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Review of the PhD thesis: "Network Formation of Sulphur Cured Natural Rubber / Butadiene Rubber Blends" by Thomas B. Hanel

1. Formal background

The official letter from Wrocław University of Science and Technology, signed by the Vice-Rector for Research, Professor Andrzej Trochimczuk, dated 25th of November 2019, inviting to take duty of the reviewer of the PhD Thesis of Mr. Thomas Hanel MSc, Eng..

The work has been supervised by well known specialist in polymer blends, composites and nanocomposites, prof. Jacek Pigłowski, who was supported by dr. Konrad Szustakiewicz., the assistant supervisor.

2. Introduction

Rubbers are known for the relationship between macroscopic stress and deformation of network chains, governed by the network density, which in rubber compounds depends on chemical structure and physical properties of the constituents. Therefore in case of rubber blends certain degree of heterogeneity of the spatial distribution of crosslinking points might be expected. The main target of this work was to study the networking behavior and phase morphology of natural rubber and polybutadiene rubber separately and in mutual blends, which inter alia led to elaboration of a mathematical tool for vulcanization curve prediction.

3. Work contents

The dissertation contains 199 pages and has been divided into five chapters and is completed by "Conclusions and Outlook", list of references (224), the list of abbreviations and the list of publications. Before the first chapter the Candidate presents in 5 pages "Motivation for the thesis and work program" and 12 pages "Introduction into the vulcanization".

In the first chapter entitled "Pre-studies of Network Density Evaluation and experimental setup" the Candidate presents literature survey on investigation of vulcanization kinetics and crosslinking structure of the resulting network. The physical properties of polymers used in the work: HV SSBR, HS SSBR, HV BR, NR, IR are presented in Table 2. Were these properties estimated by the Candidate? Are the trade names and suppliers of the polymers known? The curing package contained N-tertbutyl, 2-benzothiazylsulphenamide (TBBS), N,N-diphenylguanidine (DPG), N,N-Diphenylguanidine, insoluble sulphur and soluble sulphur. To study the network density following methods were applied: Torque measurement by means of a MDR (Moving Die Rheometer), Stress strain measurements at low deformation, applying the "Mooney – Rivlin " correlation and mass uptake measurements by swelling in solvents.

The Fig. 20 has the tittle "Network density determination at maximum cure state" but it shows maximum torque in dependence on the temperature at which the samples were cured, which not enables estimation of the network density. It needs explanation. The conclusion that "The network density (@maximum cure state) is almost independent of the temperature" is in my opinion disputablebecause of the results obtained by the "Mooney – Rivlin " correlation (Fig. 22). Would it be possible to present during the public defense numerical data for the Figures 21 and 22? Further it is claimed that the time-domain-NMR (TD-NMR) might be the most reliable method for estimation of the network density because it relates closely to the atomic structure of network.

The Chapter II focuses on curing mechanism of NR and BR. At the beginning the Author presents briefly a literature overview on rubber vulcanization and mathematical approaches used for describing its kinetics. The Candidate underlined that interaction between different accelerators was

still not fully explained and later in this dissertation he contributed to explanation of this process. The investigation od curing behavior of natural ruber (NR) followed the sensitivity analysis scheme created for different concentrations of sulphur and TBBS – DPG accelerators. As in similar experiments, it was found, that the investigated vulcanization reaction followed the Arrhenius relation. Obtained correlations between crosslinking agents and curing and reversing behavior are typical and the results do not differ from expectations. In this chapter a numerical tool for adjusting kinetical parameters to fit the calculated vulcanization curve to the experimental results is applied, which was developed in a cooperation with Gabriele Miliani from Politecnico di Milano. Statistical analysis performed by using of the Response Surface method led to the conclusion, that the interaction between both accelerators TBBS and DPG plays such a small role that it could be neglected during numerical evaluation of the reversion percentage and torque maximum.

Curing behavior of cis butadiene rubber (BR) was investigated like in the case of NR, using the same vulcanization system over a range of curative concentrations and temperature. The findings are generally similar. On the page 67 it is written, that "Compared to NR , BR cures at a slightly lower speed, at the same curative concentrations" but on the page 74 there is a stronger statement : "The values are in accordance to the general findings of the networking behavior of BR compared to NR and emphasize the significant higher reactivity of the NR. What is true, slightly or significant? Besides, all units in a scientific work should be given accordingly to the International System of Units SI, for example in kJ/mol and not in kcal/ mol (Table 7).

The next problem, curing mechanism of NR/BR blends is investigated in the chapter III, which begins with a literature review (9 pages) on curing and morphology of these blends. The literature results pointed on immiscibility of NR and BR phases in the blends with higher crosslink density in the BR phase, whereas NR showed higher reactivity. The experimental work was done at four temperatures on pure BR and NR, at different blend ratio and with different concentrations of sulphur and TBBS-DPG accelerators, accordingly to the Design of Experiment Principle. This approach should enable multifunctional correlation between input parameters and obtained results, and in fact

trend indicators (no clear influence, increase, decrease, slow decrease) were found for activation energy, maximum torque and time to reach it, crosslink density and sulphur chain length distribution. Additional interesting results about crosslinking kinetics and morphology were collected from DSC and AFM investigations. The distribution of polysulfidic to mono-/disulfidic bridges was estimated by the swelling method. Was it performed accordingly to the procedure depicted in the Fig. 19 on page 35? The results of numerical simulations were close to the experimental curve if solubility of sulphur and accelerators was taken into account, which finding is a valuable contribution of the Author to the simulations. The next important issue is NMR characterization of network morphology of the blends. In elastomers, cross-links prevent fully isotropic orientation fluctuations which is detected by Multi Quantum Time Domain NMR (MQ-TD-NMR), a powerful tool for investigation of network structure. As I understand the results presented on pages 118-123 origin from the PhD thesis of M. Farina (2015). IF it is this case, it belongs to the literature review at the beginning of this chapter. Were M. Farina's results published ?

Chapter IV deals with the determination of curative solubility and migration. It was started by swelling of DCP-precured samples in sulphur, TBBS, DPG and zinc-octoate. Next, samples based on different rubbers were assembled and kept under pressure at a constant temperature. The migration of curatives was followed by X-ray fluorescence analysis. This experimental approach was quite ingenious and allowed for calculation of corresponding diffusion coefficients.

The last Chapter V introduces achieving miscibility between two rubber phases by macromolecular cross-metathesis (MCM). This research was performed in collaboration with the University of Salerno. Which part of this work, presented in chapter V, was performed by the Candidate? Is it the sub-chapter 4? I ask this question because Thomas. B. Hanel does not authorize the article [228] with the details of the collaboration.

At the end the Author presents well thought out conclusion and outlook. Especially valuable is the conclusion about lack of correlation between polymer morphology and vulcanization which should be following strictly the principle of single monomer reactivity.

4 . Methodology, clarity of research and scientific correctness

The Candidate has proposed methodology typical for rubber research to solve the scientific problem defined. The standard measurements have been completed with the most sophisticated analyses like MQ TD NMR, AFM, DSC, X-ray fluoroscence chromatography However, not all experimental techniques have been described at length. The material is clearly and concisely presented. However, it happens that information on theoretical background is a part of an experimental section. The results discussed are illustrated by relevant tables, figures, schemes and pictures. They have been generally prepared in an informative way, being readable and of good quality.

5. Conclusion

My opinion about the reviewed dissertation is very positive. The Candidate has a very good command of rubber technology andengineering. He mastered, or at least is familiar, with several experimental techniques, useful in the investigation of elastomers and demonstrated skills and efficiency in writing scientific papers. He knows how to plan experimental work, to select the most suitable techniques, and he can interpret results obtained in mature and critical way, what has been reflected by five publications. The Candidate has already become an independent researcher, carrying out scientific studies by himself.

In the final conclusion I hereby state, that the reviewed dissertation by Mr. Thomas B. Hanel fulfils the common and legal Polish requirements for the PhD degree (Polish law „O stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki", Dz. U. Nr 65, poz. 595, z dn. 14 marca 2003 r.). Based on this statement I make a request to the High Scientific

Council of the Discipline Chemical Sciences of the Technical University of Wrocław of its hearing to the public defence.

Nomination for awarding

In addition, I am asking to award the doctoral dissertation of Mr. Thomas B. Hanel. I support my request with high quality of scientific content of the thesis, excellent writing and his very high ranking publication (Scotti R., Susanna A., D'Arienzo M., Di Credico B., Giannini L., **Hanel T.**, Morazzoni F., et al., "ZnO nanoparticles anchored to silica filler. A curing accelerator for isoprene rubber composites", Chemical Engineering Journal, 275, **(2015)**, pp. 245-252) – assigned 200 points on the List of scientific journals and reviewed materials from international conferences together with the assigned number of points published by the Minister of Science and Higher Education on December 18, 2019.

Mr. Thomas B. Hanel is an active researcher, an author of at least 12 articles, his Hirsch index is 9. He is an inventor of numerous patents, including 3 new patents from the year 2020 on rubber tyres.

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