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COMMENTS ON THE PHD THESIS ELABORATED BY RAMIN HOSSEINNEZHAD FROM THE CENTRE OF MOLECULAR AND MACROMOLECULAR STUDIES, POLISH ACADEMY OF SCIENCES, ON "BIOCOMPOSITES WITH NANOFIBERS GENERATED BY SHEAR AND SHEAR INDUCED CRYSTALLIZATION", UNDER THE SUPERVISION OF DR HAB. IURII VOZNIAK

BASIC INFORMATION ABOUT THE CANDIDATE

Ramin Hosseinnezhad received a Bachelor of Science degree in Chemical Engineering from the University of Tazbir, Iran in 2010 and a Master's degree in Chemical Engineering-Polymer from Sahand University of Technology, Iran in 2012. From 2012 till 2013 he was employed as Teacher Assistant at Sahand University of Technology, from 2013 – 2018 he was Research and Development Specialist at Mazandaran Wood and Paper Industries and from 2018 till now he is employed as Scientific Research Specialist at the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences in Łódź. He is co-author of 7 papers published in international journals, one patent application, and 6 contributions presented at international conferences.

ASSESSMENT OF THE DOCTORAL DISSERTATION

The PhD thesis of Ramin Hosseinnezhad is aimed at the development of the concept of in-situ generation of "green all-polymer" nanocomposites, where the nanofibers of one biopolymer are formed inside the second biopolymer during shear processing in a melt. The thesis has been completed under the supervision of dr hab. Iurii Vozniak at the research group of Professor Andrzej Gałęski. Therefore, it is not surprising that it was oriented on the subject of research excellence of this research group and fits very well with the current social needs.

The layout of the thesis is rather "classic" and includes Abstract (both in English and Polish), Introduction, State of knowledge (29 pages), Objective of the thesis, Experimental part, Results and discussion including Conclusions (93 pages) as well as the References. Thus, the appropriate balance was achieved between the literature survey and the discussion of the presented results. Moreover, a list of figures and tables, a list of publications, patent application, and presentations of the candidate, where he was co-author, as well as his academic biography were attached at the end of the dissertation

The literature survey (with 274 references) is well written and reflects the current state of knowledge related to the subject of the thesis. It includes four major aspects: (i) the concept of microfibrillar composite, (ii) polymer nanofibers formulation from melt processes, (iii) hybridization of microfibrillar composites, and (iv) shape memory microfibrillar composites. The biodegradation properties of the materials constituted the subject of the thesis were not discussed.

Based on the analyzed state of knowledge the objective of the thesis has been formulated and the plan of the research performed, including the following steps, was provided:

- studying shear-induced crystallization of different biopolymers to establish the effect of the shearing rates on the peak crystallization temperature; selection of biopolymers with remarkable increase the crystallization temperature under shear deformation;
- selection of the related pairs of biopolymers and succeeding conversion of polymer blends into in situ composites;
- formation of hybrid polymer blends and further conversion into in situ “all-polymer” composites that contain rigid and tough fibers;
- characterization of the obtained nanocomposites

One of the main goals of the dissertation was aimed at the formation of continuous nano-sized fibers characterized by the maximum aspect ratio, degree of molecular orientation, and crystallinity degree.

The experimental part of the dissertation includes a description of the materials used, sample preparation, mechanical and thermal tests performed, SEM, rheo-optical measurements, shear-induced crystallization test, SAXS, WAXS, and Shape memory tests. The research methods used were adequate to complete the scope of the dissertation. A minor remark concerns the lack of the molecular structure evaluation of the PHA used in these studies.

Results and discussion are presented in a very logical way and were devoted to the studies on the role of interfacial interaction, the effect of viscoelasticity, the effect of shear-induced crystallization, morphology characterization, mechanical and rheological properties of the materials studied, crazing-shear banding evolution process, microstructural evolution, thermal and dynamic mechanical analysis, characterization of hybrid composites studied as well as triple shape memory properties of the composites evaluated.

The performed research has shown, among others, that:

- the shear-induced crystallization of nanofibers studied is influenced by the viscosity of inclusions
- viscosity and elasticity ratios, as well as interfacial interaction, were the major parameters dominating the morphology of the dispersed polymer inclusions
- the in-situ generated PLA/PBAT (94/6) composite, compared to the respective blend, exhibited a 1.4-fold increased Young's modulus, 1.1-fold increased yield stress, 1.7-fold increased tensile impact strength, 1.3-fold increased stress at break, and 10-fold increased strain at break
- the improvement in the performance of nanocomposites was achieved through hybridization of all-polymer composites studied
- the in-situ generated shape memory composites showed drastically higher values of strain recovery ratios, strain fixity ratios, faster recovery rate, and better mechanical properties as compared to the respective blends.

Thus, the results of performed research indicate, that the main goal of the thesis i.e. the formation of "green all-polymer" nanocomposites in a single step has been achieved in the case of polymers studied. However, the open problem of the nanocomposites biodegradation in comparison to the respective blends would need further studies. Previous studies on Ecoflex® degradation in soil and on its ecotoxicological impact revealed the retention of aromatic chain fragments in the low molar mass fraction of the incubated sample (compare e.g.: Biomacromolecules 2010, 11, 839–847). Nevertheless, the thesis contains many interesting and original results. The author managed to use polymer physics in the characterization of novel composites with nanofibers generated by shear and shear-induced crystallization – using advanced instrumental techniques. Most of the results covered by the patent application are of real interest for different specific applications. The originality of the results is also proven by

their publication in international journals and by their presentation at national/international conferences.

In conclusion, the doctoral dissertation is well written, and the number of editorial errors and inaccuracies is small and does not differ from the average for this type of work. Thus, I consider that Ramin Hosseinnezhad deserves to receive the doctorate degree and in my opinion, the dissertation fulfills all requirements for Ph.D. These, stated in the Polish law (the Act on Scientific Degrees and Title). Consequently, my recommendation to the Scientific Council of CMMS PAS is to proceed into the next steps of the Ph.D. qualification procedure of Ramin Hosseinnezhad.

Zabrze, November 02, 2021