

P10. Katarzyna Bandzierz: Application of PALS to Study Structure of Elastomers

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Crosslink density, defined as a number of network chains per cubic centimeter of a sample, describes a three-dimensional structure of elastomers. Due to the fact that the crosslink density influences to a high extent numerous properties of elastomers, its comprehension and determinability is fundamental. Hereunder, the structure and packing of macromolecular chains, and the number and length of crosslinks between them, influence the size of free volumes. However, the structure of elastomers can be highly complicated, due to complexity of reactions which occur during high-temperature curing process. Precise characterization of structure of crosslinked elastomer systems still remains challenging. A powerful technique, which can serve to investigate the microstructure of polymeric materials is Positron Annihilation Lifetime Spectroscopy (PALS).

The subject of the study were sets of samples on the matrix of styrene-butadiene rubber (SBR), crosslinked with use of three types of curing systems – dicumyl peroxide (DCP), zinc dialkyldithiophosphate in combination with rhombic sulphur (ZDT/S₈), and N-cyclohexyl-1-benzothiazole sulfenamide with rhombic sulphur (CBS/S₈), differing significantly in the length and structure of crosslinks, but similar according to crosslink density. The room temperature PALS studies were employed to provide information on the free volumes, which were correlated with crosslink density, determined with use of equilibrium swelling in toluene and calculated on the basis of Flory-Rehner equation. The lifetime of *o*-Ps as a function of crosslink density exhibits in general a downward trend. For DCP cured samples, the shortening of *o*-Ps lifetime is very little, whereas for CBS/S₈ and ZDT/S₈, the τ_3 value considerably drops with increase in crosslink density. However, the τ_3 values are scattered and cannot be directly assigned to the formation of crosslinks and more dense packing. The intensity of the τ_3 component, i.e., I_3 decreases with increasing crosslink density, indicating on reduction of free volumes fraction. The change of I_3 value is very little for peroxide cured samples, in contrary to CBS/S₈ and ZDT/S₈. It demonstrates that the obtained data are strongly dependent on the type of curing system used – particular types of molecules, such as rhombic sulphur and/or accelerators, present in the elastomer matrix. They can significantly influence, by inhibition or quenching, formation of *o*-Ps.

These studies reveal that the obtained values from PALS for crosslinked elastomers, due to various possible types and amounts of curatives incorporated into the polymer matrix, cannot be always directly correlated with crosslink density, what is often overlooked in scientific publications.