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HR EXCELLENCE IN RESEARCH

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Review of the PhD Thesis

'Polymeric membranes and mixed matrix membranes (MMMs) for carbon dioxide separation'

by MSc Guoqiang Li

The doctoral thesis which I had a great pleasure to review is titled 'Polymeric membranes and mixed matrix membranes (MMMs) for carbon dioxide separation'. It was conducted by MSc Guoqiang Li under the supervision of Professor Wojciech Kujawski. Dr hab. Joanna Kujawa, NCU Prof. was a co-supervisor.

The PhD thesis was performed at The Nicolaus Copernicus University in Toruń, at the Department of Physical Chemistry and Polymer Physical Chemistry. The Department Head is Professor Wojciech Kujawski.

1. Thesis content

The presented PhD thesis follows a classical structure. It has been composed in accordance with the academic standards. It is written in English. It consists of 204 pages. It is organized in the following sections: abbreviations and nomenclature, introduction, conducted research, conclusions, future

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work and research directions, references, abstract (in English and Polish), list of publications included in the PhD thesis, academic achievements of MSc Guoqiang Li, statements of co-authors (in Polish and English) and copies of the above-mentioned publications.

The doctoral thesis was prepared in the form of a thematically consistent series of six publications. Although these papers are multi-authored, in all of them, MSc Guoqiang Li is the first author. His contribution of the above-mentioned works is substantial and crucial. Indeed, according to attached declarations it was between 45 and 65%. The obtained results were published in specialized journals, such as: International Journal of Greenhouse Gas Control, Membranes, Polymers, Materials, Chemical Engineering Research and Design as well as RSC Advances. It should be emphasized that the current Impact Factor of these journals is high and ranges between 3.4 and 5.0.

2. Quality of the work

The literature review presented in the first Chapter is well-structured. It perfectly introduces the reader to the scientific topic of the PhD thesis. Indeed, it describes the issue of biogas purification as well as it demonstrates that membrane technologies have both great potential and practical value in the industrial gas separation processes. Moreover, in this part, a very detailed and valuable characterization of polymeric membranes and mixed matrix membranes has been presented. Overall, the bibliographic references are adequate. MSc Guoqiang Li cited 108 works, of which articles published in the last 5 years constitute 63% (68 items) of all literature. Hence, it can be concluded that MSc Guoqiang Li demonstrates the knowledge of the most important and current issues in the field of both membrane technologies and gas separation, and the PhD thesis was based on a very good and detailed literature overview. It is also confirmed by the publication of very extensive review paper by MSc Guoqiang Li which is part of the presented PhD thesis. More precisely, the article presents an in-depth analysis of the development of hollow fiber membranes used for gas separation processes.

The membrane gas separation is a well-known technology since it was first established in the 1980's in order to remove CO_2 from natural gas. Nevertheless, MSc Guoqiang Li rightly noted that nowadays, investigations focused on the membrane materials, fabrication techniques as well as the optimization of the membrane gas separation processes are highly demanded. The introduction ends with a presentation of the five most important goals of the work undertaken. The main objectives of the PhD thesis can be synthesized around the following tasks: fabrication and characterization of hollow fiber membranes as well as the fabrication and characterization of flat sheet mixed matrix membranes. The objectives have been well defined and clearly presented. It is important to note that the aim of the PhD thesis was very ambitious and seamlessly aligns with the ongoing research trends in the fields of membrane technologies and gas separation processes. MSc Guoqiang Li dealt excellently with his tasks and demonstrated an ability to formulate innovative ideas for investigating polymeric and mixed matrix membranes dedicated for carbon dioxide separation.

The second Chapter demonstrates research conducted in the thesis. More precisely, it demonstrates the most important results which have been presented in the above-mentioned articles by MSc Guoqiang Li. This Chapter is divided into two subchapters. The first subchapter focuses on the fabrication and characterization of hollow fiber membranes. The second one, describes detailed studies on the fabrication and characterization of flat sheet mixed matrix membranes. The experimental works have been appropriately directed towards addressing aims of the PhD thesis. The obtained results were reported competently. The quality of the Figures and Tables used to concisely present the selected results is very high. Analysis of the experimental data is deep. The discussion and interpretation are at the high scientific level. It is worth mentioning that each subchapter ends with key findings, which are clearly presented.

The third Chapter concisely and synthetically presents the most important conclusions. This section is written correctly, very clearly and concisely presents the results obtained. As the important, interesting, and

significantly original achievements of the presented PhD thesis I consider demonstration that in the case of polyetherimide hollow fibers fabricated by using a dry-jet-wet spinning technique and PDMS/PEI TFC-HFMs by using the dip-coating method:

- The membranes pore structure, skin layer thickness, the wall thickness, outer diameter, and gas permeance are influenced by several factors, such as the polymer concentration, bore fluid flow rate, and the composition of bore fluid,
- Gas permeance and CO_2/N_2 ideal selectivity of PDMS/PEI TFC-HFMs is influenced by the spinning conditions,
- The thickness of PDMS layer, gas permeability, and CO_2/N_2 ideal selectivity are predominantly influenced by the concentration and composition of coating solution and the coating time.

In turn, in the case of fabrication of Pebax® 2533-based HF-MMMs and flat sheet mixed matrix membranes, as the important, interesting, and significantly original results I consider demonstration that:

- The incorporation of proper amount of fillers into the Pebax® 2533 matrix increases the CO_2 permeability and the ideal selectivity of the prepared mixed matrix membranes,
- Incorporation of too high amount of fillers incorporated into Pebax® 2533 matrix results in the adverse effects on the gas separation performance of mixed matrix membranes,
- ZIF-8-PEI@IL is characterised by enhanced compatibility with polymer matrix and enhanced gas separation performance,
- MIL-GO-2-Pebax® 2533/PVDF mixed matrix membranes show increased CO_2 permeability and the CO_2/N_2 ideal selectivity.

Finally, the fourth Chapter presents the recommendations for future work and research directions. MSc Guoqiang Li rightly indicated that further scientific works are necessary. Indeed, results showing the membranes properties used to separate gas mixtures would be very interesting. In addition, MSc Guoqiang Li clearly pointed out that further utilization of metal

organic framework in the preparation of mixed matrix membranes is highly recommended.

There is no doubt that the results obtained in the presented PhD thesis have the high application potential. *Therefore, I would like to kindly ask MSc Guoqiang Li to answer the following questions: Is the possibility of using the tested membranes on an industrial scale being considered? Are there any indications that these membranes will maintain the desired properties during long-term use? Is MSc Guoqiang Li going to investigate such aspects?*

The presented PhD is of exceptional overall quality. It is rich in content and understandable. MSc Guoqiang Li proved that he can successfully share obtained results both by publishing scientific articles as well as by giving oral presentations. I would like to emphasize scientific achievements of MSc Guoqiang Li. It must be stressed that MSc Guoqiang Li is an co-author of 23 papers published in the International Journals with the total Impact Factor equal to 152.9. It is an excellent result. In addition, MSc Guoqiang Li participated in five research projects and was co-author of 10 lectures presented at conferences. Finally, it should be pointed out that MSc Guoqiang Li significantly expanded his professional and scientific network completing five international internships.

3. Originality

The doctoral thesis is an outstanding contribution to the development of membrane technologies. Indeed, it demonstrates a significant amount of original and innovation work. The proposed methods and obtained results show the highest level of novelty that can be found in the field of polymeric membranes and mixed matrix membranes for gas separation. An important point which should be noted is that the originality of the PhD thesis is also proven by high quality publication achievements. As it has been indicated earlier, the results obtained by MSc Guoqiang Li have been presented and discussed in detail in the peer-reviewed scientific articles.

4. Conclusions

In conclusion, I hereby declare that the doctoral thesis entitled 'Polymeric membranes and mixed matrix membranes (MMMs) for carbon dioxide separation' written by MSc Guoqiang Li fulfils with great excess the requirements for doctoral dissertations according to the paragraph 187.2 of the Act of 20 July 2018 – The Law on Higher Education and Science (Journal of Laws of 2018, item 1669 as amended). Therefore, I strongly recommend that the Discipline of Chemical Sciences Council of the Nicolaus Copernicus University in Toruń approves MSc Guoqiang Li for public defence of the PhD thesis.

I hereby recommend the presented doctoral thesis for distinction. It is justified by the high quality of results obtained, reliable and systematic implementation and innovative solutions with high application potential. It should be pointed out that the presented approach is very promising and may significantly contribute to the wider use of membrane technologies for gas separation. Finally, I would like to point out admirable scientific achievements of MSc Guoqiang Li.

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