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Review of the doctoral dissertation by Vahid Rahmanian
entitled ***"Polyethylene Nanocomposites with Carbon, Nanofillers: Similarities and Differences''***

prepared under the academic supervision of prof. Andrzej Gałęski
in Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Division of Polymeric Nanomaterials.

The review was prepared on the basis of a letter no. L.Dz. 2/SN/2023 of September 14, 2023, from the Head of the Research Office, Scientific Center for Molecular and Macromolecular Studies, PhD Barbara Jeżyńska.

The assessment was prepared on the basis of a doctoral thesis submitted to me entitled: *"Polyethylene Nanocomposites with Carbon, Nanofillers: Similarities and Differences*" covering the PhD student's work on 112 pages.

General information about the doctoral thesis and scientific achievements

The doctoral dissertation of Vahid Rahmanian, submitted to me for evaluation, entitled "*Polyethylene Nanocomposites with Carbon, Nanofillers: Similarities and Differences*", was carried out, as I mentioned, at the Center for Molecular and Macromolecular Studies under the supervision of prof. Andrzej Gałęski. The work was carried out as part of the research project titled "*Cavitation of polymer nanocomposites*", headed by prof. Andrzej Gałęski financed by the National Science Center. The project was implemented at the Polish Academy of Sciences in Division of Polymeric Nanomaterials.

The doctoral student is a co-author of 7 international publications, three of which concern the issues discussed in the doctoral thesis (including Polymers, Macromolecules, Polymer Composites, Biosensors, Water).

1. Introduction

The intensive development of polymer mixtures results from the possibility of obtaining qualitatively new materials by mixing existing large-volume polymers and is associated with many possibilities of physical and chemical modification. Research directions and applications of mixtures focus on areas where materials with potentially the best properties can be obtained. Creating mixtures of nanofillers with existing polymers is also much faster than developing and producing new polymers.

Polymer nanocomposites are increasingly used in various industries, mainly in the automotive and packaging industries, where they replace multilayer materials, aviation and electrical engineering, which are difficult to recycle. These applications are the result of the following properties: low density, high mechanical, thermal and barrier properties.

Thermoplastic polymers are a group of polymers with the widest range of applications and a production scale of over 280 million tons per year. Most of them are partially crystalline polymers, such as polyethylene, polypropylene, polyamide, poly(methylene oxide), poly(ethylene terephthalate), polylactide. The properties of these materials depend largely on their internal structure. The internal structure of the solidified polymer, including the supermolecular structure, lamella sizes, and crystalline phase content, results from both the nature of the macromolecules (molecular weight, side groups, chains) and the forming process. Among polymers and their composites, including nanocomposites, mechanical properties are particularly important, because products made of polymer composites are practically always subject to external forces and should behave under their influence as expected. Although, as is known, partially crystalline polymers and composites based on them have been used for years and intensive research has been carried out on their deformation process and the factors determining it, the state of knowledge is still not complete and there are aspects that require clarification. The main reason for the incomplete state of knowledge is the above-mentioned complicated and diverse internal structure of polymers, making analysis difficult, where the structure typically contains both crystalline elements in the form of lamellas and an amorphous phase, often together forming larger spherulitic structures. Phenomena observed in recent years but not sufficiently analyzed included the occurrence of cavitation in some polymers, understood as the creation of a large number of cavitations (holes) inside the polymer during its deformation in the solid state. The first observations of the formation of holes came from the 1970s.

In recent years, there has been a lot of research work carried out by the team of professors Gałęski and Pawlak on determining when the cavitation phenomenon occurs, in what materials, what is the mechanism of cavitation formation, why not all polymers cavitate, to what extent the nature and conditions of deformation (rate, temperature) influence on the formation of holes and whether the fact of creating numerous holes changes the properties of the polymer, which is why research on this phenomenon was initiated in 2004.

In polymer nanocomposites, the presence of nanofillers in the polymer matrix can have a significant impact on the cavitation behavior, thereby leading to improvement or deterioration of mechanical properties. An interesting phenomenon is the fact that some nanofillers can act as stress concentrators and promote cavitation by creating local stress cavitations at the point of contact with the polymer matrix or at defects within the fillers. On the other hand, fillers can also hinder cavitation by strengthening the matrix and providing additional resistance to hole growth.

The cavitation behavior of polymer nanocomposites during tensile testing has attracted great research interest in recent years. Studying cavitation phenomena can provide insight into the fundamental deformation and fracture mechanisms of polymer nanocomposites, and may also aid in the design and optimization of their mechanical properties for various engineering applications. The literature describes the results of research on the mechanical properties of polymers, which depend on many variables, such as the parameters of a single chain and the organization of the supermolecular structure. Macromolecular materials have a complex, hierarchical structure that needs to be explored in order to properly use the possibilities they offer. The deformation mechanics of such materials is determined by the structure of crystalline polymers and their nanocomposites, mainly because they contain two phases with significantly different properties, crystalline and amorphous. To create materials that meet the necessary rigorous standards, it seems necessary to investigate the processes governing plastic deformation of polymers.

Until now, it was believed that cavitation is a secondary result of the deformation of some materials and has little or no effect on the final deformation of the material. Among other things, research conducted at the Center for Molecular and Macromolecular Studies of the Polish Academy of Sciences allowed for a better understanding of a number of issues related to the formation of discontinuities in materials and showed that cavitation is an important, unavoidable phenomenon that often conceals the actual mechanisms of deformation.

The main goal that the PhD student wanted to achieve in his work is to continue the research carried out in Professor Gałęski's team on the cavitation phenomenon occurring in polyethylene-based nanocomposites, in particular to investigate the type of cavity nucleation occurring during the deformation of these nanocomposites. This proves the novelty of the issue researched by the PhD student, and also gives us a full picture of the scientific and technical difficulties the PhD student had to face.

2. Structure of a doctoral thesis

Vahid Rahmanian's doctoral dissertation titled "*Polyethylene Nanocomposites with Carbon, Nanofillers: Similarities and Differences*" is of an experimental nature and concerns the analysis of elements contained in polymers, such as nanoparticles, stabilizers or low-molecular fractions (oligomers), which can have a significant impact on the intensity of the cavitation process.

As part of the work, the research material was purified and the influence of selected admixtures or nanoparticles on the onset and intensity of the cavitation process was examined in order to determine the function of the described additives in cavitation nucleation. The experimental results allowed the PhD student to detect whether cavitation during the deformation of polymer nanocomposites occurs in a homogeneous or heterogeneous manner, similarly to the case of small molecular liquids.

The research results obtained by the PhD student will enable better management of phenomena such as eliminating cavitation where it is undesirable, enabling a better understanding of the process of cavity formation during deformation of crystalline polymer nanocomposites, and controlling cavitation when its presence is needed.

The dissertation was prepared at the Center of Molecular and Macromolecular Studies of the Polish Academy of Sciences Division of Polymeric Nanomaterials under the supervision of prof. Andrzej Gałęski. It contains 112 pages in English, which includes: 3 chapters of the theoretical part (numbered from 1 to 3) and 3 chapters of the experimental part (numbered from 4 to 6), with chapter 6 being conclusions from the experimental part. At the beginning of the work, the PhD student posted summaries in English and Polish. The literature includes 217 items from domestic and foreign sources, including books and scientific publications. It can be concluded that the proportions between scientific studies and other items included in the literature are correct. There are many literature studies of a fundamental nature for the study of nanocomposites, in particular the phenomenon of cavitation in polymeric materials.

The doctoral thesis begins with a synthetic introduction containing general information on the phenomenon of cavitation in polymer nanocomposites under tensile load. Next, the PhD student described the issue of strengthening polymers by adding nanofillers selected from a number of different nanomaterials: carbon black, multi-wall carbon nanotubes (MWCNT), cellulose nanocrystals, carbon nanotubes, graphene, carbon nanofibers, nanoclay, fibrous nanoclay-sepiolite, nanosilica, carbon nanofillers, various oxide nanoparticles metals and inorganic particles such as hydroxyapatite and nanocarbonate. In the introduction, he also described the selected polymer matrix - HDPE and the method of obtaining HDPE-based nanocomposites. He also described the processes occurring during tensile deformation of HDPE, mainly micronecking and the phenomenon of cavitation in HDPE nanocomposites.

In chapter 2 entitled "*Basic concepts*" the PhD student presented detailed information on the structural properties of semi-crystalline polymers, as well as general concepts regarding the mechanical properties of polymers. This chapter consists of two subchapters, the first one is divided into 5 subchapters and the second one into 3 subchapters.

The third chapter entitled "*Objective of the research*", in which the PhD student specified the purpose and scope of the work.

The fourth chapter is devoted to the experimental part, which begins the first subchapter devoted to the characteristics of the raw materials used in the research. In section 4.2, the PhD student described the preparation of HDPE-based nanocomposites using a mini-co-rotating twin-screw extruder. Subsequently, in this chapter he described the preparation of test samples in the form of 1 mm thick foil at a temperature of 180°C using a press with the possibility of cooling. In section 4.3, the PhD student characterized the devices used for research: instruments for plastic deformation tests, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Dynamic Mechanical Analysis (DMTA), Nuclear Magnetic Resonance (NMR), Small-angle X-ray Scattering (SAXS), Impact strength (Izod test), Polarized Light Microscopy (PLM).

In the fifth chapter entitled "*Results and discussion*", the doctoral student presented an extensive analysis of the obtained research results, which he included on pages 57 to 98.

The conclusions reached by the author are interesting and correctly formulated from a scientific point of view. It is also important that the results of the work have practical implications and can be used by industry.

3. Characteristics of the doctoral dissertation

The research results and their analysis refer to important and current issues, not only from the scientific point of view, but also from the application point of view. The research work was carried out using specialized machines and devices located at the Center of Molecular and Macromolecular Studies of the Polish Academy of Sciences Division of Polymeric Nanomaterials. They allowed the PhD student to conduct in-depth research on the topic of the dissertation.

The first research part begins with subchapter 5.1 entitled "*Graphene and reduced graphene oxide nanocomposites*" devoted to the characteristics of graphene (G) and reduced graphene oxide (rGO) and HDPE-based nanocomposites with the addition of this nanofiller. In this subsection, the PhD student described in great detail the SEM and WAXS studies of the nanofiller, and then the crystallization of HDPE/graphene nanocomposites was monitored by detecting heat flow in the DSC apparatus during cooling. Subsequently, he performed mechanical tests in static stretching of HDPE+G and HDPE+rGO nanocomposites as well as impact tests. What is impressive in this chapter is the structural and X-ray analysis of both nanofillers and nanocomposites, which, as you can guess, was performed by the PhD student under the professional supervision of the supervisor, Professor Gałęski.

The next research part of the doctoral dissertation (chapter 5.2) was devoted to polyethylene nanocomposites with other carbon nanofillers and their comparison with nanocomposites containing graphene and reduced graphene oxide. As part of this work, the PhD student examined the impact of the presence of selected nanofillers (carbon black, graphene, nanodiamonds with an average grain size of 50 nm, nanodiamonds with an average grain size of 100 nm, fullerene and multi-wall carbon nanotubes) on the crystallization process, mechanical properties in static stretching, Izod impact strength and cavitation phenomenon.

The last part of the work is "*Conclusions*", and the most important conclusions presented in the summary include:

- based on TEM observations of an ultra-thin cross-section of graphene and rGO nanocomposites, good dispersion and adequate wettability of these nanofillers' plates through the HDPE matrix were observed;
- it was observed that graphene platelets nucleate HDPE crystallization, while reduced graphene oxide did not;
- a slight increase in the yield strength of graphene nanocomposites was observed, but no such effect is observed in the case of nanocomposites containing rGO;
- plastic flow during tension is subject to fluctuations: the intense neck deformation zone migrates from one end of the neck to the other, which causes stress fluctuations. The reason is the interplay of orientation strengthening and softening by the heat generated during plastic deformation;
- fracture in Izod impact strength measurement of nanocomposites occurs by debonding of HDPE from graphene or rGO and by fast radial spreading of fracture from debonded particles. The radial zones are freely spreading until impingement with neighbors when the travel of crack tip is slower, farther from the notch;
- in tensile drawing of nanocomposites the debonding occurs even before the yielding is reached. The debonded nanoplateletes are the source of intense cavitation. The number of cavities in

nanocomposites is higher for higher concentration of nanoplatelets. The sizes of cavitation pores are above 25 nm as it is judged from SAXS experiments. All smaller pores were healed by surface tension. In contrary, whitening of nanocomposites indicates that cavitational pores can reach the size of the light wavelength. Finally, there is only a small difference between graphene and rGO nanocomposites in the nucleation of crystallization of HDPE;

- the solidification process, crystal structure formation and crystallization nucleation of nanocomposites with all-known carbon nanoparticles were investigated in details. Only carbon nanotubes and graphene induce the nucleation of polyethylene crystallization by 3-4°C higher than the other carbon nanofillers whose grains do not show the ability to nucleate;
- nanofiller agglomerates behave differently. Comparison of the number of nuclei produced with the number of introduced nanoparticles confirms these observations;
- the impact strength of nanocomposites shows a 30-40% increase for carbon black, nanodiamonds, fullerene and carbon nanotubes, while a decrease of 25-30% for both lamellar nanofillers;
- the behavior of the nanocomposites and polyethylene during tensile deformation was investigated. Polyethylene cavitates above the yield stress while polyethylene nanocomposites show an increase in cavitation intensity for all nanofillers except for nanodiamonds and reduced graphene oxide. These results show that the filler nanograins detach from the polymer during deformation, while nanodiamonds and reduced graphene oxide adhere strongly to polyethylene and do not contribute to increased cavitation. It appeared that the cavities of both origins: from HDPE alone and by detachment from the nanofillers are larger than 10-15 nm;
- no smaller cavities were detected by SAXS in tensile deformed samples under fixed strain. The cavitation pores having 10-15 nm in diameter are formed suddenly in a single step. This value is surprisingly close to the thickness of the amorphous layer. It is suggested that, similar to ordinary liquids, the surface tension of amorphous phase of polyethylene collapses smaller caverns;
- during stretching, the stress of 21 MPa would counterbalance the 7 MPa closing pressure. Such stress is generated close to the yield point. Any smaller cavities would require larger stress and would collapse under the action of surface tension. This shows that the cavitation behavior of the amorphous phase of polyethylene at nanometer scale bears similarity to an ordinary liquid;
- from the presented reasoning it follows that the stress at fixed strain is not sufficient to keep open the cavities smaller than 10-15 nm.

Particularly noteworthy is the thoroughness of the research work carried out by the PhD student, which required him to master modern research methods: DSC, SEM, DMTA, NMR, SAXS and PLM. They were properly adapted to the issues and problems he had to solve. It is known that the use of specialized equipment and the interpretation of measurement results cannot be entirely attributed to the PhD student, because it always requires cooperation with specialists, and above all with the Supervisor, the results of which are presented in co-authored works complementing the achievement.

As a reviewer, I have a few editorial comments:

- error in the numbering of figure number 1, page 16;
- Fig. 5 and Fig. 6 illegible, pages 18, 19;
- page 21, the solitary title of subchapter 2.1.4.;
- captions in Fig. 19 illegible, page 35;
- Fig. 23 on page 4 and the caption on page 47;
- Fig. 24 on page 47 and the caption on page 48;
- Fig. 41 should be on one page, not two (pages 66 and 67);
- Fig. 42 should be on one page, not two (pages 68 and 69);
- Fig. 43 should be on one page, not two (pages 70 and 71), no markings a and b;
- Fig. 48 should be on one page, not two (pages 76 and 77);
- table 4, page 77 power of 10 divided;
- table 5, page 81, not very legible, no average result and standard deviation of impact strength tests according to Izod;
- Fig. 50 should be on one page, not two (pages 82 and 83);
- Fig. 51 should be on one page, not on two (pages 84 and 85), the captions in the chart windows are not very legible, maybe it would be worth marking them a, b, c, d, e, f, g and explaining the markings in drawing caption;
- Fig. 52 should be on one page, not three (pages 86 - 88), the captions in the chart windows are not very legible, maybe it would be worth marking them a, b, c, d, e, f, g and explaining the markings in the caption drawing;
- Fig. 54, page 90, no markings a and b;
- Fig. 54, pp. 94-97 no markings a - g;
- literature - different font.

and scientific comments:

- the description of Young's modulus results is limited. The author only gave a range of change in Young's modulus value without considering how a given nanofiller affects this parameter. In my opinion, changing the value from 600 to 800 is very significant. Are the values obtained consistent with other analyses?

It should be emphasized that these comments are of a debatable nature and do not affect the substantive value of the dissertation.

4. Summary

To sum up, Vahid Rahmanian's doctoral thesis titled "*Polyethylene Nanocomposites with Carbon, Nanofilers: Similarites and Differences*" is a description of a coherent scientific achievement, and therefore meets the formal requirements contained in applicable statutory provisions. The paper describes innovative research directions worth continuing. In turn, the dissertation submitted for evaluation is carefully prepared with only a few editorial mistakes.

Finally, I would like to add a remark that the reviewed doctoral thesis by Vahid Rahmanian entitled "*Polyethylene Nanocomposites with Carbon, Nanofilers: Similarites and Differences*" proves the author's high competence in the preparation and testing of HDPE-based nanocomposites with the addition of selected carbon nanofillers. I state without any doubt that the dissertation submitted to me for evaluation fully meets the conditions specified in the Act of March 14, 2003 on academic degrees and titles and degrees and titles in the field of art (consolidated text in the Journal of Laws of 2017, item 1789) and the Regulation of the Minister of Science and Higher Education of January 19, 2018 on the detailed procedure and conditions for carrying out activities in the doctoral procedure, in the habilitation procedure and in the procedure for awarding the title of professor (Journal of Laws of 2018, item 261), therefore I am applying to the Council Scientific CBMiM PAN in Łódź for admission of the PhD student to further stages of the doctoral process.