33	0.36	44	24
	0.2	0.22	0.30	0.33	48	25
	1.0	0.21	0.27	0.30	46	26
2	0.1	0.17	0.27	0.30	56	26
	0.2	0.15	0.25	0.28	58	27
	1.0	0.18	0.36	0.39	63	23
9	0.1	0.20	0.28	0.31	50	25
	0.2	0.21	0.33	0.36	54	24
	1.0	0.23	0.35	0.38	53	23

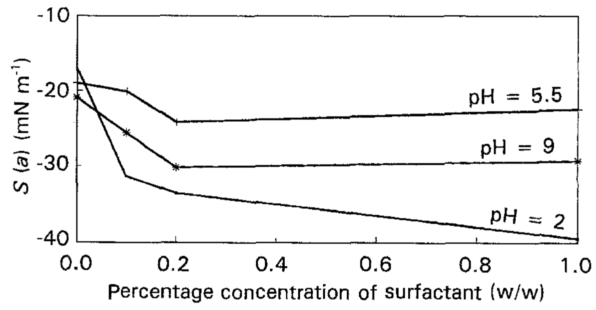

Figure 5 The spreading coefficients of E-glass fibres modified in surfactant solutions of increasing concentration: (-■-) pH = 2, (-□-) pH = 5.5, and (-*-) pH = 9.

4. Conclusion

The glass-fibre surface was extensively modified, especially by the treatments in a strong acidic solution resulting in large changes in the surface composition of the E-glass fibres (cf. the ESCA results). The alkaline treatment of E-glass fibres did not result in any changes in the surface composition, even though the surface characteristics were clearly modified (cf. the Wilhelmy balance method and the zeta potential).

It was also apparent that only a fraction of the surface was covered by the surfactant. It thus seems that adsorption to the specific sites on the glass fibre surface is sufficient to produce a macroscopic hydrophobicity.

The effect of the surface conditioning in solutions of different pH seemed to be greatest for the acidic solutions giving rise to increased adsorption of the surfactant on the glass-fibre surface. It should be noted that the surface treatment in a strong acidic solution produced glass fibres that were brittle and fragile.

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