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Oponentský posudek disertační práce "Behaviour of the Interface of Low Toughness Materials" (doktorand: ing. Martina Halasová)

The focus of this Ph.D. thesis is the characterization of microstructure and mechanical properties of silicon oxycarbide (SiOC) based fiber-reinforced composites and the interpretation of the results in terms of the properties of the two phases and the interface between them. This is a highly timely topic that doubtlessly deserves a detailed investigation.

In her thesis the candidate first summarizes the "State of the Art". This 35-page introductory chapter provides basic general information on the materials used (matrix and reinforcement) and the microstructures commonly encountered in fiber-reinforced composites. With respect to the topic of this work this discussion is mainly focussed on amorphous polymers and polycrystalline ceramics, for both of which brittle fracture is typical. Processing methods and mechanical properties are summarized, including interfaces, toughening mechanisms and failure modes in polymer matrix composites (PMCs) and ceramic matrix composites (CMCs). After a short formulation of the aims of this work, the 20-page chapter entitled "Experiment" gives detailed information on the materials (both commercial and laboratory-made) studied and the characterization techniques used for their investigation, including specimen preparation, microstructural and fractographic characterization (optical microscopy, laser confocal microscopy, SEM, TEM) and mechanical tests (indentation hardness, elastic modulus and relaxation behavior, static and dynamic elastic moduli measurement by three-point bending and impulse excitation, flexural static and impact strength, and fracture toughness). The "Results" are presented on 55 pages, followed by 10 pages of "Discussion" and a 2-page "Conclusion". In these chapters the candidate presents and discusses in great detail the characterization of matrix materials and composites, as well as the interface, and interprets the mechanical properties with respect to the composition and microstructure of the materials.

The thesis is written in fluent and proficient English, with an acceptable number of typos (with the only important one being "Voight" on pp. 6 and 20, which should be "Voigt") and a relatively small number of grammatical or stylistic deficiencies (mainly missing or redundant English articles). Also the number of formal deficiencies is small. For example, Equation 2.5 occurs twice (on p. 20 and on p. 57), on p. 82 the numbering of equations is a little confusing (Equation 3.3 follows 3.5), and also the fact that the equations in Chapters 3 and 4 are denoted as 2.1, 2.2 etc. and 3.1, 3.2 etc., respectively, is not so nice. The values of elastic constants should not be given with two decimals precision (which is definitely too high). The list of references could have been prepared with a little more care. Book and journal titles should be written either with capital letters or with lower case letters, but not a mixture of both, and incomplete citations (e.g. refs. 51 and 61) should be avoided. Moreover, if it was an official template that has been used to create the citations in this work, I would strongly recommend changing or ignoring it in future works.

As far as contents are concerned, this work is a very complex and detailed in-depth study of the microstructure, fractography and mechanical properties of fiber-reinforced composites, based on a large amount of carefully performed experimental work. I highly acknowledge this amount of work that has evidently been done by the candidate and consider the experimental results of this work a valuable contribution to our knowlegde of fiber-reinforced composites. The results are presented in a logical sequence and discussed with due care. It is clear, however, that even in a nice work like this certain details have been overlooked or certain interpretations are disputable.

From the viewpoint of theory I have one general remark:

1. As indicated in the text several times, the author is fully aware of the fact that her materials are not isotropic. However, there is no clear statement of the symmetries involved. In particular, a major part of the text does not make a clear distinction between transversally isotropic composites and orthotropic composites, although e.g. from 4.2.1 and 4.2.2 it is clear that both types have been considered in this work. While the introductory chapter ("State of the Art") only mentions orthotropic symmetry, major parts of the later text ("Results") seem to refer to transversally isotropic symmetry. What I also miss in this work is a clear statement of the fact that the complete description of elastic properties of these materials would require 5 independent elastic constants in the case of transversally isotropic materials and 9 independent elastic constants in the case of orthotropic composites. It would be useful to refer to the full stiffness matrix in the first place and then to comment on the types of elastic constants that are accessible to measurement for these two types of microstructures by the different test methods used. It is clear that for this purpose the impulse excitation technique is not optimal for characterization and also 3-point-bending and tensile tests can only provide partial information (ultrasonic techniques would probably be a better choice in this case, but I understand that this is a question of available equipment). Maybe the author could comment on some of these points during the discussion.

Detail issues are the following:

2. (p. 5) The statement that "in fibre reinforced composites, the constants become orthotropic" is not necessarily true. The stiffness tensor can also be transversally isotropic, when all fibers have the same orientation, as indicated by Figure 1.4 on p. 6. (More precisely, not the constants become orthotropic, but the stiffness tensor.)
3. (p. 5) What is the "strengthening coefficient" in Figure 1.3. Why are the units [MPa]?
4. (p. 6) The parameters vf and vm in Equations 3.1 and 3.2 are not volumes, but volume fractions (otherwise the equations would not be correct from the viewpoint of dimensions). Much more important, however, is the fact that Equations 1.2 and 1.3 are not valid for the ultimate tensile strength and for mass! Note that "strength" is not a material property in the strict sense, i.e. is not defined as a coefficient in a linear constitutive equation. Therefore the validity of these equations cannot be proved and is pure speculation. For density only 1.2 is valid (but not 1.3!), and this mixture rule determines the density exactly (i.e. 1.3 has no meaning for density!).
5. (p. 6) Figure 1.4 curve 2, i.e. the "lower bound" does not represent the elastic modulus of an aligned fiber composite in the transversal direction, but only the elastic modulus of a sandwich composite (laminate) in the normal direction (i.e. perpendicular to the layers).

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6. (p. 6) Why does the author agree with Campbell's statement (see ref. 19) that "the effective volume ratio of the reinforcement is considered maximum up to 60–70 %". In my opinion this is a realistic maximum for particle composites, where the maximum packing fraction is around 64 % (for random close packing of monodisperse spheres), but for aligned fiber composites much higher volume fractions are thinkable and should be possible. Note that in fiber composites with aligned (i.e. unidirectionally oriented) fibers the maximum packing fraction for infinite fibers is 91 % for closest packing and still 78–82 % for random packing. At least in theory.
7. (p. 19) The mass is *not* given by "the" rule of mixture (at least not by the same as density).
8. (p. 20) The "rule of mixture", Equation 1.2, is the "Voigt model" (not Voight!). The two are the same. Therefore it is inappropriate to say that "the modulus obeys both rule of mixture and the Voight model". Please note, however, that in the transverse direction fiber composites do not obey the Reuss model (see point 5 above). The Reuss model is obeyed only by sandwich composites (laminates) perpendicular to the laminae (layers)!
9. (p. 20) Is there any mathematical proof for the validity of the "mixture rule for strength" in Equation 2.5 of Section 1.4 on p. 20 (note that by mistake there is another "Equation 2.5" on p. 57)? As far as I know, such a proof does not exist (see point 4 above), and I would assume that Equation 2.5, if interpreted as a mixture rule for strength, is wrong. Please confirm my assumption or present arguments or evidence that convince me of the opposite.
10. (p. 48) In Table 3.7 the thermal expansion coefficient is cited with units [W/mK], which is an obvious error. However, the values of 0.031–0.038 appear to me extremely low for the thermal conductivity (and extremely high for the thermal expansion coefficient). This should be clarified.
11. (p. 49) If the composite is "unidirectionally reinforced", it is not orthotropic, as stated several times in previous passages. Also Figure 3.13 indicates that some of the composites studied in this work are not orthotropic, but transversely isotropic. This point should be clarified.
12. (p. 54) Equation 2.1 for the evaluation of Archimedes measurements is not correct (as can be easily seen from the dimensions). The density on the r.h.s. should be in the nominator (not in the denominator) and is the density of the liquid (not the solid). Moreover, Equation 2.1 determines the bulk density only in the absence of open porosity. In the general case "m_air" in the denominator has to be replaced by "m_air_saturated", i.e. by the weight of the isopropanol-saturated sample in air. Also the last sentence on p. 54 is not very clear and should be explained.
13. (p. 55) What kind of "elastic modulus" is the tangent slope of the unloading curve in Figure 3.10? In other words, does the "indentation elastic modulus" measured in this way correspond to one of the more common elastic moduli E (tensile modulus), G (shear modulus) or K (bulk modulus), at least in the case of isotropic materials? If not, is it usually closer to E, G or K? Or is it just a quantity for relative comparison that cannot be related to any of the common elastic moduli (E, G or K) at all? Please comment.
14. (p. 55) Does the tangent slope in Figure 3.10 depend on the maximum force applied? How precise is the determination of the tangent slope? (Note that the unloading curve is nonlinear, see also the curves in Figure 4.14 on p. 72!) Please comment.
15. (p. 62) What is the "running average" in Figure 3.15. If it is the cumulative average calculated in order to smooth the curves, beginning from the origin (i.e. zero force and zero deflection) it is not clear to me, how its intial slope can be so smooth, while the "original curve" heavily oscillates. This should be clarified.

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16. (p. 73) What kind of standard deviation is shown for the indentation elastic modulus in Figures 4.15, 4.16 and 4.17? Do these error bars take into account the principal difficulty to reliably determine the tangent slope of the unloading curve? (see also question 14 above)
17. (p. 81) If the fiber content would be really 58 wt.%, as written twice in the text (probably this is just an oversight), the calculations in Equations 3.2 and 3.5 would be wrong, because volume fractions, not mass or weight fractions, have to be used in these mixture rules! The corresponding volume fractions would be 0.397 and 0.603, and thus the density would be 1.86 g/cm^3 instead of 2.12 g/cm^3, and the Young's modulus would be 38 GPa instead of 52.26 GPa. With respect to the repeated occurrence of this problem I believe that there is just a double misprint in the text (i.e. 58 wt.% should probably be 58 vol.%). In fact on p. 50 the author mentions a content of 58 vol.% of fibers. This should just be checked and confirmed.
18. (p. 81/82) Equation 3.5 is an estimate for the value of the tensile modulus (Young's modulus) of the composite in the axial (longitudinal) direction, i.e. measured by uniaxial tension (static) or longitudinal vibrations (dynamic) in the direction of fiber alignment. That means the flexural modulus of the composite (measured in 3PB or with flexural vibrations) should be between this upper bound (Voigt bound) and the lower bound (Reuss bound). However, the measured value (68.41 GPa) is significantly higher than the upper bound (52.26 GPa when assuming 7.058 GPa for the matrix or 54.30 GPa when assuming 11.88 GPa for the matrix, assuming a fiber content of 58 vol.%, not wt.%, in both cases). The author explains this by the hypothesis that the fiber fraction in the specimen measured is higher than average, e.g. due to inhomogeneity. In order to discuss this hypothesis, however, it would useful to calculate the fiber fraction that would be necessary to make the upper bound, Equation 3.5, higher that the experimental value.
19. (pp. 87/88) What is the meaning of "normalized strength" in the graphs of Figure 4.33 on p. 87 and "normalized energy" in Table 4.3 on p. 88? Normalized with respect to what? Moreover, I would expect normalized quantities to be dimensionless. These are not. Why?
20. (pp. 96-98) What is the "nominal impact stress" and "nominal impact strength" in Figs. 4.42, 4.43 and 4.44? Are these the same as the "normalized" quantities mentioned above?

The 30-page short version of this thesis provides a useful concise summary of the experimental findings, wisely avoiding most of the disputable issues mentioned above. The candidate may select some of the aforementioned issues and briefly comment on them in her presentation.

Despite these partly disputable issues, which concern mainly terminology and interpretational details, it has to be emphasized again that this thesis is obviously based on careful experimental work and that it doubtlessly provides valuable new insight into the microstructure, fractography and mechanical properties of fiber-reinforced composites, including the central role of the interface in determining the fracture behavior of these composites. Therefore **I consider this work a valuable contribution to extend current knowledge in this field.** The objectives have been clearly achieved, and without doubt this work fulfils the requirements posed on a Ph.D. thesis. **Therefore I recommend this thesis for defense and for awarding the title "Ph.D."**

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