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## Oponentský posudek disertační práce “Mechanical Reinforcement of Bioglass<sup>®</sup>-Based Scaffolds“ (doktorand: Luca Bertolla)

This thesis treats a timely topic on which there is considerable interest in the international research community. Mechanical weakness is one of the major drawbacks of Bioglass<sup>®</sup> scaffolds used for bone tissue engineering, and overcoming this deficiency would significantly improve the performance and enhance the range of applicability of these materials in vitro or possibly even in transiently load-bearing applications.

The approach chosen in this work consists essentially in preparing Bioglass<sup>®</sup> foams via the traditional replica technique and coating the as-sintered foams with polymers. It seems that in this work a polymer composite coating based on PVA and microfibrillated cellulose has been applied for the first time. The work describes processing issues, including rheology, microstructural characterization and mechanical property measurements and contains also a numerical part on finite element modeling and an extra part in which the feasibility of using BN reinforcements has been tested in combination with spark plasma sintering.

The work contains 90 text pages subdivided into 7 Chapters, including Theoretical background (27 pages), Methods (14 pages) and Results and Discussion in two separate chapters (together 40 pages). In my opinion the separation of Results and Discussion was not a happy choice. Nevertheless, the thesis clearly fulfils the aims formulated in Chapter 3, the results correspond to the requirements of a PhD thesis and the data obtained may be used as sound benchmarks for further research in the field. The candidate lists four journal papers, three of which are listed on the Web of Science.

With this wide range of topics, it is clear that there are certain details that have been overlooked.

Concerning formalities I have the following detail remarks:

1. The paper contains a relatively large number of misprints, small grammatical mistakes and stylistic errors that cannot be commented here.
2. Table captions should be above the tables, not below.
3. All abbreviations used, including those that appear trivial or self-evident to the author, should be defined upon first appearance, e.g. “H.r.” in Table 2, 9 and 12, CPMD on p.27 (reference missing).
4. No attempt has been made to unify terminology. For example, on p. 26 the author talks about “fracture strength“ in the text, while Table 3 clearly distinguishes between “compressive“ and “tensile“ strength and on p. 30, the author even uses the old-fashioned term “modulus of rupture“, as if the author is afraid of clearly stating that this is the



- “flexural strength“ (and the indices „cr“ denote “crushing strength“). This inconsequence in terminology makes reading a little uncomfortable.
5. Many symbols are used in different meanings throughout the work, while on the other hand the same quantities are sometimes denoted by different symbols; apparently no attempt has been made to unify the symbols and to avoid double assignment of symbols for quantities of different meaning, e.g.  $C_1$  and  $C_2$  in equations 7, 10 and 11,  $\rho_b$  in equations 16 and 17 and  $m$  for the Weibull modulus in equation 30 and the “quasi-Newtonian“ viscosity on p. 78. In Tables 9 and 12 the densities are denoted as  $d$  while in the equations as  $\rho$ .
  6. In Table 9 and 12 and in the text on p. 65 the units of fracture toughness are not correct.
  7. Some quantities used in equations are not defined, e.g.  $\Delta T$  and  $E$  in equation 3,  $C_1$  and  $C_2$  in equation 7. Indices are often used without necessity, e.g.  $S_I$  in equation 4.
  8. Reference numbers on pages 30-33 seem to be incorrect.
  9. The references contain a large number of typesetting errors and lack formal unification; many of the references are incomplete or presented in unacceptable form and would certainly not be adequate for journal publication (8, 42, 43, 47, 53, 60, 69, 70, 88, 92, 96, 127, 142, 172, 175, 176, 179, 202, 217).

Concerning details of content I have the following remarks:

1. On p. 13 the definition of “tissue engineering“ seems to be too restrictive. Tissue engineering comprises not only regeneration, but also replacement of damaged tissues by tissues grown in vitro (e.g. using stem cells). Also the term “artificial biological substitutes“ seems not to be very good.
2. On p. 13, “zirconia femoral heads“ are mentioned; however, since the crash of the market in zirconia hip joint implants around the year 2000 (Saint Gobain) these are not produced any more.
3. On p. 14, bone is described as a composite containing high elastic modulus mineral “fibres“; this is misleading, because it gives the wrong impression that the shape of hydroxyapatite particles in bone can be described by a single aspect ratio. This is not the case. Hydroxyapatite particles in bone are nanosized laths, that cannot be adequately described by a single aspect ratio, but are much closer to triaxial ellipsoids.
4. In my opinion Figure 1 (on p. 16) describes tissue engineering in vitro, not in vivo, as claimed in the text.
5. On p. 18 (short version p. 6) the crystalline phase  $\text{Na}_2\text{CaSi}_2\text{O}_6$  is mentioned without a mineral name, while later, on p. 23 (short version p. 8),  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  is explicitly mentioned and defined as “combeite“. On the other hand, on p. 85  $\text{Na}_2\text{CaSi}_2\text{O}_6$  is identified as “combeite high“ (i.e. high-temperature combeite?), but the formation of  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  is mentioned as well, in addition to a phase  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_6$  (probably a misprint), which is claimed to be “isostructural to the high temperature form of  $\text{Na}_2\text{CaSi}_2\text{O}_6$ “ and even a phase of composition  $\text{Na}_2\text{CaSi}_6\text{O}_{16}$ , for which no reference seems to be cited in the text, although urgently needed. All this is very confusing. A small table in which the possibly occurring crystalline phases are listed (together with the two rhenanite phases), would solve all these problems. Unfortunately the student does not give a table of this kind in his work. I would highly recommend showing such a table (showing



- at least the density, symmetry and temperature stability ranges of all these crystalline phases) as a slide in the presentation.
6. On p. 23 the description of starch-based techniques is not correct. “Rice flour“ is not automatically rice starch and “gelling agents“ are usually not added in these techniques.
  7. On p. 25 the statement that replica foams can be considered as “orthotropic with a transversal isotropic behavior“ is self-contradictory. Orthotropic materials have 9 independent elastic constants, transversally isotropic ones have 5. Irrespective of this, however, the author in this work implicitly assumes isotropic behavior, i.e. only 2 independent elastic constants. The author should make this clear.
  8. On p. 25, the reported “average connectivity of 4“ is claimed to confirm the adequacy of the tetrakaidecahedron structure to represent the foam cell. However, in random materials 4 triple junction lines must necessarily meet at one point (quadruple node = vertex), that means X-ray CT is not needed to confirm this. The key point, not mentioned here by the author, is that the tetrakaidecahedron cell results in a space-filling arrangement.
  9. On p. 30 the author cites (with incorrect reference numbers, should be [94] instead of [90,91]) the empirical finding by Hagiwara & Green of a value of 0.3 for  $C_I$  (for replica foams with hollow struts), without however mentioning the fact that the Gibson-Ashby value for this constant is 1. In fact, a value different from 1 is just an empirical correction that makes the GA relation, which is one of the most interesting relations of this kind, useless for smaller porosities. Moreover, the meaning of the sentence „Nevertheless, due to the reduced magnitude of displacements in the elastic region, acquired data are not always reliable.“ is not clear. The author may comment on these points in his defense.
  10. On p. 31 the author repeats the common misunderstanding that the Gibson-Ashby cell is a unit cell for a cubic model. Actually, the problem is that the GA cell is a nice schematic model, but *cannot* be used to build up a cubic structure (the GA structure is orthotropic, i.e. has 9 elastic constants). It is thus not an alternative to the Kelvin cell, as Fig. 11 suggests. However, this is a misunderstanding very common in the literature and the author cannot be blamed for this mistake.
  11. On p. 35 the author reports an elastic modulus of 146 GPa (!) for microfibrillated cellulose. Is this realistic? What do other authors think about that?
  12. On p. 37 the author cites a very special micromechanical model (with the slightly misleading statement in the first line of section 2.5 that Ouali et al. “developed“ percolation theory). It is highly regrettable – and one of the major deficiencies of this work – that the author did not take into account micromechanical models in a more systematic way. This cannot be done without Hashin-Shtrikman bounds. Why use a very special percolation model with empirical parameters when much more rigorous – and simpler – models are available?
  13. On p. 38 the author repeats a common misunderstanding prevailing in the literature, that spark plasma sintering involves electric spark discharge and the occurrence of a “plasma“. In fact, SPS is just a misnomer (should be called “electric-field assisted sintering“ or the like) and has nothing to do with a real “plasma“. However, this is a misunderstanding very common in the literature and the author cannot be blamed for this mistake.
  14. On p. 38 it is claimed that the Young’s modulus of 110 GPa is comparable to that of compact bone. This is not true. (110 GPa is comparable with Ti-based implant materials, but not with bone, not even with compact bone.)



15. On p. 45, are the compositions of the alumina-based foams really in vol.% or in wt.%?
16. On p. 47, if the boron nitride particles are high-energy ball-milled with zirconia balls, has the phase composition been checked after milling? Is there no milling wear debris?
17. On p. 48, it should be emphasized that equation 16 holds only if open porosity is absent.
18. On p. 49,  $\rho_s$  is in general not the “apparent density“, but the bulk density (i.e. the density including closed and open pores). “Apparent density“ is a concept that is well defined as well, but has a different meaning, viz. the density including only closed pores.
19. On p. 49, the mixture rule (equation 20) is wrong. The effective density is calculated as the volume-weighted arithmetic mean, not the mass-weighted arithmetic mean!
20. On p. 51 the description to equation 25 is confusing. Is it for Martens or Vickers? Moreover, since  $A_s(h)$  is function of the indent height  $h$  ( $h_m$ ?), it cannot be at the same time a constant (26.43).
21. On p. 51, the key information for using equation 26 is whether central or Palmqvist cracks are assumed. Please add this information and clarify in the presentation. Is there some way to check whether central or Palmqvist cracks are present? Has this been done in this work? (See also the claim of Palmqvist cracks on p. 86.) Please clarify in the presentation.
22. On p. 51, following equation 27, the meaning of notch angle and notch depth is not clarified. Please explain.
23. On p. 52, equation 28 is wrong. Instead of the second  $b$  there should be the thickness (height) of the bar; moreover, the correction factor does not account for the finite thickness, but for the finite length of the bar.
24. On p. 61, the measured density is  $2.53 \pm 1.53$  g/cm<sup>3</sup>. Please explain the large scatter.
25. On p. 72, are the elastic modulus values in Table 14 from tensile or from compressive tests? Does the author have an explanation for the statement that “the slope-approach generally underestimates the real stiffness“?
26. On p. 78, in my opinion there is an error in the calculation of the “quasi-Newtonian“ viscosity  $m$  (called  $\eta$  in Table 18); the difference cannot be two orders of magnitude (0.0043 versus 0.650 Pas – units are missing on p. 78), see Figure 47a and 47c and Table 18! This should be rechecked!

The 35-page short version of the thesis has evidently been prepared with greater care, although some of the aforementioned points refer also to the short version. The candidate may select some of the more important topics mentioned above and comment on them in his presentation.

Despite these objections in detail, which are mostly problems of the elaboration of the written version of this thesis and seem to be partly the result of time restrictions, the work as a whole is based on a sound philosophy and treats a highly important topic of materials science. It provides many significant results, based obviously on careful experimentation, on which future research in this field may be built. Therefore **I recommend accepting this thesis and award Luca Bertolla a Ph.D. diploma.**

Prague, 3 December 2015

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