University
of Bielsko-Biala

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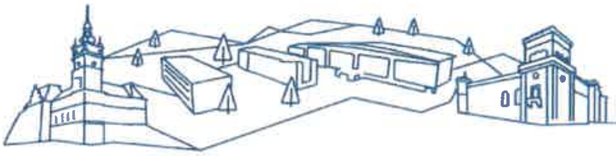
Dr hab. Czesław Ślusarczyk, prof. UBB
Faculty of Materials, Civil
and Environmental Engineering,
University of Bielsko-Biala,

Comments on the PhD thesis elaborated by Vahid Rahmanian from the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, on „*Polyethylene Nanocomposites with Carbon Nanofillers: Similarities and Differences*" under the supervision of Prof. dr hab. Andrzej Gałęski

Polymeric materials have been filled with synthetic or natural inorganic compounds for many years to improve their properties or reduce costs. In recent years, carbonaceous nanofillers (CN) have attracted significant attention due to the remarkable enhancement of the polymer matrix's mechanical, heat-resistance, gas barrier, thermal, and electrical conductivity properties. The intensive research carried out to date clearly shows that CN should be recognized as an excellent candidates for reinforcing or functionalizing polymers. However, the mechanisms responsible for these impressive changes have yet to be fully understood, especially when the polymer matrix is crystallizable.

The research object of the PhD thesis of Vahid Rahmanian is high-density polyethylene (HDPE) nanocomposites with all recognized CN: carbon black (CB), carbon nanotubes (CNT), fullerene, graphene, reduced graphene oxide (rGO) and nanodiamonds (ND). The main aim of the thesis is to investigate the influence of these nanoadditives on the mechanical properties of nanocomposites, with particular emphasis on the cavitation phenomena occurring during tensile



43-309 Bielsko-Biała, ul. Willowa 2, POLAND
Phone: (33) 827-92-01, fax: (33) 827-93-55
Regon: 072728961, NIP: 547-19-43-784
cslusarczyk@ubb.edu.pl, www.ubb.edu.pl

testing. Since the mechanical properties, including cavitation, strongly depend on the multi-scale morphologies of the polymer matrix, another goal of this thesis is to determine the influence of the amorphous phase in the production of discontinuities during the deformation process. The nanocomposites examined in this work were obtained using a tween screw extruder with identical temperature profile, compounding protocol, and passing through 1 wt% masterbatch, identical for all samples. Such experimental design allows for comparing similarities and differences between individual nanoadditives in their impact on the tested properties of nanocomposites. This is an excellent advantage of the reviewed work and proves the PhD student's ability to plan an experiment.

The layout of the thesis includes *Abstract* (both in English and Polish) and seven chapters, namely: *Introduction, Basic concepts, Objective of the research, Experimental section, Results and Discussion, Conclusions* and *References*. Moreover, a list of publications where Vahid Rahmanian was a co-author and his academic biography was attached at the end of the dissertation. Five publications, three of which he is listed as the first author, were published in high-impact journals. Two publications were also submitted to high IF journals.

In the first two chapters, the Author of the dissertation presented a great deal of his fundamental knowledge. The *Introduction* contains short information about polymer nanocomposites with particular emphasis on HDPE nanocomposites, morphology and tensile deformation of this polymer, and cavitation phenomena in HDPE nanocomposites. Some topics mentioned in the *Introduction* are presented in detail in the next chapter *Basic concepts*. This chapter is well-written and reflects the current state of knowledge related to the subject of the thesis. It includes four major aspects: (i) the structure of the HDPE unit cell and the lamellar structure of this polymer, (ii) the Lauritzen and Hoffman theory of polymer crystallization, (iii) basics of small-angle X-ray scattering (SAXS) method and data analysis of SAXS, (iv) cavitation in polymers.

Based on the analyzed state of knowledge, the objective of the thesis has been formulated in the next chapter, *Objective of the research*. That was discussed by the Reviewer above in the second paragraph of the review.

The *Experimental section* of the dissertation includes a description of the materials used, preparation of nanocomposites, and equipment used. It should be emphasized that the dissertation covers a wide range of nanocomposites. The following nanocomposites were prepared: HDPE/Graphene, HDPE/rGO, HDPE/CNT, HDPE/ND(100nm), HDPE/ND(50nm), HDPE/CB, HDPE/Fullerene, all with the concentrations: 0.1, 0.3, 0.5, and 1 wt%. The nanocomposites thus obtained were subjected to mechanical (tensile and Izod) tests and examined using the following methods: Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMTA), Small-angle X-ray Scattering (SAXS), Scanning Electron Microscopy (SEM), Polarized Light Microscopy (PLM) and Nuclear Magnetic Resonance (NMR). Noteworthy is the interesting use of the SAXS method to determine the size of voids formed due to the cavitation phenomenon as a stress function. For this purpose, the deformation of samples during the tensile test was interrupted and fixed using specially designed frames that immobilized the samples at the chosen strain and enabled the recording of SAXS patterns of stressed samples.

The first part of the chapter, *Results and Discussion*, discusses the research results for nanocomposites HDPE/Graphene and HDPE/rGO. First, the nanoadditives themselves were characterized. Using the SEM and SAXS methods, it was found that the average thickness of the platelets is around 7 nm for graphene and 12 nm for reduced graphene oxide, while lateral dimensions were determined to be 1 μm and 10 μm for graphene and reduced graphene oxide, respectively. Transmission electron microscopy (TEM) allowed for the conclusion that the platelets are dispersed in HDPE so that no vacancies are between platelets and polymer bulk. Results obtained for nanocomposites HDPE/Graphene and HDPE/rGO show that:

- Graphene platelets accelerate nucleation of HDPE, which resulted in a shift of crystallization onset and crystallization peak (on DSC thermograms) toward higher temperature as the concentration of graphene increases;
- The average thickness of lamellae, calculated based on the Gibbs-Thomson equation, is equal to 22.9 nm for neat HDPE and 25.3 nm for the nanocomposite HDPE/1% Graphene;
- These values are higher than the values (18 – 19 nm) obtained from the distribution of lamellae thicknesses, determined using the Crist-Mirabella method;
- Unlike graphene, rGO exhibits weak nucleating properties for HDPE crystallization. DSC thermograms of both pure HDPE and all HDPE/rGO nanocomposites have a similar crystallization onset and a similar crystallization peak location;
- Mechanical properties and the course of tensile deformation of HDPE/Graphene and HDPE/rGO nanocomposites depend on the type and content of nanoadditives. The yield stress, which is about 18 MPa for pure HDPE, increases to about 22 MPa when the graphene content is 1 wt%. In contrast, both nanofillers have a moderate negative effect on impact strength. An increase in their concentration increases the number of defects in the structure, which leads to a decrease in impact strength by approximately 20%. Defects

in the structure of nanocomposites were clearly presented in the dissertation in SEM micrographs;

- The introduction of graphene and rGO into HDPE facilitates the formation of cavities originating in the amorphous phase of HDPE during tensile drawing. This effect causes an additional increase in volume strain compared to pure HDPE, the value of which increases up to 60%. For comparison, an increase in volume strain to approximately 40% is observed in pure HDPE.

The cavitation phenomena occurring during the tensile deformation of nanocomposites have been investigated in more detail using 2D-SAXS measurements. This method allowed the Author of the dissertation to determine changes in the lamellar structure of HDPE and to estimate the contribution of formed voids depending on their size. For this purpose, the SAXS curves were analyzed using Guinier approximation. Pore sizes were found to be in the range of 25 nm to 80 nm, with pores of size 80 nm having a more significant share. The SAXS method also showed the absence of cavities smaller than 25 nm.

The second part of the chapter, *Results and Discussion,* contains the research results on nanocomposites containing other carbon nanoadditives. The discussion of these results was based on comparing the selected properties of these nanocomposites with the properties of HDPE/Graphene and HDPE/rGO nanocomposites, and the results were selected due to the research method used.

Using polarizing optical microscopy (POM), the nucleating abilities of various nanofillers were compared. Based on the observations, the number of structural elements of HDPE in 1 cm^3 of the nanocomposite was estimated and compared with the number of such elements in pure HDPE. It was found that the number of HDPE structural elements formed during crystallization increases, depending on the type of nucleant, from about 22 times (for CB and ND(50 nm)) to about 5000 times (for CNT). In order to properly assess these results, it is necessary to refer to the actual number of nanoparticles introduced into the nanocomposites, which depends on their type. Such analysis showed that the most effective nanoadditives are CNTs, for which approximately 17 particles are needed for the nucleation of one HDPE crystalline element, followed by graphene (43 particles) and ND(100 nm) (68 particles). The least efficient in terms of the number of particles needed for nucleation of a single HDPE crystalline element is fullerene ($8.3*10^7$ particles) and CB ($1.8*10^5$ particles). According to the Author of the dissertation, the different ability to nucleate the crystalline phase of HDPE results from the crystallization mechanism. Only nanoparticle agglomerates with niches, obtuse cubbyholes, and cavities are capable of nucleation. Their presence causes a decrease in the energy needed for the formation of a primary nucleus of polyethylene. Due to their flexibility, such kinks, nooks, and crannies are primarily observed in CNTs and, to a minor extent, in fullerene, forming loose pockets when two or more particles aggregate. The above observations were confirmed in DSC tests, in which only for HDPE/CNT and HDPE/Graphene nanocomposites the formation of crystallization nuclei was observed 2-3 °C earlier during melt cooling than in nanocomposites with other nanofillers.

The properties of the HDPE matrix dominate the stress-strain behavior of nanocomposites investigated. The mechanisms pertinent to HDPE, modified due to the presence of nanoparticles, are responsible for their plastic deformation. It is best seen in the yield. The yield stress increased compared to pure HDPE for all nanocomposites except for rGO and fullerene. The highest values were observed for nanocomposites with graphene and CNT because those nanofillers nucleated the crystallization of HDPE, leading to an increase in the size of crystallites and the resulting increase in the yield stress. In turn, Izod tests showed impact strength's dependence on the nanofiller particles' shape. For flat particles (graphene, rGO), the impact strength value decreased by 20% compared to pure HDPE. For the remaining nanofillers, the value of this parameter increased from 30% to 50%. The observed differences were explained by SEM micrographs, well interpreted by the Author of the thesis.

The analysis of the relationship between the volume strain and the local strain showed, similarly to nanocomposites with graphene and rGO, that the introduction of other nanofillers (except 50nm ND and 100nm ND) also causes that the volume strain significantly exceeds that of plain HDPE. This effect is caused by the formation of additional cavities due to the debonding of the nanofillers from the HDPE matrix. It is best visible for nanocomposites with the highest 1 wt% content of nanoadditives.

The following subsection presents research results on the cavitation phenomenon in pure HDPE. This research gave a new, interesting result, changing the current view of this phenomenon. Namely, only cavities of sizes of about 20 nm were observed, and smaller cavities with sizes of 10-15 nm were not observed. This result is inconsistent with the view that the cavitation phenomenon is initiated by small-sized cavities, which then increase with increasing deformation. The research presented in this work showed that cavitation pores with diameters above 15 nm are formed rapidly in a single step, without intermediate stages. Additionally, it was found that the sizes of these cavitations are almost equal to the thickness of the amorphous HDPE layers. The Author of the dissertation rationally justified the observed phenomena based on the analysis of its main factors, which are the surface tension and the negative pressure arising as a result of the crystal plastic resistance. A summary of these theoretical considerations is presented as a model of the phenomenon, shown in Figure 55. These results constitute an essential element of the novelty of the reviewed work.

In nanocomposites, the cavitation process begins in the polymer matrix but also occurs due to the debonding of filler grains from the polymer. For all nanocomposites investigated, regardless of the type of nanofiller, no cavitation pores with sizes smaller than 15 nm were found. Apparently, in nanocomposites the cavitation phenomena are also determined by the properties of the polyethylene matrix.

The last subsection of the chapter, *Results and Discussion,* presents 2D-SAXS curves and discusses the texture development of HDPE, the redistribution of nanoparticles, and the appearance of cavities during tensile deformation. This section is short and does not analyze the results quantitatively but is limited only to qualitative considerations.

The chapter entitled *Conclusions* skillfully summarizes all the most important results of the work. This chapter is well-edited and gives a clear overview of the dissertation's achievements. The dissertation ends with a list of references, including 217 items (positions 13 and 16 are the same).

Critical remarks:

1. The most significant shortcoming of the reviewed work is the incomplete presentation of the research results for nanocomposites containing carbon nanofillers other than graphene and rGO. In particular, for these nanocomposites, there is no information on the distribution of the crystal thickness, G(l), using the Crist Mirabella method. For the nanocomposite containing 1 wt% of graphene, a double peak of this distribution was observed (Fig. 37 p.62), indicating the existence of two populations of crystallites. For the HDPE/rGO nanocomposite, this effect did not occur. The question arises: What about other samples? Does this effect occur for 1 wt% content of other nanofillers?

2. The theory of small-angle X-ray scattering (SAXS) is discussed in too much detail in the thesis. Aspects of the method that were not used, e.g., interface distribution function (IDF), were also presented. Instead, no attention was paid to the lack of a uniform marking of the scattering vector. The following symbols for this quantity are used in this work: s (eq. 1.8 p.24), q (eq. 1.10 p. 26), S (Fig. 46 p. 73, error in the definition of S), h (e.g. 6 p.75).

3. On page 54, the Author gives information: *"The curves were subjected to background and Lorenz adjustments."* However, it seems to the reviewer that the background was not cut off from the SAXS curves, as evidenced by the curves in Figures 54 and 56. In these figures, the scattering intensity in the "tail" of the curves increases significantly, while after the background is cut off, it should drop to zero. It is an essential issue because an incorrect background cut-off causes a change in the angular position of the peak, which leads to incorrect results when applying Bragg's law. On page 93, it is stated that the distances between the scattering objects are below 15 nm, and Figure 56 shows that the peak location occurs at about 20 nm and even more (?)

4. On page 75, the distribution of cavity sizes was analyzed using the Guinier approach. The use of Guinier approximation is a challenging task in practice. There need to be details about this method in the work, e.g., appropriate charts from which information about the distribution is obtained. The Author generally does not provide information about the computer programs he used to process SAXS data.

5. Figure 35 presents the correlation functions obtained for graphene and rGO powders. What is the interpretation of the determined distances of 81 and 91 nm? To what structure can such periodicity be attributed? Moreover, the Author states: *"the average thickness of the platelets is around 7 nm for graphene and 12 nm for the reduced graphene oxide..."* (p. 58). Further analysis indicates that this is the thickness of a single layer. Is it possible? It appears that the given thicknesses refer to some aggregates composed of monolayers. The reviewer believes a wide-angle X-ray scattering (WAXS) method would better characterize these powders. In the WAXS curves for rGO, there is a peak for the scattering angle $2\theta \approx 10^\circ$, from which the average number of monolayers in the grain of the tested powder can be estimated.

6. There are many editorial mistakes in the text of the dissertation; among others, different numbers of figures are mentioned than the actual ones (for example, p. 35, Fig. 14 instead of Fig. 19, p. 58 Fig. 2 instead of Fig. 35, p.61 eq. 5 instead eq. 4, p.75 Fig. 12 instead Fig. 47).

Final Conclusions

The doctoral dissertation elaborated by Vahid Rahmanian on *"Polyethylene Nanocomposites with Carbon Nanofillers: Similarities and Differences,"* submitted for review, was completed with much work and demonstrates his high mastery of scientific theory, research methods, and the literature on the subject. The results of the research carried out in this work bring many new facts and enrich our knowledge, including the properties of polymer nanocomposites with carbon nanoadditives. They also allow for the assessment of similarities and differences in these properties depending on the type of nanofiller. The critical remarks reported in the review do not reduce the positive assessment of the overall dissertation.

Thus, Vahid Rahmanian deserves to receive the doctorate. His dissertation fulfills all requirements for Ph. D. that are stated in the Polish law (the Act on Scientific Degrees and Title). Consequently, I submit to the Scientific Council of CMMS PAS a recommendation allowing Vahid Rahmanian to proceed to the next steps of the Ph. D. qualification procedure.

26.10.2023 Ślusarczyk