

## **Review of PhD-thesis: “ Influence of network structure on properties of elastomers”**

**By: Katarzyna Bandzierz**

**Promotor: Prof. Dr hab. Inż. Dariusz M. Bieliński, Politechnika Łódzka, Łódź, Poland**

First I would like to express my appreciation for the invitation to review the PhD-thesis of Katarzyna Bandzierz. I greatly enjoyed reading the thesis: an impressive piece of work and congratulate her with the results. It does add more insight into the already long existing technology of rubber/elastomer vulcanization, which on the other hand still offers many unresolved questions; a situation which – I presume – will last forever. Consequently, it is not realistic to expect that the present PhD-thesis does answer all questions and so there are indeed still many points open for discussion.

I feel pleased though to recommend Ms. Bandzierz for promotion to Doctor of Science on basis of the present thesis.

However, my role of reviewer is to make some critical comments, resp. request clarifications on various points in the thesis, which I will do hereunder.

### **Introduction**

On page 6 the PhD-candidate states that “new curatives are constantly synthesized and introduced into the market”. I dare say, that that is a bit exaggerated, without giving examples for this statement. In the last 20 years I remember just about one: Vulcuren, as treated in Chapter 4. Not many. Does the candidate have other examples in mind?

### **Chapter 2, Literature review**

On page 11 it is stated that acc. to IUPAC a crsslink is defined as “A small region in a macromolecule from which at least four chains emanate, .....”. Is the candidate sure that it is four and why? Don't three chains also have the potential to form a permanent network? Ref. for example the use of three-functional co-agents for peroxide vulcanization, like e.g. triallyl-cyanurate (TAC) or Trimethylolpropane-trimethacrylate (TRIM) and others.

Page 13 and repeatedly later in the thesis: For the reviewer, who spent a large proportion of his professional life in the development and application technology of EPDM-rubber, it is a bit embarrassing to read that the M in EPDM would stand for "monomer". The candidate is recommended to check the ISO-standard 1629: “Rubbers and latices – Nomenclature”, which states that the M stands for “rubbers having a saturated carbon chain of the polyMethylene type”. The saturated polyMethylene main-chain is the prime reason for the superb ozone- and thermal-stability of this elastomer compared with e.g. Natural Rubber (NR) or Styrene-Butadiene rubber SBR, PolyChloroprene rubber (CR) and the like. Here the R stands for “rubbers having an unsaturated carbon chain, e.g. natural rubber and synthetic rubbers derived at least partly from conjugated dienes”, leading to reduced thermal and ozone-stability.

On page 16 in the middle, the reviewer would like to add that it are primarily the **secondary amines**, which may form carcinogenic **secondary N-Nitrosamines** being resorbed in the body to eventually lead to carbonium-ions, which attack DNA. Primary N-Nitrosamines are too short lived to cause any damage; tertiary N-Nitrosamines are stable and not reactive. All accelerators which contain secondary amines in their chemical structure, like the thiurams, but



also dithiocarbamates and e.g. di-isopropyl-mercaptobenzothiazyl sulfenamide, are potentially carcinogenic. See also in later chapters of this thesis.

Page 16, 3 lines from the bottom: the formation of Zinc-stearate resulting in “solubilized zinc” is just one of the explanations for the role of stearic acid. On the other hand, there are examples (e.g. in EPDM) where in the absence of stearic acid the vulcanization reaction proceeds as well as in presence thereof. The diffusion speed of accelerator moieties is of the order of  $10^{-11}$  m<sup>2</sup>/s, or 10 μm<sup>2</sup>/s, which accounts for enormous distances during vulcanization times of several 10's of minutes. Long enough for such accelerator moieties to migrate to ZnO-particles to pick up a Zn-ion and jointly migrate back to another position to act as catalyst for the vulcanization. It is therefore not really proven, that the reaction of ZnO with stearic acid to form “solubilized zinc” (Page 17, first line and Page 19, first line) is critical for the curing process.

Page 22: To be exact, the abbreviation CV stands for “Conventional Vulcanizing”, SEV for “Semi-Efficient Vulcanizing” and EV for “Efficient Vulcanizing”.

Page 24, last sentence of par. 2.2.3: It is worth mentioning, that it are particularly the 1,2-vinyl moieties in the butadiene-monomers which are really prone to radical crosslinking, resulting in appr. 10 crosslinks per peroxide-radical. This is the main reason for the mentioned crosslink clusters.

Page 25, last sentence before figure 2.5: The reviewer would not use the word “idealization” for the relationships between crosslink density and various properties, but “schematically”, as these relationships are real!

Page 26, Table 2.4: “Fatigue life” increases and then decreases: see Figure 2.5.

Page 28, par. 2.3.1.5: The reviewer considers the explanation of why the modulus and hardness increase with crosslink density a bit simplistic. He would have expected a bit more explanation about how the elasticity of crosslinked rubber comes from entropy-decrease: the basic property of rubber-elasticity, and that  $E = \nu kT$ , where  $E$  is the modulus,  $\nu$  = the number of elastically effective network chains (or simply the crosslink density),  $k$  = Boltzmann's constant and  $T$  = absolute temperature.

Page 29, par. 2.3.1.9: The thermal stability of elastomer materials depends of course primarily on the type of elastomer: see earlier statement on M- and R-rubbers.

Page 31: I fully agree with the statements made by the candidate that the Mooney-Rivlin  $C_1$  constant is only assumed to be dependent on the crosslinks and trapped entanglements, the  $C_2$  constant suggested to be associated with the contribution of trapped entanglements, as the Mooney-Rivlin theory is based on continuums mechanics without a direct link to a polymer network-model. Therefore any relation to crosslinks and entanglements is purely accidental.

Page 38: Somewhere it should have been indicated in the text, that  $M_c$  in Figure 2.7 is inversely proportional to crosslink density.

Page 41, 3<sup>rd</sup> line from bottom: “2-propane” should read “2-propane-thiol”.



the dithiocarbamates, having a similar or even higher reactivity (although much worse processability).

Both TMTD, ZDMC and ZDT belong to the class of ultra-accelerators, typically needed for elastomers like EPDM, which is difficult to cure with sulfur because of its low level of unsaturation. The use of these as main accelerators in SBR is actually quite uncommon.

Furthermore, with TMTD splitting into two ZDMC-molecules, it might be justified to compare TMTD and ZDT on a 2:1 molar basis in the following of the thesis, rather than on 1:1 molar basis, which would as well result in a higher reactivity of ZDT, as corresponds to practical experience.

All this confirms indeed the statement of the candidate, that stating the classical 'curatives amounts in phr' does not account for these factors and that it is therefore insufficient and better to calculate in moles: Page 84 and last conclusion on page 98.

Page 78, line 6: change "dispersity" into "polydispersity".

Page 79, Table 3.2: Why are TMTD and ZDT compared in equimolar quantities and S<sub>8</sub> not, while after all S<sub>8</sub> is the real crosslink-former?

Page 83, Figure 3.1, and page 84, middle of the page: In the perspective of the argument given above, that TMTD can be considered as generating two dithiocarbamate species, the conclusion may well be that ZDT is in fact much more reactive towards crosslink-formation, because in effect the TMTD-formulations contain double amounts of reactive accelerator species (dithiocarbamates) on a molar basis.

The candidate unfortunately did not provide cure-curves or details on scorch time and t<sub>95</sub> – optimum cure times for the various compounds, which would have been helpful in the interpretation of the various data.

Pages 85 – 98: It is quite conspicuous, that the effect of the ZDT-curing system in comparison with the TMTD-system is much stronger on: the Static as well as Dynamic T<sub>g</sub> if plotted against the Crosslink density achieved; similar for the free volume change, the density change and the onset of degradation temperature. But most interesting is the lower tensile strength vs. crosslink density in figure 3.7 for ZDT vs. TMTD. Although I do agree with the candidate that there is probably a difference in the degree of modification of the molecular chains in the sense of bulky side-groups generated by pending accelerator-moieties, could also the degree of polysulfidic vs. disulfidic, vs. monosulfidic crosslinks generated play a role here? The fact that the tensile strength vs. crosslink density in Figure 3.7 is significantly lower for the ZDT-system than for the TMTD-system might well indicate a predominance for shorter sulfidic crosslinks for the ZDT-system. The shorter sulfidic crosslinks, in particular the monosulfidic are less flexible on a molecular scale, resp. more stable, and so can less easily accommodate large deformations. In effect peroxide-cured rubber compounds are also always lower in tensile strength for the similar reason that the C-C-crosslinks are less flexible and more stable even than monosulfidic crosslinks: see also page 124, figure 4.13 (b), for which on page 125 exactly this explanation is given. The statement made on page 94, lines 9 – 11: "..... the crosslink structures are similar in both investigated series, ....." may be questioned. This is an assumption and not proven with e.g. thiol-amine chemical probes, like in Chapter 4.

Page 50, line 11: Is the polybutadiene really cold-emulsion-polymerized at -20 °C? First: water freezes at 0 °C, so significant amounts of freezing-point decreasing substances must have been added (methanol or ethylene glycol?). Further, emulsion polymerization of butadiene is practically never done anymore these days, except as the start of emulsion-polymerization of High Impact Polystyrene. The polybutadiene latex-particles have poor rubbery properties, but still good enough for impact-modification of Polystyrene. Even anionically solution-polymerized polybutadiene can only in limited quantities be used for real rubber/tire applications: Michelin has a plant of their own. It still does not excell in rubber properties. Practically all Polybutadiene is these days polymerized with Ziegler-Natta solution polymerization. The references [143] and [144] are all pretty old afterall: 1948 and 1951, times when Ziegler-Natta and possibly anionic polymerization had not been discovered yet. So this is a bit out-of-date.

Page 59, 6 lines from the bottom: A “specific interaction” often quoted is the little heat released by the formation of a crosslink, raising the temperature locally on molecular scale and so promoting another crosslink-formation close-by.

Page 64: Another technique worth mentioning is Network Visualization as developed by the Tun Abdul Razak Research Center (TARRC) in the UK. The technique makes use of swelling the network in styrene and later on crosslinking the styrene radically, so catching the swollen network in polymerized polystyrene. After microtoming and staining the nanoscopic inhomogeneities can be visualized with Transmission Electron Microscopy. The developers first thought they saw the crosslinked network, but therefore the resolution is not good enough. But inhomogeneities are well visible.

Page 65, 2.7.1.2: it is “Williams” and not “William”. (The present reviewer was a Post-doc with Ferry and has known Williams personally).

### Chapter 3

Page 78, Materials: Can the candidate explain in more detail why the particular materials were chosen for this study:

- The SBR KER 1500 must, by its 1500-code be an emulsion-polymerized SBR. Emulsion-polymerized elastomers may contain appr. 5 wt% left-over emulsifiers, giving all sorts of interactions which may interfere with a fundamental network-study. Why was no solution-polymerized SBR used: much cleaner till max 0.5 wt% non-rubber? See later in the thesis.
- Why were the particular two accelerators chosen?
  - (a) Tetramethylthiuram disulfide (TMTD): a real “old” accelerator, severely N-Nitrosamine forming and therefore under pressure to be replaced by non-carcinogenic alternatives. It is well known that TMTD in reaction with ZnO splits in two Zn-dimethyl dithiocarbamates (ZDMC), which are the real accelerating species: see e.g. the PhD-thesis of P.J. Nieuwenhuizen: “New Perspectives on Sulfur Vulcanization: reactions and homogeneous catalysis concerning Zinc Dithiocarbamates”, University of Leiden, June 25, 1998, and extensive literature quoted therein concerning the above reaction path. See also: P.J. Nieuwenhuizen et al., Rubber Chem. Technol. 70, 368-430 (1997). So, one molecule of TMTD splits in fact in two ZDMC-molecules.
  - (b) 2-Ethylhexyl zinc dithiophosphate (ZDT), has gained special interest over the last decades because it is a non N-Nitrosamine forming alternative to

## Chapter 4

Similar as in Chapter 3, with the wide variety of curatives tested in the present chapter, it would have helped the interpretation of the various results a lot if details on cure-data had been provided.

Page 112, Figure 4.3: Does the candidate have an explanation why the Tan delta curve increases for the non-crosslinked sample at high temperature? This raises a point which also pertains to the other figures covering tan delta: the height in Figure 4.6; the width in Figure 4.7 and the tan delta height at 70 °C in Figure 4.8. In effect, tan delta is the ratio between two quantities: the loss modulus  $G''$  and storage modulus  $G'$ , each depending separately on the crosslink density. It would have been very helpful for the interpretation of the phenomena if the dependency of both quantities independently on crosslink density could have been given. The reviewer is therefore not in a position to judge that the largely different width of the tan delta peak in Figure 4.7 for TBzTD and Vulcuren "can be caused by the large amounts of TBzTD and Vulcuren present in the sample" and whether "Consequently, the molecular movements during the glass transition process occurred over a broad range of temperatures".

Page 119: The candidate expresses the expectation, that short crosslinks (monosulfidic or C-C) should reduce the free volume considerably, and that longer crosslinks (disulfidic and polysulfidic) should result in a larger size of free volume. However, the opposite seems to be true, as demonstrated for the crosslinkers DCP, TMTD and TBzTD. To state therefore that "This **proves** that the crosslink structure **probably does not influence the free volume size**" is not quite appropriate. Could it be, that the inhomogeneity of the crosslink network, as discussed earlier, plays a role here?

## Chapter 5

Page 137: Why were the swollen samples as put in the aluminum DSC-pans completely submerged in excess cyclohexane. The consequence was, that there is always a large peak to be seen in e.g. Figure 5.1, of the pure cyclohexane and that the freezing point depression can only be discerned as a minor bump. Would putting the swollen networks in the pans without excess cyclohexane have had a major influence on the freezing point measurements?

Chapter 5 as a whole: Overall I do agree with the candidate that the technique of freezing point depression is nice but not sensitive enough to discern differences in network structure of the materials investigated.

## Chapter 6

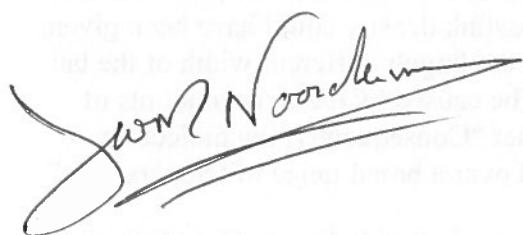
The radiation yield of crosslinking: 0.076  $\mu\text{mol}/\text{J}$  (for the E-SBR containing 23.5% bound styrene) may be low in comparison with other elastomers: Table 6.2, but also in comparison with the results of Witt [14] in Table 6.3: for 23.5% bound styrene, one would have expected a  $G_x$  of  $\pm 0.20 \mu\text{mol}/\text{J}$ . Apart from the arguments given for this disparity by the candidate, could the emulsifier-residues contained in the SBR have had an effect in this respect?

A handwritten signature in black ink, appearing to be 'JW', is located in the bottom right corner of the page.

## Chapter 7

Admittedly, there are so many assumptions and adjustments to the Tao-Eldrup model necessary in order to interpret the data, that the question seems justified in how far the results in this chapter really contribute to an increased understanding of crosslink structure of the vulcanized rubber. The reviewer agrees in this respect with the conclusions from the candidate on page 192.

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