

REVIEW

Of the Thesis of
Ing. Richa Saggar

“Processing and properties of 1D and 2D boron nitride nanomaterials reinforced glass composites”

The synthesis of new nano-phases, such as carbon nanotubes and graphene, combined with the use of new densification routes, such as spark plasma sintering, has opened up the possibility of developing new glass/ceramic nanocomposite materials with potentially high fracture toughness. The main objective of the present doctoral thesis was to develop new structural glass nanomaterials reinforced by various kinds of boron nitride based nanofillers, i.e. different structures of BN nanotubes (BNNTs) and/or BN nanosheets (BNNs). The research constitutes a fundamental systematic study of the effect of different BN-based nanofillers on the densification and mechanical properties of one of the most widely used glass, borosilicate glass (BS). The present doctoral thesis is therefore very timely and highly original in nature. I highly appreciate the fact that the BNNs were not sort of a commercial product, but they were produced in the lab and subsequently used to reinforce the glass matrix. This contributes significantly to the nanomaterial processing field. Indeed, the thesis is the first study on the incorporation of BNNs in a glass matrix. The originality and innovation of the work lies in the integration of novel and interesting materials physics at the nanoscale, and characterisation and processing to achieve the objective of the thesis.

Theoretical background of the thesis provides a nice introduction into the topic and was prepared with sufficient number of literature data, but in my opinion it could have been a bit longer with more details provided (currently on 27 pages). In particular, incomplete information on the works previously done is provided. For example, when talking about previously reported works, it is insufficient to say something like “they used CNTs (or graphene, or BNNTs, or...) in any particular matrix and obtained better properties.” For the benefits of readers, it would be better if the information also included how much of the reinforcing agents was used, what properties they investigated and, most importantly, how significant was the contribution. In addition, it is a shame Ing. Saggar took the role of an inactive observer and she did not critically discuss the results previously obtained by others. Particularly, the extensive number of papers on the reinforcement of brittle matrices by nanofillers has been published with discrepant results. Some candidate insights on the topic would

have been pretty much appreciated. In the last point, although the thesis is focused on development of a new style of glass nanomaterials, the literature survey covers both glass and ceramic materials reinforced by nanofillers. That would be fine, but I do not understand why in some of the subchapters, there are only works on ceramics rather than glasses given as examples (very often seen in the 2.3 part "Sintering of glass ceramic composites"). This brings up the question how relevant are these sintering techniques for manufacturing new glass materials if no work on glass is given as a reference? In the results and discussion parts of the paper, the author said the BN-fillers could hinder the viscous flow of the glass during sintering. However, no theory on sintering of glass is given in the theoretical background, and the readers could get an impression this part of thesis is focused more on ceramics rather than glasses. Many of the results obtained by others are just reported; I miss any concluding part at the end of the theoretical background, which would compare and summarise all the works with the conclusion that incorporation of what type of reinforcing agents led to the best improvement in glass and/or ceramic matrices. Based on this, it is not clear what are some measurable indicators of progress beyond the current state-of-the-art that the present PhD aimed to achieve (e.g. what fracture toughness value could be consider as significant improvement of the state-of-the art, etc.....).

However, the experiments were carried out in such a way that some of these problems could be solved. In her experimental program, Ing. Richa Sagggar produced 4 different types of glass nanomaterials with different loading of the BN-based reinforcement (2.5 and 5 wt% of BNNTs or BNNSs). The densification and mechanical properties were compared to the reference pure borosilicate material. All the materials were produced using a relatively new advanced consolidation technique, Spark Plasma Sintering (SPS). The main part of the experimental work was then focused on the investigation of fracture behaviour of these materials; mainly fracture toughness, but also strength and wear resistance. The experimental program was very well planed and perfectly executed. It is obvious that Ing. Sagggar used and became familiar with numerous experimental methods; many of them were used in the collaboration with foreign Institutions (mainly Queen Mary University of London in the UK, Institute of Materials Research in Slovakia, or Joint Glass Centre of Institute of Inorganic Chemistry in Slovakia). This has definitely contributed to the scientific outputs of the present work. Some examples are SEM, TEM, X-ray diffraction methods for crystalline phase characterisation, EDS for chemical analysis, Zeta potential for electrostatic charge of the particles, and TGA for investigation of the onset of the oxidation of BN nanofillers. The elastic modulus was investigated using the impulse excitation resonance method and hardness was assessed by the Vickers method. The fracture toughness was determined using both indentation and Chevron notched beam techniques. The strength was measured in three-point bending mode using standard flexural strength specimens. Special attention was given to the wear resistance of the materials, which was characterised by single pass scratch resistance and unlubricated ball-on-disc experiments, combined with profilometer and confocal microscope measurements to determine the wear profile.


With this work, Ing. Richa Saggar contributed to the understanding of the influence of BN-based 1D and 2D nanofillers on the development of structural borosilicate glass. Some of the important questions, which I am sure can be all answered during her PhD defence, have not been clearly addressed. A simple example is presented in the following: One of the main conclusions of the work is that the BNNSs provided better reinforcement than their nanotubes counterpart (BNNTs); ~ 30 vs. 45% for BNNTs and BNNSs, respectively. The quantitative extent of the improvement was assessed in comparison with the reference pure borosilicate glass. However, I have difficulties in understanding why the results were compared to the two apparently different monolithic pure borosilicate glasses. For the BNNTs- part of the work, the pure BS showed the fracture toughness of $0.85 \text{ MPa}\cdot\text{m}^{1/2}$ while in the BNNSs- part the reference BS material had "only" $0.76 \text{ MPa}\cdot\text{m}^{1/2}$. In both cases, it was the same BS matrix the results are compared to, wasn't it? According to the description of the experiments, the pure BS was prepared using the same borosilicate powder and same consolidation technique in both cases. If the results of fracture toughness of BNNSs-reinforced BS glasses had been compared to the same value of fracture toughness of pure BS as BNNTs-composites, the "toughening" would have been in a similar level and the difference between BNNSs and BNNTs would be less significant.

In summary the doctoral thesis represents a systematic and well conducted scientific work in the new and very promising field of the material science, nanomaterials. It gives a consistent and valuable basis for the designing and further development of new brittle materials reinforced with nanofillers. This work will have a significant impact on the processing of these materials. Ing. Richa Saggar has published/co-published 4 scientific papers in well-recognised ceramics journals. This is a hint for the international recognition of his work.

The experimental work is outstanding with some of modern advanced characterisation techniques used. The work is the first study on the influence of BNNSs on a glass matrix. Moreover, for the first time, two very important and popular styles of reinforcement, 1D (BNNTs) and 2D (BNNSs) were studied and compared. The fracture toughness of the borosilicate glass matrix was reinforced at least by 30%, what can be considered as a significant achievement in this field. Therefore I believe the candidate successfully achieved all the tasks of the thesis proposed on the pages 43 and 44. In contrast the critical assessment of this work is too short and a little weak. Nevertheless, and especially taking into account the international recognition, the work is in summary excellent.

The reviewer proposes to award Ing. Richa Saggar the academic title of "philosophiae doctor".

Kosice, 06.12.2016


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