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Role of silane coupling agent and polymeric film former for tailoring glass fiber sizings from tensile strength measurements

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Tensile strengths of differently sized E-glass fibres have been characterised using a bimodal Weibull two parameters cumulative distribution function. By comparing unsized fibres, pure silanes, different film formers, and silane/film former combinations, a comprehensive summary on the healing effect for surface flaws in relation to the type of sizing emulsion has been obtained. The great influence of the film former, which is the main component of the sizing by weight, was shown to affect both the healing of initially occuring flaws in the unsized fibre and the possibility of creating new defects. Besides the single influence of the film former, the synergetic effect of silane and film former polymer has been shown. In fact, the presence of sizing influences both the population of flaws on the fibre surface and the structure of the interphase, which will be created from the impregnation with a polymer matrix. Data from statistics of fracture as a function of the nature of sizings were discussed according to the literature on stress corrosion of E-glass filaments.

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1. Introduction

Glass fibre-reinforced polymers became very attractive materials in many areas of industrial applications because of their excellent mechanical performances/cost ratio. Many studies have been performed in recent years on the role of the interface/interphase region in determining the mechanical properties of these materials. The structure of this region and thus the mechanical properties depends strongly on the coating applied on the fibre surface before association with a polymer matrix.

The sizing has to protect the fibre during handling thus to enable processing, and to improve the adhesion and wettability of the fiber surface by the molten polymer or reactive mixture of monomers. In general, it consists of a water-based formulation containing a film former, a coupling agent and auxiliary components [1]. In most cases, the coupling agent is an organofunctional alkoxysilane which can react at the glass surface with the hydrolysed silanol groups and favour the chemical coupling with the sizing as well as with the surrounding polymer matrix in order to promote the interfacial adhesion strength [2]. The sizing is applied during glass fiber processing from an aqueous emulsion e.g epoxy, poly(vinyl acetate), etc. or a solution [1].

Since the structure of the deposited layers resulting from a silane coupling agent solution is well known [2–5], as well as the resulting polymer/sizing interface [6, 7], the structure of the sizing layers obtained from industrial processing, i.e including a film former, is still not investigated comprehensively. Nevertheless, it is known that the film former in conjunction with the silane governs the wetting behaviour, the resulting interphasial structure and most of the properties of glass fiber based composites materials [8, 9]. While the influence of coupling agent on the interfacial mechanical properties has been the subject of numerous papers, the effect of the nature of the film former itself is very poorly documented. By changing its chemical nature and molar mass, and by leaving out the silane coupling agent, Scholtens *et al.* [10] showed that the film former plays a crucial role in the level of fibre matrix

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"adhesion". Its effect may be larger than that of the silane. It should be noted here that the film former is the main component of the sizing in mass percentage.

The addition of a polymer in the fiber surface treatment was first done in order to protect the fiber during handling, and to promote the wetting of bundles by the reacting comonomers during processing. It appears then that this component could also be used to improve fiber-reinforced composite properties, such as impact resistance for instance, without affecting the other properties of the materials [11]. The concept of tailored interface has given new insights in the field of composites materials [11–13]. The use at the interface of a polymer which is compatible or not with the matrix [12], or the design of elastomeric interphases [13] can lead to materials exhibiting enhanced and tailored mechanical properties. Modification of interphases can also be envisaged by means of the synthesis of new functionalized polymers and coatings, such as functionalized silicone in epoxy/glass fiber composites for instance [11].

The film former, as well as the auxiliary agent, are thought to modify the structure of the silane deposit but very little is known about their exact effect and contribution. Jones [3] reported that the silane can act as surfactant for the colloidal polymer particles in the sizing emulsion. It was till now assumed that the coupling agent diffuses to the interface providing an interfacial region which is similar to that inferred from the fundamental studies with pure silane coupling agents [3]. Recent studies [14, 15] demonstrate that the structure of interphases resulting from pure silane and silane film former combination treatments are very different. In fact, the use of γ-aminopropyltriethoxysilane (APS) as 1wt % solution of water for coating E-glass fiber with and without film former shows that the interfacial adhesion as measured with the microbond technique is higher when the reactive monomers are applied on a glass surface treated with a pure silane treatment [14]. Nevertheless, the film former plays a major role in the durability of interfaces, since the sized fiber displays a much stronger resistance to hydrothermal treatment than the silane-treated one [15]. Those behaviours are not well understood due to the poor knowledge of the properties of the interphase region as well as the nature and extent of this interphase which requires *in situ* analyses. On the other hand, numerous scientific fields are concerned, such as inorganic/organic hybrids, polymer blends and compatibility, micromechanics and the accompanying issue of relating the results with macromechanical properties. Another difficulty is the small scale involved, which makes experiments with single fibre models both difficult to perform and difficult to interpret [14].

Progress in the understanding of interphase structure — composites materials properties and especially durability relationships implies the development of tools for determining the nanoscale and molecular structure and properties of the deposit/sizing on the fibre. The development and use of new direct characterisation methods for interphases in polymer composites is still in an early stage [9]. Besides this, application oriented research is directed towards the development of user-friendly methods for quantification of interfacial effects derived from the differently surface treated fibres. The relation between "fundamental" adhesion determined by using thermodynamic surface characterisation methods and "practical" adhesion has been shown recently [16]. Other relevant data have been obtained for an elastomeric interphase [17] but also for sized glass fibers [18] from direct mechanical characterisation of the fibers. Informations upon the deposit were obtained through a statistical treatment of the data, but also by considering linear elastic fracture mechanics concepts. The combination of probabilistic and deterministic approaches is a very powerfull way to provide information at different scales, from the components in the sizing solution/emulsion, i.e hydrolyzed and condensed species, suspension droplets, etc. to the healing of surface flaws by the coating layers [18]. Moreover, the influence of the film former on the mechanical properties of glass fibers, which in turn may affect the behaviour of the resulting composite, is often neglected compared to the well documented effect of surface finishs on the properties of carbon fibers [19, 20].

The aim of this paper is to highlight the effect of film formers in glass fiber sizings. Using a methodology developed previously [18], the mechanical characterization of fibers is used as an indirect analysis of the effect of the surface treatment consisting of both pure γ-APS or pure film formers and different γ-APS coupling agent/film former combinations in comparison with unsized glass fibers. Thus, this paper deals with the combination of different approaches which were done independently on statistics of glass fibres fracture, physico-chemistry of surface treatment of sizings, and stress corrosion of glass.

2. Experimental

2.1. Glass fibres

E-glass fibres were made at the Institute of Polymer Research Dresden by using a continuous spinning and sizing pilot equipment at industry-comparable processing conditions. The temperature of the bushings was 1200°C. The diameter of the filaments was controlled by the processing speed and varied between 12 and 15 μm for all samples at 1000 m/min for winding the continuous filament yarn on a spin cake. Just immediately after spinning the equipment enables to apply the sizing onto the virgin filaments after a short cooling period. The sizing was continuously applied from the sizing bath with a rotating roll.

The production of "unsized" fibres necessitated to use distilled water in the sizing bath. A 0.3 wt% aqueous solution of γ-APS (A1100 from Witco Corporation-OrganoSilicons Group) was used both to make the pure silane treated fibres and the completely sized ones. All film formers were applied from 3 wt% aqueous solutions. Auxiliary components such as lubricants, antistatic agents, etc. were avoided in all sizing emulsions.

The polyurethane (PU-Neoxil 9851) and the polyvinylacetate (PVAc-Vinnapas EP 400) film formers were provided by DSM Italia Srl and Wacker-Chemie GmbH, respectively. Protolube 3974 was taken from

TABLE I Average tensile strength and standard deviation of different types of glass fibres at a gauge length of 50 mm

Designation	Sizing	Average tensile strength [GPa]	Standard deviation [GPa]
0	Unsized	1.42	0.61
APS	γ-aminopropyltriethoxysilane (APS)	1.78	0.45
PU	Polyurethane film former	1.08	0.39
PP	Polypropylene film former	1.82	0.61
PVAc	Polyvinylacetate film former	1.01	0.59
APS/PU	γ-APS/polyurethane film former	1.82	0.43
APS/PP	γ-APS/polypropylene film former	2.01	0.44

Sybron Chemicals Inc. as an example for polypropylene film former (PP). The particle size distributions of the film former dispersions were determined with dynamic light scattering (PCS). The average particle sizes were 80 nm for PP, 600 nm for PU and 950 nm for PVAc (polydispersities of 0.45, 0.11, and 0.2 respectively).

The spin cakes were dried directly in an oven at 100°C for 2 hours. The single-fibre specimens were taken directly from the spin cakes without any further mechanical loading by additional textile processing steps.

TABLE II Values of the shape (m) and scale (s) unimodal Weibull two-parameter cumulative distribution function of differently sized glass fibres

Designation	m	s	r
0	2.83	1.59	0.92
APS	3.96	1.98	0.97
PU	3.3	1.21	0.95
PP	3.25	2.03	0.96
PVAc	2.16	1.09	0.88
APS/PU	5.03	0.68	0.94
APS/PP	3.83	2.21	0.58

2.2. Mechanical testing

Single filaments were extracted from the bundles without any selection prior testing. Single fibre tensile tests were carried out using a Zwick Z 010 testing machine, operating with a cross-head speed of 1 mm min^{-1} at a temperature of 23°C and a relative humidity of 50%. The single-fibre specimens were mounted in a rectangular paper-box and fixed with an epoxy adhesive. Special care was taken during handling in order to avoid creation of additional defects and changes in the flaw distribution. At least 50 specimens of each sample were prepared, but those ones which failed close to the clamps have not been considered. All tests were conducted at a gauge length of 50 mm.

3. Results

3.1. Tensile strength

Average tensile strengths for a sample size of about 40 to 50 and a 50 mm gauge length are given for each type of fibres in Table I. Lowest strengths were determined for the fibers sized with film formers based on PVAc and PU and for the unsized glass fibres. The average values for γ-APS, γ-APS/PU, γ-APS/PP, and also PP demonstrate the increase of strength due to a well-acting sizing treatment.

3.2. Weibull treatment

The statistical treatment of the data has been reported in detail elsewhere [18]. Data were first fitted using a Weibull unimodal cumulative distribution function, in order to distinguish the respective flaw distribution:

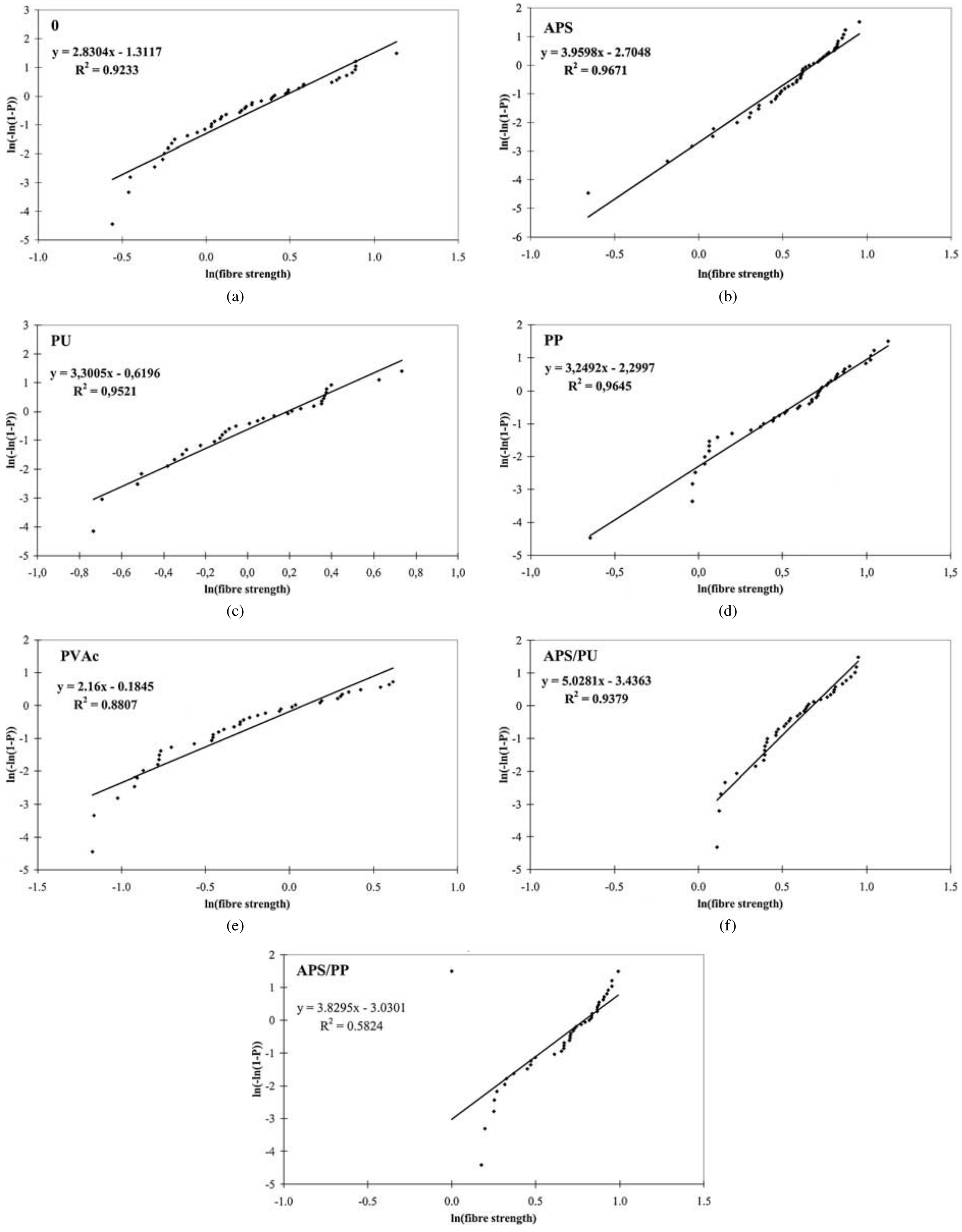
$$P(\sigma) = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{1}$$

where P is the cumulative probability of failure of a fibre at the applied stress σ and m is a shape parameter or the Weibull modulus. σ_0 is a scaling parameter. Details concerning the significance of the shape and scale parameters and their relation with flaws characteristics, i.e severity and separation, can be found in reference [21] and [18], respectively. Fig. 1 displays the experimental probability of failure of the differently sized fibres vs. theoretical unimodal cumulative distribution function. The corresponding shape and scale parameters determined by a classical least-squares method are given in Table II. It can be seen that only γ-APS treated fibers exhibit a single population of defects.

The two-parameter bimodal Weibull cumulative distribution function used for further fit the experimental data is given by:

$$P(\sigma) = 1 - p\exp\left[-\left(\frac{\sigma}{\sigma_{01}}\right)^{m_1}\right] + (1-p)\exp\left[-\left(\frac{\sigma}{\sigma_{02}}\right)^{m_2}\right] \tag{2}$$

where m_1, m_2, σ_1, and σ_2 are the shape and scale parameters of the corresponding population of defects respectively. p is the mixing parameter, i.e the fraction of failures due to the most severe (type 1) defects. In such a description, it is assumed that no interaction occurs between type 1 and type 2 defects. The results given in Table III and Fig. 2 enable to appreciate the goodness of fit of the model. The proportion of the first type of defects, attributed to severe surface flaws is 20% in average. Those results are in agreement with a previous study devoted to glass fibres strength [18]. Nevertheless, even without considering any selection of the filaments from the bundle, the experimental protocol can lead to the use of the stronger fibres as the weakest ones will break during preparation. As a consequence, with the uncoated fibres, the average population will be



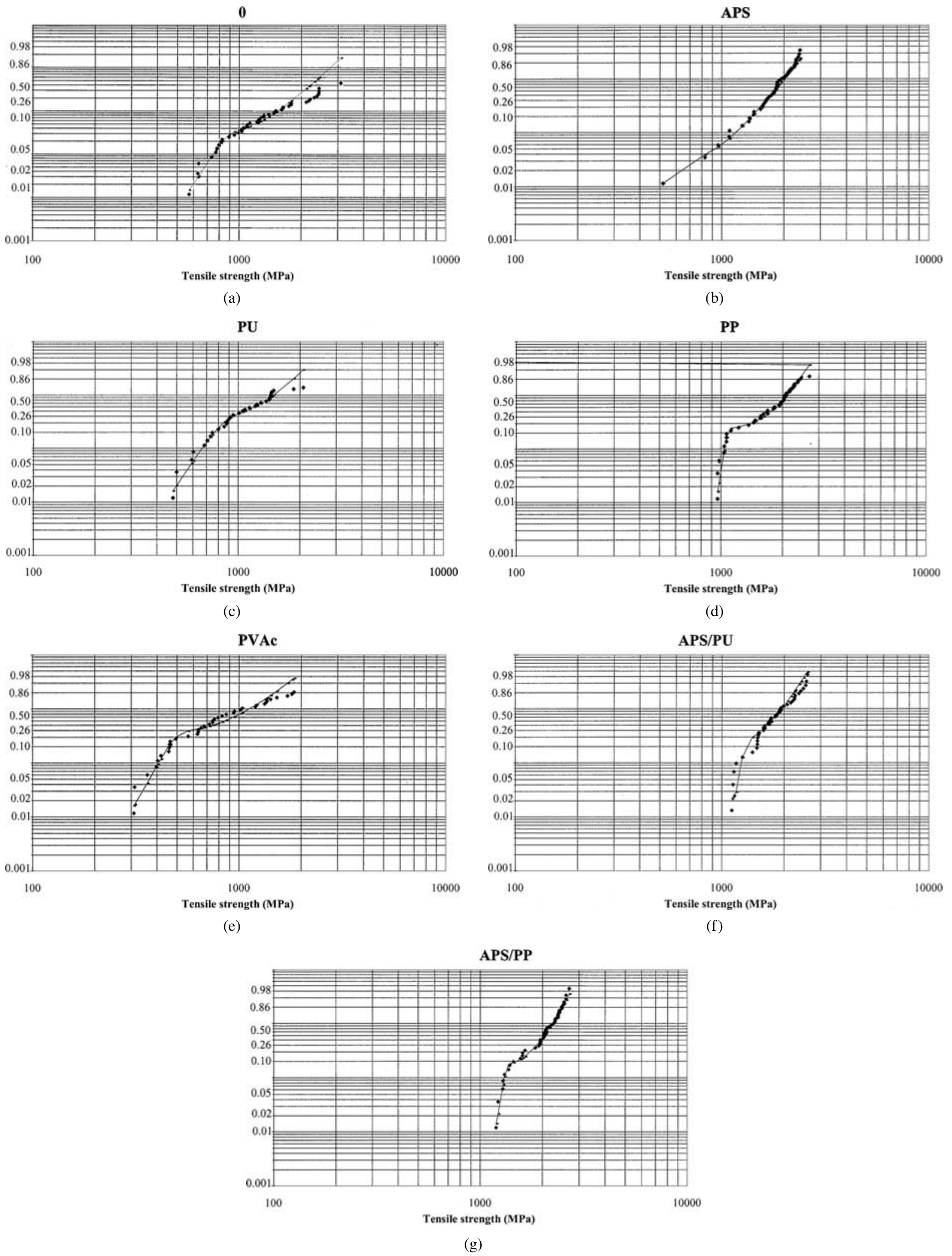
(a) (b) (c) (d) (e) (f) (g)

Figure 1 Experimental probability of failure for differently sized fibres (a – 0, b – APS, c – PU, d – PP, e – PVAc, f – APS/PU, g – APS/PP) as unimodal cumulative distribution function.

weak. This fact needs to be considered and gives one of the limits of the study.

3.3. Analysis based on the linear elastic fracture mechanics (LEFM)

To obtain information about dimensions of the flaws, the general shape of a surface defect according to the presence of a surface treatment was assumed to change due to the effect of the sizing, which increases the crack tip radius. By using the relation between the toughness, the fracture strength, and the crack dimension for a single-edge notch specimen [18], the size of the surface defects for fibres exhibiting 2 failures modes could be estimated. Such values are summarized in Table IV together with the particle sizes in the solution determined by PCS. For unsized fibres, flaw dimensions of



(a) (b) (c) (d) (e) (f) (g)

Figure 2 Experimental probability of failure for differently sized fibres (a – 0, b – APS, c – PU, d – PP, e – PVAc, f – APS/PU, g – APS/PP) as bimodal cumulative distribution function.

type I distribution are from 200 nm to 400 nm approximately. The fibers sized with PU film former displays a similar behaviour, as values of shape, scale and mixing parameters are similar. This film former applied as sizing alone does not improve the fibre properties (Tables I and III). The case of PVAc which weakens the fiber will be discussed later.

APS fibres display only a unimodal distribution. This effect can be related to the fact that the proportion by weight of APS in the sizing solution remains low. The small particle size in the solution enables healing a great part of the defect content, but in turn cannot give a thick polysiloxane layer leading to a great increase of the crack tip radii.

TABLE III Values of the shape (m_1, m_2), scale (s_1, s_2), and mixing (p) parameter of the bimodal Weibull two-parameters cumulative distribution function of differently sized glass fibres

Designation	m_1	s_1	m_2	s_2	p
0	9.47	1.44	4.35	5.5	0.22
APS	7.01	1.21	4.84	5.98	0.02
PU	6.30	1.84	4.11	5.93	0.27
PP	32.45	1.25	5.82	5.41	0.20
PVAc	8.59	0.86	3.21	6.59	0.27
APS/PU	179.88	1.30	6.17	4.75	0.17
APS/PP	31.05	1.56	7.33	4.70	0.14

TABLE IV Flaws dimensions obtained from the LEFM treatment and particle size distribution as determined from PCS for the different systems

Designation	Flaws dimension (nm)	Particles size (nm)	Polydispersity
0	200–400	–	–
APS	–	–	–
PU	200–450	600	0.11
PP	125	80	0.45
PVAc	500–1400	950	0.2
APS/PU	95	–	–
APS/PP	75	–	–

Interesting modifications were obtained for APS/PU, APS/PP and PP. A threshold is observed, which corresponds to flaw sizes of 95, 75, and 125 nm, respectively, as obtained from the LEFM treatment. This can be attributed to flaws which are not healed by the surface treatment, i.e. not filled by the aggregates or micelles of the sizing emulsion. The flaw dimensions for PP obtained from the LEFM treatment (125 nm) are in good agreement with the values of the particles size as measured by PCS (80 nm – polydispersity 0.45).

4. Discussion

4.1. General statements

As discussed earlier [18], an unimodal Weibull function supposes that the failure is governed by one type of defect. When considering several categories of defects, it does not result in a straight line. The extreme values should represent two straight lines with different slopes, and the slope change is an indication of multimodal distribution. Such dependencies are given in Fig. 2 for the different surface treatments considered except for the pure silane treatment APS. Thus, it demonstrates that two populations of flaws for a gauge length of 50 mm are found and in agreement with fundamental studies. By taking both modes into account, the effect of surface treatment of the glass fibres, i. e. the physicochemical interactions between the sizing components and the glass surface and also possible effects of processing of fibres can be evaluated.

Fig. 3 displays a comparison as bimodal cumulative distribution function for fibres differing from their sizing. The only unimodal distribution can be found for APS sized fibres which can be attributed to a reduction of flaw severity due to the concept of healing surface flaws by the deposited sizing particles. In the case of APS the severe surface flaws disappear from the three-dimensional graded network resulting from the interaction between the organosilane and the glass fibre surface [18]. Compared with APS, the unsized and the PU sized fibres represent lower shape and higher scale parameters indicating more severe flaws and a higher heterogeneity. Lowest s_1-values have been determined for PVAc sized fibres due to both the high particle sizes in the poly(vinylacetate) dispersion hardly able to fill surface flaws and the possibility of creating additional flaws by hydrolysis, i.e. acidic corrosion followed by weakening the fibres.

On the contrary, sizings on the basis of PP increased the shape parameter after a threshold, which is either due to the low particle size of the PP dispersion or a synergy effect with APS. A special contribution might also be achieved in this case by smaller particles as indicated by the wider particle size distribution. The synergistic effect between coupling agent and film former can also be observed for the APS/PU system.

4.2. Effect of the sizing formulation

It is assumed that the flaw distribution for fibres of the same diameter is similar after the spinning process. Separation of type I defects for APS-treated fibres is narrower than those for unsized and PU-sized fibres and

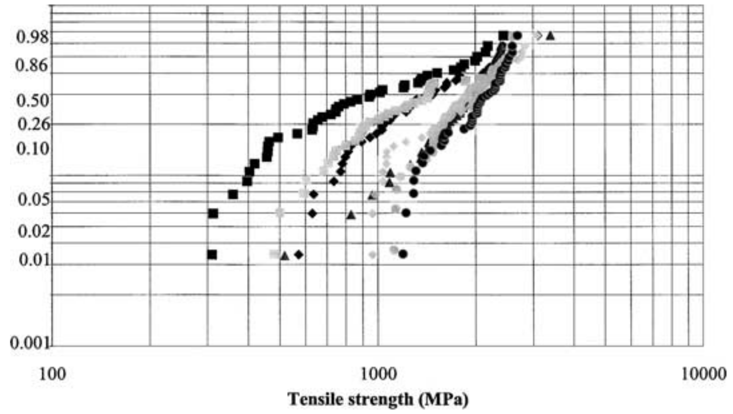


Figure 3 Comparison of probability of failure as bimodal cumulative distribution function for differently sized fibres: 0 ◆, APS ▲, PU □, PP ◇, PVAc ■, APS/PU ○, APS/PP ●.

flaws are less severe as revealed by the values of the shape and scale parameters. This effect can be associated with the healing of the surface flaws caused by the APS, which penetrates the surface defects and has been crosslinked in it. Compared with previous findings [18], the concentration of γ-APS in the aqueous solution is much lower (0.3 wt%) and also the hydrodynamic radii of hydrolysed γ-APS should be much smaller than 150 nm, as reported by Ishida [22] for 1 wt% aqueous solution. Thus, a unimodal distribution was determined for APS and no threshold occurred, indicating that a great part of surface flaws could be healed by γ-APS. On the contrary, the PU-sized fibre behaves similar to the unsized one, indicating a threshold at a slightly lower tensile strengths. If flaw distributions between 200 and 400 nm are expected for the unsized fibre from linear elastic fracture mechanics determination, this seems to assist the concept of critical dimension, since an average particle size distribution of 600 nm was determined for the PU dispersion. The similar behaviour between unsized and PU fibers is thus attributed to the particle size of PU in the solution which does not enable flaws to be healed. Such a phenomenon may also occur for PVAc fibres, since the particle size is even greater than that of PU (950 nm). The case of PVAc is interesting. This film former, which is used against shrinkage in polyester based composites, weakens the fiber. This might be caused by the slightly acidic behaviour of the polyvinylacetate dispersion, thus the partial hydrolysis and following crosslinking of the polyvinylalcohol during the drying step of the fibres [23]. The weakening of fibres by using a PVAc sizing can also be attributed to the formation of acetic acid and is fully consistent with previous studies [24, 25], the approach of strength of glass developed by Charles [26], and the Fox thermodynamic analysis [27]. This effect is usually compensated in complete sizings due to the influence of basic aminosilane. In fact, Metcalfe and Schmitz showed that acidic solutions were more detrimental to strength of E-glass fibres than alkaline ones. The stress corrosion involves ion exchange mechanisms occurring at the glass surface. The weakening phenomenon can be also associated to the hydrophilic behaviour of PVAc. As a consequence, this water on the surface contributes to the chemical mechanisms and leads to the futher corrosion of the glass fibre weakening the tensile strength. The same phenomenon can be proposed for PU-based film former. The PVAc film former increased the surface roughness of the fibres significantly as was determined by atomic force microscopy in comparison with other sized fibres [28].

A threshold value at higher tensile strength, which corresponds with flaw dimensions of about 75, 95, and 125 nm, was determined for APS/PP, APS/PU, and PP in the same order. Although the polymer as the main component of a sizing by weight increases the tensile strength of APS/PP and PP sized fibres, which can be explained by the healing effect of the small particle sizes in the PP dispersion, in the APS/PU sizing the expected "negative" effect of the large particle sizes was suppressed by the known healing effect of the APS. The coupling agent may act as surfactant in the polymer emulsion, leading to smaller particle size which in turn are able to fill a greater amount of flaws. This effect, combined to the hybrid nature of silane coupling agents, which enable chemical links with the glass surface/crack tip, is thought to explain the benefit effect of the coupling agent/film former combination. It is thus inferred that film former and silane act *synergistically*. Besides the population of flaws, the built-up of the complex coating layer, i. e. homogeneous arrangement of silane and film former or as islets, silane at the bottom or on top or vice versa, might have great influence on the interphase layer to be built during composite formation. On the other hand, the selection of silanes and film formers depend on both the compatibility and the reactivity with the matrix polymer. This approach taking into account the presence of the nature of film former in addition to the silane coupling agent in the surface treatment of E-glass fibres can be combined with the accurate studies of stress corrosion of E-glass filaments as a function of the nature of glass composition combined with stress corrosion models [24].

5. Conclusion

The mechanical characterization of differently sized glass fibres has shown the great influence of silane coupling agents and film formers on both tensile strength and Weibull parameters determined from single fibre tensile tests. Using the opportunity to compare unsized fibres, pure silanes, different film formers, and silane/film former combinations, a comprehensive summary on the healing effect for surface flaws in relation to particle size distribution and wetting/spreading onto the surface could be pointed out. Thus, the synergetic effect of silane and film former polymer has been shown which creates both the basis for the population of flaws on the fibre surface and for the "interphase state", which will be formed when contacted with polymer matrix for composites.

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