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Bydgoszcz, 11.05.2024r.

# Review of
# Doctoral thesis of Tomy Muringayil Joseph, MSc
# entitled „Copolymerisation studies of cardanol-based monomers towards the development of novel thermoplastic elastomers via ATRP"

**Basis for the development of the review**

The review was prepared on the basis of a letter of March 26, 2024 sent by the Chairwoman of the Chemical Sciences Discipline Council of the Gdańsk University of Technology, Prof. Agata Kot-Wasik.

**Subject of the review**

The doctoral thesis submitted for review by Tomy Muringayil Josephm, MSc. addresses an important and timely issue in the field of technologies based on alternative materials to traditional materials dependent on fossil sources.

The doctoral thesis submitted for review was written at the Department of Polymer Technology of the Gdańsk University of Technology, under the scientific supervision of Prof. Józef Haponiuk and Dr. Kattimuttathu Ittar Suresh.

It should be emphasized that the assessed doctoral dissertation presents very valuable research results of an applied and cognitive nature. Moreover, it fits perfectly into the global research trend regarding the development of new techniques and the search for new, easily renewable sources of raw materials.

**Choosing the topic of the doctoral thesis**

Mr. Tomy Muringayil Joseph's research conducted as part of his doctoral thesis concerns the current and intensively researched research area of designing new polymer materials. Modern materials are subject to high operational requirements, which, in turn, often force the development of new technologies and the search for new sources of raw materials. In particular,

polymeric materials are an example of a dynamically developing group. Their properties and structural characteristics enable the implementation of innovations and pioneering methods, ensuring the implementation of advanced technological solutions.

The basic raw material for the production of polymers is crude oil, which is a non-renewable raw material and whose resources are decreasing rapidly. Plastics produced from mining fuels pollute the natural environment very much because, among others, are characterized by extremely long decomposition times. Innovative polymer production technologies are methods that fully meet environmental requirements. The aim is to reduce energy consumption and increase production efficiency. Analyzing the development of the plastics industry over the last several decades, it seems that plastics (and polymer-based materials in particular) will continue to be in the spotlight. These materials are ideal for implementing new discoveries and ideas of scientists. They also have a real contribution to solving humanity's current and future challenges.

There is a common trend towards modifying polymeric materials to improve their biodegradability, chemical and mechanical resistance, ease of processing and transport. Reducing the dependence of plastics production on crude oil and reducing effective greenhouse gas emissions are also of great importance.

The development of the plastics industry cannot be at the expense of the degradation of the natural environment. The principles of clean production encourage minimizing the amount of waste generated in production processes, and at the same time force the search for raw materials from renewable sources. In this context, it is important to develop new technologies for producing innovative materials. Their production, use, and subsequent disposal will have minimal adverse impact on the natural environment.

Therefore, I consider the choice of the research topic to be purposeful and very valuable, both in scientific and technological terms. The topic of the doctoral thesis submitted for evaluation concerns an important research area, especially in recent years, which is polymeric materials containing a natural by-product - cardanol. The chemical modification of cardanol allows it to be copolymerized with styrene using the ATRP technique. This leads to the synthesis of copolymers based on renewable raw materials to optimize their properties.

The reviewed doctoral thesis fits perfectly into current trends in research on materials of natural origin. The research carried out is based on sustainable technology and covers important aspects that bring measurable cognitive and utilitarian benefits. In addition, they meet the challenges faced by modern materials science.

**General characteristics of the dissertation**

Mr. Tomy Muringayil Joseph's doctoral thesis is a scientific work in which experimental research is of key importance. However, it should also be highlighted that it is the result of properly conducted literature studies.

This doctoral thesis has a conventional layout, with the division of chapters typical of scientific theses. The author systematized the presented issues correctly. The structure of the chapters, as well as other editorial elements, is well thought out, logical and coherent. This enabled the Author to justifiably implement the research concepts indicated in the thesis. I positively assess the dependence between the title of the thesis, its structure and substantive content.

The doctoral thesis has 135 pages. It was divided into two main parts - literature and experimental. The literature part covers 57 pages, while the experimental part covers 78 pages. This proves the correct balance of theoretical knowledge and research performed as well as discussion of obtained results. This thesis is characterized by the classic structure of doctoral theses in engineering and technical sciences. It contains: table of contents, list of the most important abbreviations, introduction, literature part, aim and scope of the work, experimental part (including a description of the research methodology with a discussion of the obtained results), summary and conclusions, bibliography, list of figures and tables and a summary in Polish and English. The work contains a total of 38 tables and figures: 8 of them concern the analysis of literature references, while 30 describe the PhD student's achievements. This comparison confirms that the aspect of enriching the state of knowledge prevails over the analysis of the current state, which is the correct relationship. The illustrations and tables presented are characterized by a high level of graphic design - they are transparent and easy to interpret.

The thesis consists of 5 main chapters and subchapters, making the table of contents extensive, detailed and exhaustive. The titles of chapters and subchapters were formulated correctly and consistent with their content. The chapters are preceded by a short introduction, which is a traditional introduction to the topic, outlines the background of the research problem, and thus justifies the purposefulness of the undertaken research direction. It introduces content that is important from the point of view of the research idea's belonging to the selected discipline and the formulation of the research problem. The bibliography contains 164 items. The selection of individual items is appropriate and includes a list of the most important literature on the subject of research from recent years, indicating understanding of the subject at a global level. The thesis ends with a list of the PhD student's research achievements, which include

publications (24) and participation in conferences and workshops (12), of which the PhD student was a co-author. The thesis raises no objections from the formal point of view.

**Substantive assessment of the dissertation**

This doctoral thesis concerns the synthesis and characterization of the properties of cardanol-based polymers and copolymers obtained using atom transfer radical polymerization (ATRP).

In the further part of the literature analysis, cardanol was characterized. It was one of the raw materials used by the PhD student in the experimental part. It is obtained from anacardic acid, which is the main ingredient of Cashew Nut Shell Liquid (CNSL). In turn, CNSL is a by-product of cashew nut shell processing. There are many possible applications of cardanol due to its molecular structure and functional groups. One of the greatest advantages of cardanol is the ease of chemical modification to obtain the desired structure changes. As a result of modification, high-quality polymer materials can be obtained, including: for use as coatings or adhesives. Most of the structure changes are related to the modification of the hydroxyl group in the aromatic ring or the modification of the unsaturated side chain. The molecular structure of cardanol, especially the unsaturation in the hydrocarbon chain, influences the ease of forming polymerization chains. Moreover, the side chain influences the hydrophobic properties of the polymer. This makes the coating based on it more resistant to water and external factors, and at the same time has increased adhesion.

Then, key information related to the Atom Transfer Radical Polymerization technique was presented. ATRP is an important technique that allows you to obtain precisely defined molecules. Minimizing the termination step is possible by keeping most of the polymerization centers in an inactive form. Activation of polymerization centers occurs by transferring a halogen atom from the polymerization center to the ATRP catalyst (activator), generating a radical in the polymerization center and a deactivator molecule. The activator is a strong reducing agent, so it easily undergoes an oxidation reaction to form a deactivator.

A very important element of the thesis is the identification of the characteristic features of the atom transfer radical polymerization (ATRP) technique, i.e. strict control of average molecular weights, low dispersity of the obtained polymers and the introduction of various functional groups into the polymers at different places in their main chains.

Summarizing the literature part, I can say that it is logical and focuses the reader's attention on the issues raised in the main part of the thesis. The author comprehensively described all theoretical content discussed. He demonstrated professionalism and knowledge of

the subject matter. In my opinion, in some places it goes a bit too extensively beyond the main topic of the thesis.

The main aim of the experimental work presented by the PhD student in the reviewed thesis was to develop a method and evaluate the properties of a copolymer derived from cardanol, which was a by-product of cashew nut processing.

The author included a description of the activities to achieve the set scientific aim in the part presenting the conducted research. It was divided into several chapters presenting individual research stages. This was a very good solution, considering the large number of studies that the Author carried out.

The first stage of research work can be called the preparatory stage, because the PhD student initially focused on a detailed discussion of issues related to all raw materials used in the research, techniques for obtaining monomers, methods of their purification and implemented research procedures and measurement methods. I have no objections to this description because it indicates that Mr. Tomy Muringayil Joseph has very extensive theoretical knowledge.

Then, research was carried out, which constitutes a kind of introduction to further research. Namely, they concern the copolymerization behavior of styrene and pentadecylphenyl methacrylate (PDPMA) using atom transfer radical polymerization (ATRP) at different monomer ratios. The course of the reaction and the products obtained were thoroughly characterized using modern research methods. The $^{1}H$ NMR nuclear magnetic resonance method supplemented with data obtained from the Fineman-Ross (FR) and Kelen-Tüdős (KT) methods and size exclusion chromatography (SEC) were used. DSC and TGA were used to study side chain crystallization and thermal stability. The morphology of the obtained compounds, rheological properties and adhesion characteristics were also comprehensively analyzed. A detailed analysis of the results obtained during the research allowed the PhD student to formulate appropriate conclusions important for further research. The PhD student paid attention to, among others: that while the PDPMA sequence length showed consistency at different monomer ratios, the styrene sequence length showed a decrease with increasing initial PDPMA content in the system. Moreover, the obtained copolymers showed differentiated glass transition behavior and increased thermal stability with higher styrene monomer content. However, morphological analysis using transmission electron microscopy (TEM) showed a phase-separated morphology.

First of all, he focused on investigating the dynamics of copolymerization between styrene and cardanyl acrylate (CA) by using atom transfer radical polymerization (ATRP),

optimizing the amount of monomer. In order to observe the polymerization process and develop the characteristics of the obtained raw materials, the PhD student conducted a number of advanced studies, which led him to interesting conclusions. The use of $^{1}H$ NMR and the Fineman-Ross (FR) and Kelen-Tüdős (KT) methods enabled a comprehensive understanding of the composition and behavior of the copolymer. Gel permeation chromatography (GPC) analyzes allowed to track changes in molecular weights and polydispersity. The produced copolymers had molecular weights in range from 2551 to 6934 g/mol and polydispersity values in range from 1.18 to 3.45. This confirmed the diverse nature of the synthesized copolymers and the feed-dependent changes in polymerization kinetics. Phase transformation studies of the obtained raw materials were examined using thermogravimetric analysis (TGA) at temperatures range from -50°C to 200°C at a heating rate of 10°C/min, showing maximum stability in copolymers with a high styrene content (90, 70 and 50 wt.%). In contrast, transmission electron microscopy (TEM) analysis showed a phase-separated core-shell morphology. The first one consisted of aromatic, electron-rich styrene domains, while the second one consisted of crystalline domains derived from CA.

Referring to the main part of the thesis contained in chapters II, III and IV, I think that the division of research works into individual chapters and subchapters is very accurate, and their composition is very accessible to the reader. At the beginning of each chapter there is a short introduction to the problem. Then the course of experiments, relevant results and their interpretation are presented.

Chapter V of this thesis is very interesting. It constitutes a kind of summary and thus the end of the conducted research. At the same time, it discovers new research areas related to the use of atom transfer radical polymerization (ATRP), identified by the PhD student, which are worth exploring. I count on the PhD student's activity in this area in the future. It should be emphasized that the implementation of the research planned by the PhD student and the analysis of the obtained results required not only a large amount of work with appropriate precision and care, but above all, extensive knowledge necessary for the optimal selection of devices, materials and techniques in order to obtain the highest quality results. The results achieved by the PhD student prove that he had such knowledge and skills. Knowledge of modern research techniques and the ability to thoroughly interpret the obtained results and their quality confirm the validity of the used solutions. Moreover, they indicate his good preparation for experimental work. I would like to take this opportunity to ask the PhD student to clarify certain issues that were missing in the reviewed thesis:

1. Among naturally occurring phenols, cardanol is a plant phenolic lipid extracted from cashew nut shells obtained from cashew trees. These trees are cultivated, among others: in India, Vietnam, Brazil, Indonesia. The degree of unsaturation in the chain varies depending on the source of origin.
2. Has the efficiency of the obtained cardanol-based compounds been tested? This is an important economic aspect in the case of commercialization of this results.
3. Has an economic analysis of polymers and copolymers developed by the PhD student been carried out? I'm mainly interested in estimating the costs of obtaining new materials based on the by-product of cashew nut shell processing.

**Conclusion**

In terms of the application of sustainable technology, the issues of easy acquisition and price of raw materials, as well as the method of conducting individual reactions taking into account the principles of green chemistry, are very important. In this context, the choice of the topic and research assumptions of the PhD thesis is extremely appropriate, because the research was aimed at obtaining new monomers from an easily renewable source, which may constitute an attractive alternative to the monomers obtained from crude oil currently available on the market. The topic of the research work is consistently discussed and implemented in the content of the thesis. It is also worth emphasizing the interdisciplinarity of research in the area of basic research and applied research.

To sum up this review and taking into account the requirements for doctoral thesis, it should be stated that in the case of Mr. Tomy Muringayil Joseph's thesis:

- The reviewed doctoral thesis presents the PhD student's thorough theoretical knowledge in the field of polymer technology. The PhD student has a very good understanding of the world scientific literature related to his research. He can use it skillfully.
- Mr. Tomy Muringayil Joseph, MSc demonstrated the ability to independently conduct scientific work. The reviewed doctoral thesis shows that the PhD student is able to design the research process, obtain and develop material, select appropriate methods and use them correctly, while referring to the current state of knowledge.
- Doctoral thesis of Tomy Muringayil Joseph, MSc. represent an original solution to the problem defined in the title and the purpose of the thesis.

To sum up the assessment of the doctoral thesis of Mr. Tomy Muringayil Joseph, MSc. in the context of the legally prescribed criteria for obtaining a doctoral degree, I state that these criteria have been met.

Taking into account the above facts, I confirm that all legal requirements specified in *Ustawa z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. 2018 poz. 1668 z późn. zm.)* for doctoral theses and candidates applying for a doctoral degree have been met. Therefore, I am requesting the Chemical Sciences Discipline Council of the Gdańsk University of Technology to admit Mr. Tomy Muringayil Joseph, MSc. for further stages of the doctoral process.

Joanna Bawiec-Sadowska