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PRELIMINARY CHARACTERIZATION
OF GLASS FIBER SIZING

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ABSTRACT

Glass fiber surfaces are treated with sizing during manufacturing. Sizing consists of several components, including a film former and a silane coupling agent that is important for adhesion between glass fibers and a matrix. Although the sizing highly affects the composite interface and thus the strength of the composites, little is known about the structure and chemistry of the sizing. A part of sizing was extracted by soxhlet extraction. The fibers were subsequently burned and some fibers were merely burned for analysis of glass fiber and sizing. The results showed that the analyzed fibers had amounts of bonded and physisorbed sizing similar to what has been presented in literature. An estimated sizing thickness was found to be approximately 100 nm. It is indicated that an epoxy-resin containing film former and a polyethylene oxide lubricant are present, yet no silanes or other sizing components were identified in the extractant.

1.   INTRODUCTION

Reinforcements in fiber composites are mainly glass or carbon fibers, although aramid, polyethylene and cellulose fibers are also used. Carbon fibers are superior by having the highest stiffness and tensile strength as well as a rather low density. However carbon fibers have the disadvantage of the price due to expensive raw materials and a complicated manufacturing process. Glass fibers are not as strong as carbon fibers but much cheaper to manufacture. This is the reason why glass fiber composites take a first place as the most widely used material for wind turbine rotor blades (Brøndsted, Lilholt and Lystrup 2005). When looking into manufacturing of a mechanically strong material to be used for wind turbine blades, certain requirements should be met: high material stiffness, a low density and a long fatigue-life. These

properties are crucial to obtain optimal performance regarding aerodynamic, gravity forces and material degradation (Stevens 1999).

The handling and the performance of glass fibers and glass fiber reinforced composites both depend highly on the applied surface treatment (sizing) of the fibers. Despite the importance, the nature and properties of the sizing and the interface in the composites are poorly understood and documented in the literature (Thomason 2012). Sizing is an important part of composite materials and its chemistry is considered to be crucial to the properties of the composites. The exact composition of the full sizing is often hidden as commercial recipes by manufacturers. It can be the reason why comprehensive understanding of the full sizing structure is not reported in the literature. Only a simplified structure is suggested by Liu, Thomason and Jones (2008) consisting of a mixture of silane polymer chains bonded to the fiber surface and physisorbed in the sizing layer together with a film former. Figure 1 shows a conceptual view of a cross section of sizing on a glass fiber.
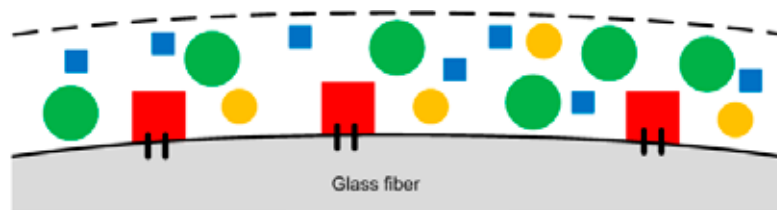

Fig. 1: Simplified illustration of the sizing layer. (■) Bonded organosilane polymer, (■) free organosilane oligomer, (●) film former and (●) other sizing components.

Little is known about the chemistry of the full multi-component sizing as the focus in the literature is often on one component: the silane coupling agent which is believed to be primarily responsible for the adhesion between glass fibers and a matrix (Plonka, Mäder, Gao, Bellmann, Dutschk and Zhandarov 2004). Organosilanes are obvious as coupling agents between the inorganic surface of glass fibers and the organic matrix since they contain both silica and organic functional groups being capable of forming bonds to both materials (Plueddemann 1981; Shokoohi, Arefazar and Khosrokhavar 2008). Many organosilanes have been investigated for their adhesive properties towards matrices used in composite materials (Ivashchenko 2009). Organosilanes with amino or epoxide groups are suggested to be especially well functioning with epoxy matrices (Shokoohi et al. 2008; Jones 2010).

The organosilanes can bond to each other by condensation reactions of the hydrolyzed alkoxy groups (silanol groups) and to silanol groups on the glass fiber surface. The possibility of crosslinking arises since functionalized trialkoxysilanes are the most used. The reaction of organosilanes forms polymers of different lengths while the reaction between organosilanes and silanol groups on the glass fiber surface leads to a chemical bond between them. Non-bonded polymers will be physisorbed in the sizing layer. The bonding of organosilanes as small oligomers and larger polymer chains in the sizing layer governs a complex network (Wang and Jones 1994; Liu et al. 2008; Jones 2010).

Organosilanes dominate only 10% of the many-component sizing. In fact the main component is the film former that represents approximately 79 % (Gorowara, Kosik, McKnight and McCullough 2001). The film former is added to ease the handling by providing good processing characteristics. The film former protects against fiber-fiber damage but also keeps the fibers together in a strand. The film former along with organosilanes set the efficiency of the wetting.

The choice of film former depends on the compatibility with the utilized polymer matrix. So the number of different film formers is connected to the number of available polymer matrices. The most commonly utilized film formers are: polyurethanes, polyvinyl acetates, polyesters, polyalkenes and epoxies (Dwight 2000; Thomason 2001; Zinck 2001; Rudzinski, Häussler, Harnisch, Mäder and Heinrich 2011). The extractable part of the silane is considered to be able to diffuse into the matrix together with the film former (Jones 2010).

In this paper, a preliminary characterization result of the glass fiber sizing is presented. To investigate the sizing, commercially available fibers as received are compared with fibers washed in a soxhlet for 24 h to remove extractable sizing and/or with fibers burned at 565°C for 3 h to remove organic components.

2.   EXPERIMENTAL METHODS

The fibers used in this investigation were E-glass fibers (a tex number of 1200, 17 μm diameter of monofilament, moist content ≤ 0.10% and sizing content in the range of 0.45-0.70%) supplied by Jushi (Chengdu, China). Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was conducted on a Perkin Elmer spectrum 100. The analyses were performed from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans per sample. Extracted samples were dissolved in acetone before placed on the ATR crystal. The acetone was subsequently evaporated prior to analysis. Two pure organosilanes were used as reference materials to identify characteristic bands: 3-aminopropyltrimethoxysilane (abbreviated 3-APTMS, 97%, ρ_{APTMS} = 1.03 g/ml) and 3-glycidoxypropyltrimethoxysilane (abbreviated 3-GPTMS, ≥98%, ρ_{GPTMS} = 1.07 g/ml) both from Sigma-Aldrich (Steinheim, Germany).

Extraction of sizing combined with burning of glass fibers is often used as a method to obtain values of the amount of loosely bound and physisorbed sizing. Extraction will remove the physisorbed organosilanes and a film former. Burning the fiber will remove all organic materials and organic functional groups leaving the part of the sizing that is strongly bonded to the fiber surface e.g. through Si-O bonds. By comparing the obtained value with the value of the amount of sizing that can be extracted, a distribution of loosely bound and physisorbed sizing can be calculated. The amount of strongly bonded sizing can be calculated only if the total amount of sizing is stated by the manufacturer (Tanoglu, Ziaee, McKnight, Palmese and Gillespie 2001).

The burn-off experiment was performed with fivefold determination. Before burning, the fibers were dried in a vacuum oven at 0.2 bars and 80°C for 2 h. Five dry crucibles with 10 g of dry fibers were placed in a furnace at 565°C for 3 h. The fibers were weighed to determine the moist content and loss on ignition (LOI) after burn off.

The acetone extraction was based on the work of Tanoglu et al. (2001), see Fig. 2. A similar approach is taken by Zhuang, Burghardt and Mäder (2010), Mallarino, Chailan and Vernet (2005), Feih, Wei, Kingshott and Sørensen (2005), Gorowara et al. (2001) and Liu et al. (2008). The extractable sizing was removed from the fibers by soxhlet extraction in spectroscopic grade acetone (Sigma-Aldrich, Steinheim, Germany) for 24 h. Each extraction was done with approximately 10 g of fibers. The fibers were weighed before and after the extraction and the drying to calculate the amount of the extracted sizing.
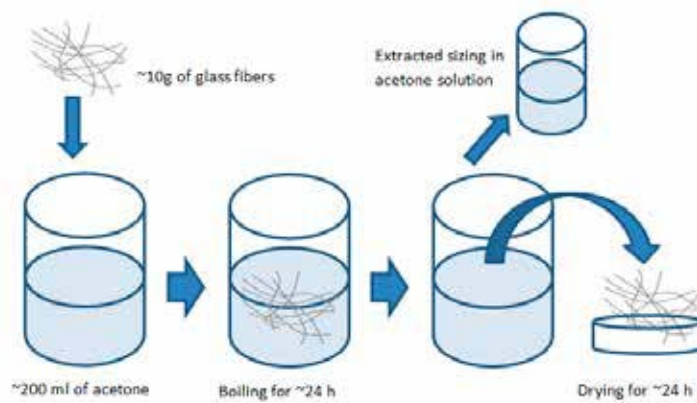
Fig. 2: A schematic presentation of the extraction process.

3. RESULTS AND DISCUSSION

It is reported that the amount of sizing varies and is in general in the range of 0.2-2 wt.% (Wu, Dwight and Huff 1997). The extractable part of sizing is mostly film former. This is supported by an extensive investigation of different commercial E-glass rovings by Thomason (1995) showing that the extractable amount of sizing was around 80-90 % of the total amount of sizing, which was in the range of 0.2-1.0 wt.%.

The results of acetone extraction and burn-off experiments are summarized in Table 1 and Fig. 3. It was observed that after extraction the fibers seemed softer and electrostatically charged. After burning they seemed more fragile and brittle. The observations correspond with the extraction of the film former and burn off of the organic parts of the sizing on the fibers.

Table 1: Results of weight loss from burn off and acetone extraction experiments. The values are given as weight percentages, the mass loss compared to the weight before burning and/or extraction.

	As received fibers	Extracted fibers
LOI	0.630% ± 0.007	0.070% ± 0.001
Moist	0.024% ± 0.060	0.050% ± 0.041
Extracted	0.502% ± 0.098	-

The amount of removable sizing can be estimated from values given by the manufacturer; however the sizing content is presented as a range. Using the highest value it is estimated that up to 25 wt.% cannot be removed by extraction or burning at 565°C.

The extractable amount of sizing (green area in Fig. 3) can be calculated as the share that the extracted sizing represent of the total amount of removable sizing (yellow area in Fig. 3) to be in the range of 80-90 wt.%. The amount of removable sizing on the fibers is consistent with values reported by Thomason (1995); the same is valid for the amount of extractable sizing. Comparing the mass losses indicated that the amount of oligomers is negligibly small. The moist contents show a good agreement to the value given by the manufacturer.
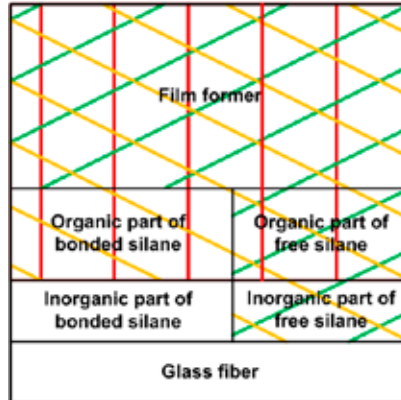
Fig. 3: A schematic presentation of the experimental results. The area covered by (∥) equals the 0.63 wt.% that is lost by burning at 565°C. The area covered by (//) equals the 0.50 wt.% that is extracted by soxhlet extraction of the fibers. The area covered by (\\) equals the sum of the mass loss from the extraction and the subsequently burning which is 0.50 + 0.07 = 0.57 wt.%.

From the diameter of the fibers and the sizing content the sizing thickness can be estimated with Equation 1 to be approximately 60 nm, assuming the densities of sizing and glass fiber to be 1 and 2.5 g/cm^3, respectively (Brøndsted et al. 2005). This thickness is reasonable, compared with the report by Thomason (1999) stating that the sizing layer is unevenly distributed with thicknesses in the range of 1 nm-1 μm.

$$t = \frac{(sizing-wt\%) \cdot r \cdot \rho_{glass\,fiber}}{2 \cdot \rho_{sizing}} , \tag{1}$$

where t, r, $\rho_{glass\,fiber}$ and ρ_{sizing} are sizing thickness, fiber radius, density of sizing and density of glass fiber, respectively. The sizing-wt.% is the weight of sizing compared to the glass fiber.

Commonly used organosilanes have either an amino, epoxy or a vinyl group attached when used with polymer matrices of epoxy or unsaturated polyester. It is reported that especially 3-aminopropylsilane, 3-glycidopropylsilane, 3-aminoethylaminepropylsilane and chlorine-substituted aminosilane have the ability to enhance the adhesion of glass fibers to epoxy resins (Shokoohi et al. 2008; Jones 2010). Thus an aminosilane (3-APTMS) and an epoxysilane (3-GPTMS) were chosen as references for comparison of FTIR spectra.

The FTIR spectra of analysed fibers are shown in Fig. 4. The spectra from analysis of fibers are not shown below 1200 cm^{-1} since any other bands are dominated by strong absorption from Si-O-Si bonds in the glass fiber that are in the region of 900-1100 cm^{-1}. The signal from silicon oxide is much stronger since the weight percentage of sizing is as low as around 0.6 wt.%. The spectra of burned and extracted fibers exhibit none of the characteristic bands found in the spectra of extracted or reference silanes. It is therefore indicated that the concentration of the extracted silanes could be below the detection limit.
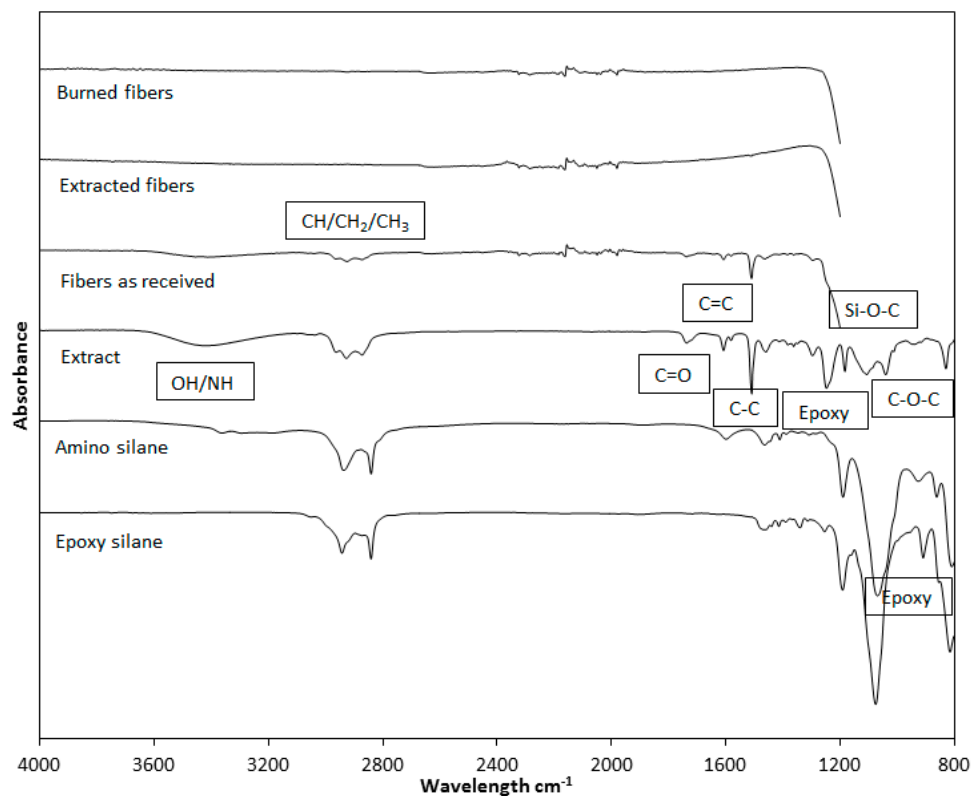
Fig. 4: FTIR spectra of as received, burned and acetone extracted fibers, the extractant and the two reference organosilanes.

The broad band between 3200 and 3600 cm^{-1} in the spectrum of both fibers as received and after extraction is assigned to stretching in N-H/O-H bonded to C and Si alike. The collection of bands around 2965-2873 cm^{-1} is attributed to stretching in C-H of CH, CH$_2$ and CH$_3$, both in aromatic and aliphatic compounds. The band at 1735 cm^{-1} corresponds to stretching of C=O in esters/carbonyl. The bands around 1100 cm are assigned stretching of C-O and Si-O which could indicate the presence of polyethylene and/or some kind of silicon oxide compounds. The bands at 1608, 1509, 1040 and 830 cm^{-1} all correspond to an epoxy resin and can be assigned to stretching in C=C of aromatic rings, C-C in aromatics, C-O-C of ethers and C-O-C in oxirane group, respectively. The bands at 1248 and 1183 cm^{-1} are also attributed to the epoxy resin. The spectrum of epoxy silane displays the characteristic epoxy band at 916 cm^{-1}. The presence of the C-O-C band can also originate from polyethylene oxide which is used as lubricant and surfactant in sizing (Salmon, Thorminette, Pays, and Verdu 1997; Dwight 2000; Gorowara et al. 2001; Macan, Ivanković, Ivanković and Mencer 2004; Zhuang et al. 2010; Rudzinski et al. 2011; Öhman and Person 2011).

4.   CONCLUSIONS

The removed amounts of sizing correspond well with the values found in the literature. Likewise is the amount of extractable sizing of 80-90 wt.% considered common in commercially available glass fibers. Comparing the sizing content to the one stated by the manufacture it was estimated that up to 25 wt.% of the sizing is not removable and must be considered strongly chemically bonded to the surface.

The absorption bands in the ATR-FTIR spectra of as received fibers and extracted sizing correspond reasonable with the presence of an epoxy-resin containing film former and a polyethylene oxide lubricant/surfactant compared to band values found in the literature.

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