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R E V I S I O N
of the PhD thesis of MSc Ramin HOSSEINNEZHAD
entitled: „Biocomposites with nanofibers generated by shear and shear induced crystallization"
The PhD thesis was submitted to the Scientific Council of Polish Academy of Sciences, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy
Supervisior: dr hab. Iurii Vozniak

The base of elaboration:

The review was commissioned by the Scientific Council of the Polish Academy of Sciences in Łódź at 20.09.2021. In the assessment of the thesis, the criteria were adopted, resulting from the binding Act of March 14, 2003. on academic degrees and an academic title as well as on degrees and a title in the field of art (Journal of Laws 65, Item 595, as amended) for doctoral dissertations.

The increasing awareness about the global environment caused that a range of new polymeric materials is being developed, especially those based on renewable resources. Unlike conventional polymers, one can convert biodegradable polymers into biomass or carbon dioxide and water. Therefore, the biopolymer blends market exhibits continuous growth. It is obvious that the usage of several polymers formed in a blend allows obtaining a number of advantages, especially, a combination of the best of their properties. Nonetheless, there are a few disadvantages of polymer blends, among all, the poor possibility over the morphology control and low interphase adhesion that obstruct the realization of high-performance blends. To overcome this problem one can convert polymer blends into all-polymer composites. The following thesis presents a novel concept of in-situ generated all-polymer nanocomposites, where the nanofibers of one polymer are formed inside the second polymer during shear

processing in a melt. The solidification of nanofibrous sheared inclusions is performed by shear-induced crystallization, all during processing. The proposed concept allowed the formation of "green all-polymer" nanocomposites in a single stage for a range of biopolymers. Herein, the primary scientific goal of the studies was to develop the methodology constituting the precise control of phase morphology of the dispersed polymer inclusions and the polymer matrix during the processing of "green all-polymer" composite via conversion of polymer blends into in-situ composites.

That is why, the proposed by the PhD student concept of "in-situ generation of all-polymeric nanocomposites" has been developed to a range of biopolymers, namely polylactide (PLA), polyhydroxyalkanoate (PHA), poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT), poly(butylene adipate-co-terephthalate) (PBAT), bio-based polyamide (PA), poly(1,4-butylene succinate) (PBS), and poly(ε-caprolactone) (PCL) is very innovative. Mr. Hosseinnezhad fabricated the series of sustainable green biopolymer–biopolymer nanocomposites. He has revealed the critical role of applying a high shear rate to precisely control the phase morphology of the dispersed polymer inclusions. In addition, within the PhD thesis triple shape memory hybrid nanocomposite was fabricated using the PLA/PBAT/ cellulose nanofibers (CNFs) blend and studied. It was found that the incorporation of CNFs boosted the conversion of PBAT droplets to nanofibers. Finally, Mr. Hosseinnezhad explained that the in-situ generated shape memory composite exhibited drastically higher values of strain recovery ratios, strain fixity ratios, faster recovery rate, and better mechanical properties compared to the blend.

The subject of the doctoral dissertation submitted for review by MSc. Ramin Hosseinnezhad is, by all means, up-to-date, since the primary scientific goal of the studies was a development of the methodology constituting the precise control of phase morphology of the dispersed polymer inclusions and the polymer matrix during the processing of "green all polymer" composite via conversion of polymer blends into in-situ composites.

1. General characteristics of the PhD thesis and its evaluation

The work consists of 194 pages of text (178 counted pages plus 14 pages at the beginning marked with Roman numerals), the layout of which also includes: bibliography, summaries in Polish and English, lists of co-authored publications and patents, list of lectures, and posters connected with PhD thesis and academic biography. There are 274 references (publications and monographs) in the bibliography.

The scope of the quoted studies is sufficient and correctly selected. The work is edited in a classic way. The thesis consists of five chapters: Introduction, State of knwledge, Objective of the thesis, Experimental and Results and discussion. In Chapter 3 the objectives of the thesis and scope of work were formulated. Completion of the thesis (subsection 5.11), in a logical and concise manner, confirms the sense and purposefulness of the thesis, which was the meaning of the dissertation, i.e. „is mainly aimed at the development of the concept of in-situ generation of "green all-polymer" nanocomposites, where the nanofibers of one biopolymer are formed inside the second biopolymer during shear processing in a melt".

A thesis is a statement belonging to the structures of deductive theories, and hypotheses belong exclusively to the structures of empirical theories. The truth of a thesis is proved by proving, and the truth of hypotheses is confirmed by research. To assess its truthfulness, the above formulation requires the implementation of research and the comparison of its results. Thus, this is a hypothesis, and its confirmation will lead to the conclusion that it is possible to prepare "green all polymer" nanocomposites containing reinforcing polymer nanofibers, and subsequently it is assumed that the proposed methodology for phase morphology controlling via in situ conversion of biopolymer blends into composites would be broadly applicable because uncontrollable structuring of incorporated phase and poor interfacial bonding are commonly encountered problems in high-performance blend preparation. In the final part of the work, the Author logically and concisely confirms the hypothesis that was the motto of the dissertation.

2. The original achievements of the thesis

MSc Ramin HOSSEINNEZHAD in his PhD thesis introduced a novel concept of in-situ generation of all-polymer nanocomposites, where the nanofibers of one polymer are formed inside the second polymer during shear processing in a melt, wherein the solidification of nanofibrous sheared inclusions was performed by shear-induced crystallization, all during processing. The presented concept allowed forming "green all-polymer" nanocomposites in a single step for a range of biopolymers. Within the thesis, the Author investigated in detail the influence of shearing conditions encountered during in situ generation of nanocomposites on the non-isothermal crystallization of biodegradable polymers. It was found, inter alia, that the viscosity and elasticity indicators, as well as interfacial interactions, are the main dominant factors in the formation of the morphology of dispersed polymer inclusions. To widely differentiate the viscoelasticity of the molding systems, Author used Joncryl ADR4400 as a compatibilizer for polymer mixtures and as a chain extender for the polymer matrix before

mixing with the second polymer. The Author has shown that there are upper and lower boundaries for viscosity and elasticity ratios that ensure efficient in situ fibril formation. The author also showed that shear increases the temperature of non-isothermal crystallization of polymer inclusions (in particular, shear at 300 s^{-1} led to an increase in the non-isothermal crystallization temperature of PBAT, PBASGT, PBS, and PHA). Moreover, it has been found that the shear-induced crystallization of nanofibers is influenced by the inclusion viscosity. Shear stress was also found to favorably affect nucleation rate and density rather than crystal growth. Besides Author has investigated the evolution of the microstructure as well as the mechanisms of plastic deformation and fragmentation of crystal lamellae for mixtures and nanocomposites.

An additional improvement in the mechanical properties of nanocomposites Author has achieved by incorporating a new hybrid configuration, i.e. interpenetrating networks of nanofibers. The hybrid network was created by combining durable, in situ generated PBS nanofibers with rigid, ready-made nanofibers obtained in a separate polyoxymethylene (POM) electrospinning process, wherein PLA was chosen as the matrix. The obtained mechanical properties with a positive hybrid effect were higher than those resulting from the additivity of the mixing rule. As a result of this research, the Author has created a triple hybrid nanocomposite with a shape memory using a blend of PLA/PBAT/cellulose (CNF) nanofibers. The in-situ fibrillation of the dispersed PBAT component favored the formation of more effective physical entanglements at the interfaces due to their greater specific interfacial area compared to the fillers dispersed in the droplets acting as physical cross-linking bonds (network nodes). The introduction of CNF increased the conversion of PBAT droplets to nanofibers during shear. As a consequence, thinner and longer PBAT nanofibers were created, causing a stronger interaction at the PLA-PBAT and PBAT-CNF interface. The in-situ formed shape memory composite showed drastically higher values of deformation recovery rates, permanent deformation rates, faster recovery, and better mechanical properties compared to the mixture.

This research is innovative and represents a rich collection of compensated knowledge related to the technology of „in-situ generation of all-polymeric nanocomposites" based on renewable resources. Particularly noteworthy is the fact that in the present work, for the first time, the possibility of forming a new hybrid configuration -interpenetrating fiber networks and its influence on the resulting hybrid effect is considered. I consider the experimental material and the way of its interpretation in the doctoral dissertation very good.

Comments and discussion

The following are the debatable and critical remarks:

1. In the thesis, the Author used Joncryl ADR4400 as a polymer chain extender. Why this one has been chosen? Is it the most widely used?
2. Page 48- Author writes „differential scanning calorimeter during heating from -100 °C to 250 °C at a heating rate of 10 °C min^{-1}, then keeping at 220 °C for 3 min" – why it was kept in 220 ºC instead of 250 ºC?
3. Page 83. Why the stress-strain curves do not run from „0"? Was it to better visualize the differences between the samples?
4. Page 87. Figure 5.25 Are these the representative curves? Or Author performed only one experiment? There is no information about it nether in the Experimental section nor the Discussion.
5. Fig. 5.45. Author labeled the Figure as „melting thermograms" – but still in the figure the info „exo up" or „exo down" should appear. The same with „cooling exotherms"
6. The Figures are not unified in the thesis: i) once you can find a come before the unit, like in Fig. 5.58, ii) immediately underneath (Fig. 5.59), the unit is in square brackets like [ºC], iii) the units are in round brackets (e.g. Fig. 5.53). it does not affect the substantive part of the thesis, but is rather an editorial error.
7. Fig. 5.60. There is no need to present the data from 0º, if the measurement has been initialized in 5º.

The writing style of the dissertation is not objectionable, although minor editorial errors have been found, eg. in a few places there are no spaces between words; in few places Authors used „0" instead of degree mark; there is no unified representation of the units: once the author writes that the density of PCL is d=1,145g/ml, while for PHA it is 1,30g/cm^3 (page 83): both are correct, however, is should be unified in the whole text; moreover according to units in few places the power is not represented by superscript like „m2" (page 87); in Table 5.5. the font is different than in the rest of the tables and in the text, etc.

The following thesis is interdisciplinary since it spans several fields of science: rheology, polymer physics, and nanocomposite technology. The quality of the study presented in the thesis is very high.

The presented critical remarks do not affect my positive assessment of the doctoral dissertation by MSc Ramin HOSSEINNEZHAD.

As part of the discussion on some of the issues presented in the dissertation, I ask the PhD student to comment on the following issues during the public defense:

1. There is no statistic data for tensile measurement to better visualize the differences between the samples (Tables 5.2, Table 5.3.)? This suggests that the experiment has been performed for only one sample (which according to the Standard is incorrect). Please explain, why in a few places (Tables) there is no statistical data for the values of Young's modulus etc. On the other hand, in the Tables where the statistic is found, then the values are rounded to various decimal places.
2. The author writes in the Objectives of the Thesis that „Moreover, from the emergence of biopolymer nanofibers one can expect economical, ecological, and recyclable benefits". Since there are no regulations for the biopolymers like PLA, or reinforced PLA. Maybe Author can explain what kind of „recycable benefits" are expected, or what kind of recycling procedure can be proposed for the materials.
3. The author writes about the applicative possibility of the prepared "green all-polymer" nanocomposites. Of course, it is an important trend in replacing commonly used fibers with bio-based ones, especially from the ecological point of view. However, since still the mechanical performance of the bio-composites are rather worse than expectable, could you please explain the application possibilities of such materials.

Conclusion

The PhD thesis presented by MSc Ramin HOSSEINNEZHAD is of a high scientific standard. The subject of work is scientifically up-to-date and attractive in terms of application. The author scrupulously used the opportunity to cooperate in a strong team of employees of The Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences (PAS). The work is edited in a clear and condensed manner. The presented results contain elements of novelty in the cognitive and utilitarian sense. The author has mastered the technique of research work very well and applied research methods adequate to its scope.

I evaluate the work positively. I state that the reviewed doctoral dissertation entitled: "Biocomposites with nanofibers generated by shear and shear induced crystallization " makes a significant contribution due to its interdisciplinary nature, through (among others) formation of „green all-polymer" nanocomposites in a single step for a range of biopolymers, investigation of the influence of shearing conditions encountered during in situ generation of nanocomposites on the non-isothermal crystallization of biodegradable polymer, and employment of this concept to produce triple shape memory hybrid composites. That is why I am applying to the Scientific Council of the Polish Academy of Sciences for its distinction. The work is edited in a clear and condensed manner. It meets

all the requirements for doctoral dissertations, resulting from the applicable Act of March 14, 2003, on academic degrees and academic title as well as degrees and titles in the field of art (Journal of Laws 2003 No. 65 item 595) and I am applying for its admission for discussion to Scientific Council of Polish Academy of Sciences.

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