Influence of the Crosslink Density and Sulfur-Length on In-Rubber Properties of Passenger Car Tire Treads

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1. Introduction

Beside the elastomer type and the chosen silica-silane system, the crosslink density and distribution are important parameters which affect the physical, mechanical and viscoelastic properties of a vulcanizate [1-3]. In accelerated sulfur-curing systems various complex reactions occur during the curing process that form either mono-, di-, or polysulfidic crosslinks, and sulfidic ring structures within the polymer chains [4, 5]. The ratio of accelerator to crosslinking agent determines the type and density of the crosslinks [6, 7].

The scope of this study is the investigation of the influence of different crosslinking densities for silica reinforced SBR/BR blends on the performance indicators of tire treads made thereof.

2. Experimental methods

Three series of compounds based on a green tire tread formulation were prepared having a conventional, semi-efficient or an efficient vulcanization system. Each vulcanization system results in a specific overall crosslink density and different sulfur rank distribution: mono-, di- and polysulfidic of nature. The overall apparent crosslink densities and distributions were measured by swelling experiments done in toluene according to Schotman and Datta, Ellis and Moore [8-10]. Propanethiol in combination with piperidine was used to characterize the polysulfidic crosslinks, hexanethiol and piperidine was used to characterize the poly- plus di- sulfidic crosslinks ("thiol-amine method" [11]).

3. Results and Discussion

The conventional curing system shows the highest overall crosslink density and has the highest Payne effect because of its high storage modulus at low strains. In contrast to this, the efficient curing system has the lowest Payne effect because a lower overall crosslink density leads to low values of the storage modulus at low strains. The polymer network, resp. the filler-filler and filler-polymer interactions contribute to the final values of the Payne effect of the vulcanized samples. At low strain level, the deformation energy is mainly stored in the filler network. This network is unstable and gradually disintegrates with increasing strain levels. At the highest strain level the polymer-filler and the remaining undestroyed polymer network are responsible for the energy storage. When the same types and amounts of filler and coupling agent are used, the differences in the filler-filler interaction can be considered as invariable. In general, the energy can be stored more efficiently in a compound with a higher overall crosslink density, because this increases the storage modulus values at both the low and high range of the strain scale. Furthermore, it is observed that with increasing content of the polysulfidic crosslinks the Payne effect becomes higher. Probably the higher percentage of mono- and di-sulfidic crosslinks can last unbroken, preventing the drop in the value of the storage modulus at high strains.

A maximum in tensile strength is pronounced for the efficient curing system, and the least visible for the conventional vulcanization system. The samples with the efficient vulcanization are also characterized by the highest values of the tensile strength, which can be caused by the lower crack propagation ability of the material with lower overall crosslink density together with a higher bond energy of the mono- and disulfidic crosslinks.

Increasing the overall crosslink density of the compounds causes a rise in the glass transition temperature by about 5 °C between the compounds with the efficient curing system and the conventional system. However, no major changes in the height of the tan δ peak are registered. Apparently, only variations in the polymer immobilization on the filler surface can lead to changes in the peak height, for instance in the case of silica differing in the specific surface area or different coupling agents.

The values of tan δ at 60 °C are decreasing with increasing overall crosslink density of the compounds. This trend is independent of the crosslink types, as at the strain level applied during the measurement the ability towards a recombination of longer poly-sulfidic crosslinks is suppressed.

The compounds with different curing systems are characterized by only a small changes in the LAT-100 side force coefficient. This could be caused by minor differences in the storage and loss moduli of the compounds at low temperatures. For similar hardness values the efficient and semi-efficient curing systems give slightly higher values of the SFC in comparison with a conventional system.

4. Conclusions

The experimental results indicate that by adjusting the overall crosslink density several in-rubber properties can be improved.

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5. References

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