Politechnika Łódzka
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Review

PhD thesis Thomas Hanel entitled " Network Formation of Sulphur Cured Natural Rubber / Butadiene Rubber Blends. "

Doctoral dissertation Mr. MSc. Ing. Thomas Hanel was made in the Department of Engineering and Technology of Polymers at the Faculty of Chemistry of the Wrocław University of Science and Technology. The dissertation supervisor is Prof. Dr Habil. Ing. Jacek Pigłowski, while the assistant supervisor is Dr Ing. Konrad Szustakiewicz. The work was done in cooperation with research teams in Milan.

The main purpose of the work is to learn about the processes of cross-linking and distribution of network nodes in the mixtures of natural rubber with butadiene rubbers. This issue is not well understood and it is known that mixtures of two or three elastomers are most often used in industrial practice. Thus, two aspects, cognitive and practical, are outlined strongly in the work.

The thesis is interdisciplinary and concerns issues in the field of chemistry, polymer technology and material engineering. It should be emphasized that the assumed goal and scope of research is very ambitious, it required the implementation of many complex and complicated research and technical procedures as well as an interdisciplinary scientific approach for its effective implementation and, as a consequence, the formulation of relevant conclusions based on the numerous results obtained.

The dissertation was presented in the form of five chapters, contains the purpose of the work, conclusions, cited literature and a set of scientific achievements. The

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whole covers 169 pages of text and 30 pages of attachments. The results are gathered in 20 tables and graphically presented in 134 drawings. Each chapter is preceded by a literature review. This information is based on 242 scientific references. The author quotes not only the latest references but also older items, tries to reach original works. The review is exhaustive, relevant items are cited.

Scientific achievements of MSc. Ing. Thomas Hanel cover a total of 5 publications and 3 papers presented in the conference materials.

From the information contained in the section "Motivation for the thesis and work program" one gets the impression that the purpose of the work was extremely clearly defined, concerning, as I have already mentioned, the determination of cross-linking kinetics, distribution of network nodes in the natural rubber / butadiene rubber mixture. The object was selected precisely and correctly. Mixtures of natural rubber and butadiene rubbers are most commonly used. The differences between these elastomers are not very significant. In terms of reactivity, they are also similar, however, the PhD student expanded the scope of research with polybutadienes differing in the content of 1,2- structure. The use of the NR / BR block copolymer is also interesting. It was recognized that there would be no fillers or plasticizers in the compositions. I am convinced that such a decision had to be made because it would be difficult to interpret the unequivocal results obtained. They would perhaps have more practical significance. However, fillers would accumulate preferentially in the BR phase, and would also affect the cross-linking kinetics and network density. TBBS (N-tert-butyl-2-benzothiazylsulfenamide) and DPG (di-phenyl guanidine) were chosen as crosslinking accelerators. They differ significantly in activity and accelerate sulphur crosslinking process differently. Noteworthy is the use of two varieties of sulphur, S_8 rhombic and polymeric, soluble and insoluble in elastomers. Zinc octoate was used instead of zinc oxide. Its presence in cross-linking teams guarantees a more uniform distribution of network nodes.

The research methodology is very diverse. Therefore, MSc. Thomas Hanel had to master the methods of network density testing, equilibrium swelling method, determination of elasticity constants and 1-H-TD-NMR technique. The course of crosslinking and crosslinking kinetics were calculated from rheometric curves. The sulfylation of nodes was calculated using the thiole-amine method. The solubility and diffusion coefficients of the components of crosslinking units were determined. Blends were tested by DSC, AFM, DMA methods. Mechanical properties during stretching were also determined. In Chapter I,

the author presents theories of vulcanization, methods for determining crosslinking kinetics and crosslinking density. Mooney-Rivlin method is described. The density of the network can be determined from the value of the first elasticity constant C_1. The Flory-Rehner method and TD-NMR are discussed. There was a good correlation between crosslinking densities calculated from equilibrium swelling and TD-NMR measurements. The phantom network model must be adopted. The conclusion seems correct because phantom networks have smaller interactions between polymer chains. In addition, the so-called "front factor" in the state equation of elasticity is smaller in phantom networks than affine networks. However, if the elasticity constants of the Mooney-Rivlin method are determined with small deformations, then the network should behave as an affine network. You may need to take Flory approach on networks that contain elements of both the affine model and the phantom network model. (Network model with constrained function model). This approach, however, goes beyond the scope and purpose of the assessed work. In addition, the PhD student rightly notes that the differences between network densities resulting from the Mooney-Rivlin and Flory-Rehner methods may depend on the adopted parameter of polymer-solvent interactions. Often, the impact parameter depends on the inverse of equilibrium swelling in the literature. The presence of permanent entanglement of chains causes that the elastic properties of the lattice sample measured at different degrees of swelling may behave slightly differently than predicted by Flory-Rehner formula. The effect of entanglement becomes smaller as the volume fraction of the polymer decreases in the swollen network. In addition, we assume the functionality of network nodes equal to 4, which may be inconsistent with reality in the case of heterogeneous sulfur crosslinking.

In chapter II MSc. Thomas Hanel described the course of crosslinking of natural rubber and butadiene rubber, and in chapter III mixtures of these elastomers. As expected, natural rubber crosslinks quickly, but with a high reversion, almost regardless of the crosslinking temperature and concentration of the crosslinking assembly. Butadiene rubber cross-links more slowly, but the crosslinking density is higher. NR / BR blend is micro heterogenic, separate phases of two rubbers are formed, despite similar solubility parameters. The author often uses the term "polarity". Perhaps it would be better to calculate the components of solubility, dispersion, polar and hydrogen bonding parameters, especially when analyzing the solubility of accelerators in elastomers. Based on the DoE results, the author concluded that increasing TBBS concentration leads in all

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cases to an increase in maximum torque (MDR) and reduce time to achieve it. The activation energy of vulcanization decreases and the sulphide nodes decrease with increasing TBBS concentration. The effect of DPG is not as pronounced as in TBBS. Increasing the amount of DPG leads to a reduction in crosslinking time and a reduction in the sulphide of the network. An unquestionable achievement is to compare the numerical calculations of the vulcanization of mixtures with real data. Using the test program based on the "cloud" - DoE, with changing the amount of sulphur, TBBS and DPG and in the crosslinking temperature in the range from 150 ° C to 180 ° C, a tool was created to predict the MDR vulcanization curve, and the density of the network of tested polymers as a function of temperature and concentrations of curatives.

Chapter IV describes the methods and results of solubility and diffusion of curatives in tested elastomers. The solubility of crosslinkers in the polymer phases significantly affects the formation and density of the network. BR and NR have different affinities for crosslinking syndromes. TBBS has a greater affinity for BR and this may contribute to further heterogeneity of the blend network. The diffusion of curatives plays a noticeable effect in the IR / BR mixture. The theoretical length of mono- and disulphide bridges is greater than the real one. This is due to the higher solubility of TBBS in the BR phase. Chapter V describes new methods to improve network homogeneity. The liquid solubility of sulphur is equal in cis-BR and IR. Insoluble polymeric sulphur breaks down into soluble sulphur and does not affect the migration of crosslinkers. For NR / cis-BR, the use of insoluble sulphur does not cause a difference in crosslinking characteristics. An interesting approach is the synthesis of isoprene-butadiene block copolymer. Metathesis reactions of commercial homopolymer PBD and PIP solutions were used. The use of the copolymer as the third polymer in the mixture leads to the compatibility effect of the micro-dispersed polymer phase in the polymer matrix, accumulating at the interface, allowing the interpenetration of the polymer chains. As a result, improved and even ideal covulcanization could be expected. The use of the IR / BR block copolymer as a "compatibilizer" partly changed the morphology but did not change the course of crosslinking. There was still a clear solubility of accelerators in BR compared to IR.

Vulcanization of pure IR / BR copolymer has revealed that vulcanization is in accordance with the principle of a single "monomer reactivity", depending on the number of allyl groups and not on the morphology of the polymer.

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In general, the work is presented correctly; it stands out with an aesthetic graphic design. Its individual components are clearly displayed, and it undoubtedly makes it easier for the reader to become familiar with the content of the dissertation. The results are interpreted correctly in my opinion. The conclusions drawn from them are fully justified.

To sum up, I believe that the doctoral dissertation of M.Sc. Thomas Hanel contains indisputable cognitive, scientific and practical data. I have no doubt that the scope of experiments, conducting research their performance as well as the form the results are presented and analyzed to the great scientific and research maturity of Mr. MSc. Thomas Hanel and are proof of a high level of preparation for independent scientific research or solving practical problems.

Due to the high scientific and application value of the work, the collected experimental data and their correct description and correct interpretation, I believe that the doctoral dissertation presented for assessment by M.Sc. Thomas Hanel excessively meets all the requirements of the Act of 14 March 2003 "on academic degrees and academic title as well as academic degrees and title in the field of art" (Journal of Laws No. 65, item 595 of April 16, 2003) and I conclude for accepting the thesis and conducting further stages of the doctoral dissertation.

Award request

I would like to ask for the distinction of the doctoral dissertation of Mr. Thomas Hanel, if the statutory conditions of distinctions at the Faculty of Chemistry of the Wrocław University of Science and Technology are met.

Mr. Thomas Hanel undertook the difficult task of learning about the processes of cross-linking and distribution of network nodes in mixtures of natural rubber with butadiene rubbers. The thesis is interdisciplinary and concerns issues in the field of chemistry, polymer technology and material engineering.

Scientific achievements of MSc. Thomas Hanel covers a total of 5 publications and 3 papers presented in the conference materials.

The collected experimental material is significant, the results are correctly interpreted. The conclusions drawn from them are fully justified. The work contains numerous elements of scientific novelty and practical solutions.

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