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Prof. dr hab. inż. Stanisław Krompiec
Wydział Nauk Ścisłych i Technicznych
Instytut Chemii
Uniwersytet Śląski w Katowicach

Review of MSc Myong Joon Oh's doctoral thesis entitled:
Development of novel silicon-based coupling agents as silica filler dispersants for „green" tire compounds".

Mr Myong Joon Oh's thesis is devoted to chemistry and technology of modern tires, which is undoubtedly a true challenge for the industry. Designing, synthesis and multidimensional examination of physicochemical properties of new coupling agents for „green" tire application is the essence of MJO's dissertation.

It is worth to emphasize that the MJO's research was realized within the framework of the project "HighChem – interdisciplinary and international Ph.D. studies with the elements of cross sector cooperation support", project number POWR.03.02.00-00-I020/17. Importantly, the above mentioned research was realized in cooperation with Synthos S.A. in Oświęcim and Synthos Schkopau GmbH in Schokpau, Germany. Moreover, the project was also a part of a scholarship programme Synthos Generation dedicated to young and talented scientist. All these facts confirm that the scientific area which MJO's thesis focuses on has been positively assessed by experts, including specialists from tire industry.

The dissertation is divided into seven chapters, which is not typical, but it is not a problem for readers and reviewers. One should add that each chapter constitutes an individual and separate entity. In Chapter 3,4 and 5 the Author presents the results of his research. In each of them we can find the main purpose, state of the art theoretical background and finally the Author's examination results. Other typical and essential elements of any thesis, namely, summaries, contents, list of NMR and HRMS analyses, quoted literature and Author's scientific achievements are present in this dissertation (166 pages in total). I noticed lack of the list of abbreviations- it is indispensable, especially due to the fact that this work is divided into isolated chapters.

Next, I am going to provide comments concerning particular fragments of the dissertation, in the order of appearance. Following the Author's description: Chapter 1 – at first, background and rationale of the research are quickly introduced, followed by aim of the thesis and description of the tasks carried out. I have no critical remarks. Namely, the Author clearly presented theoretical background, rationalization of his research and all research goals. The main objective of the project was to develop novel compounds as silica filler dispersants and investigate their influence on the behaviour of the derived SSBR/BR/SiO_2 composite materials, in reference to widely used SCAs (**Figure 1.2**). Another important goal was to

accentuate cost-efficiency and sustainability of those coupling agents during synthesis and application, in order to maximize their commercialization potential. In the subsequent parts of this thesis, the Author presents groups of compounds which were designed and synthesised, namely N-SCAs and silatrane derivatives, followed by a convincing justification of their selection. It is worth to emphasize that crucial synthetic procedures are fully innovative, which increases the value of the whole dissertation.

Moreover, key properties of the obtained elastomer samples were thoroughly characterized (rheological studies, mechanical testing, dynamic-mechanical-thermal analysis). Finally, the obtained SiO2/rubber samples were compared to reference composite materials, resulting in the establishment of some guidelines which will contribute to progression in the field of rubber compounding, useful for the other research groups striving to obtain high silica content in car tire. As far as economic analysis is concerned, it is impossible to provide realistic calculation of the whole cost of new compounds implementation to the industry. According to me, such an analysis would be realistic only during the step of implementation into industry, but in cooperation with Synthos S.A.

Chapter 2 – This part is a detailed literature review on tire compounding. Physical sense of tire performance parameters, tire testing methods and tire ingredients are discussed, which was intended to help readers better understand experimental sections in further chapters. Moreover, the historical background and recent progress on SCAs used in tire compounding are presented. In this case, I also have no critical remarks. As for positive ones, it is very well written, which enables any reviewer who is not a specialist in the tire industry to gain knowledge concerning the current state of this technology as well as challenges which scientists still face in this area. The quoted literature is fully satisfactory and really impressive. I have only one remark referring to the structures presented in Fig. 2.17: why were arrows and dashed lines used? Another issue is charge distribution. Furthermore, the structure of Zn complex shown in Fig. 2.16. is incorrect.

Chapter 3 – Here starts the first experimental chapter in this thesis. The idea of new, nitrogen-containing SCAs is presented followed by detailed discussion about molecule designing, synthesis and application potential of the studied materials in tire compounding. The results and the comments were presented in a very professional manner. However, the application tests require comments given by a professionalist. According to me, the application tests are very thorough and confirm the attractiveness of the obtained compounds for tire industry. As far as synthetic procedure is concerned, I would like to ask the Author how he overcame the problem of extreme hygroscopic properties of the compounds and susceptibility to hydrolysis, especially SiOMe groups. Secondly, were ring opening products observed in the reaction with epoxide?

Chapter 4 – This chapter begins with a critical literature review on properties, preparation and potential application of silatranes as a novel class of coupling agents. Then, a new organocatalytic protocol for obtainment of silatranes is presented, along with catalyst screening, catalyst activity studies and the reaction mechanism. The versatility and efficiency of the developed procedure is proven by a library of examples obtained. As far as the

syntheses presented in Fig. 4.1. are concerned, I suggest attempts in PTC conditions, especially using 18-Crown-6. Additionally, looking at the results given in the tables 4.2. and 4.3. I would have a similar suggestion, namely to carry out reactions in the presence of t-BuOK/18-crown-6 in THF, which might be effective. Perhaps also failed syntheses shown in Table 4.4. could be successfully realized in the presence of t-BuOK/18-crown-6 system in THF, rt. Regarding the transesterification mechanism presented in page 105, it is less realistic according to me. Namely, the formation of a four-membered transition state would be characterized with very high activation energy. It would result from the presence of very large substituent joined to all atoms which create the above mentioned transition state. According to me, this is a multi-step reaction: deprotonation of OH group by DBU, followed by nucleophilic attack at the Si atom via SN_2 or addition-elimination mechanism. Finally, proton exchange and DBU and alcohol creation take place. Moreover, charge distribution presented in figure is only formal, but not realistic.

Chapter 5 – Continuing the studies from Chapter 4, this chapter discusses the development of novel silatrane coupling agents for "green" tire application synthesized with the newly discovered procedure. The synthetic procedures are adequately described and the product physicochemical characterization is appropriate- I have no critical remarks. Maybe only arrows or dashed lines in Fig. 5.1. might be changed. As for the reactions which finished with failure, I propose to use PTC conditions during next attempts, especially for reactions 2 and 3. Next, the application test results of the obtained silatrane coupling agents are discussed, in reference to commercial silane coupling agent counterparts. Different behaviours of silane- and silatrane coupling agents in silica-filled rubber compounds with follow-up experiments were explained. The application tests are also sufficient, taking into consideration the current stage of this research. However, an in-depth analysis and assessment of this fragment requires a specialist in the technology. My competence in this area is limited and I do not feel qualified to perform such an investigation. To sum up, I would like to accentuate the fact that according to me, the Author showed the attractiveness of the obtained compounds for "green tire industry".

Chapter 6 – The last chapter summarizes key results and new discoveries made from all previous chapters. Namely, taking into consideration current trends and requirements, the main goal of the research described in this thesis was to develop novel coupling agents in an ecological and economical manner that would also allow improve overall performance of "green" tires. For this purpose, a group of novel organosilicon compounds, namely *N*-containing trialkoxysilane derivatives and *S*-functionalized silatrane derivatives was designed and synthesized. Importantly, all compounds were obtained *via* straightforward catalytic or stoichiometric transformations using widely-available, low-price chemicals only. In the next step, selected silicon derivatives were applied as silica dispersants in the preparation of tire tread materials. The key properties of the obtained rubber compounds were compared to reference samples based on TESPT or other commercial silane coupling agents. In overall conclusion, the Author claimed that combining all the results gained in the all the experimental chapters, it can be stated that the primary objective of this research has been accomplished. I share this opinion and notice that the scientific results of this dissertation are

truly at the highest level. The syntheses which finished with failure do not have any influence on my final assessment. True scientists are aware of the fact that if everything turns out to be successful, it an obvious indication that the work was characterized with low innovativity, or was even incremental. Furthermore, this thesis will certainly provide valuable information to those seeking state-of-the-art coupling agent systems, as well as basic knowledge about rubber compounding. I share the Author's opinion as far as the importance of the results presented in this thesis is concerned. The main goal of the basic research is to provide new knowledge to scientists who implement it into technology. I hope that the Author protects his innovative solutions by patent applications.

Chapter 7 (Appendix) This part of the dissertation consists of NMR spectra and HRMS analysis of the obtained compounds. I have no objections- both the spectra and HRMS analysis quality are very high.

Pages 166-168 are devoted to the Author's scientific achievements, which are impressive! Five publications in prestigious scientific journals (as a co-author), one patent (co-author), 11 times an active participant in conferences, in Poland and abroad (as a main author). It is worth to notice that the research was realized within the framework of the project "HighChem – interdisciplinary and international Ph.D. studies with the elements of cross sector cooperation support", project number POWR.03.02.00-00-I020/17, realized in cooperation with Synthos S.A. in Oświęcim and Synthos Schkopau GmbH in Schokpau, Germany. The project was also a part of a scholarship programme Synthos Generation. Taking into consideration the above mentioned circumstances, I have no doubts that MJO's academic achievements are impressive, predisposing the Author to be granted an honours degree, which I would like to apply for on his behalf.

Finally, one more comment concerning the graphical and language form of this dissertation. My assessment of these elements is really high. Obviously, some minor mistakes can be found. However, I do not tend to enumerate technical errors, since they do not have an influence on the scientific work's assessment.

To sum up, MJO's dissertation meets all legal expectations as well as standard expectations existing in the chemical community. Therefore, I recommend the Scientific Council of Chemical Sciences, Faculty of Chemistry UAM in Poznań to grant a Ph.D. degree in chemical science. Taking into consideration the exceptional scientific level of this dissertation, I propose to award MJO an honours degree. Importantly, the scientific results of this dissertation have already been partially published in prestigious scientific journals. The above mentioned scientific achievements, namely publications, patent, conferences, and cooperation with industry, rationalize and emphasize my high assessment of this thesis. Due to this fact, I do not feel forced to rationalize in much more detail my recommendation to grant an honours degree.

Stanisław Krompiec

Stanisław Krompiec
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