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Study on Elastomer's Network Structure by Dynamic Mechanical Analysis and Positron Annihilation Lifetime Spectroscopy

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Crosslinking, also referred to as curing and vulcanizing, is an indispensable process in elastomer technology. This process requires presence of curatives in the material, which at elevated temperature (130°C – 190°C) undergo transformations. As a result of these reactions, chemical intermolecular bonds develop, permanently linking the polymer chains. The crosslink density, defined as a number of network chains per cubic centimeter of a sample, influences to a very high extent numerous properties of elastomers [1]. The curatives available are abundant and characterize themselves with diverse structures and therefore various reactivity. Many of those curatives are based on sulfur compounds, rhombic sulfur or their mixture. Since the reactivity of this group of chemicals, especially at high temperature, is very complex, the structure of formed crosslinks can be diversified. Furthermore, beside the formation of effective crosslinks, the curatives can undergo side reactions leading to modification of the polymer chains: (i) sulfur chains connect to different positions on the same polymer chain, forming intramolecular cyclic structures; (ii) accelerator, sulfur and accelerator/sulfur complexes graft on the polymer chains in a form of pendent groups. According to literature, the change of properties, resulting from curing, almost entirely comes from intermolecular crosslinks and their structure [2], hence much attention is attached to detailed characterization of these two structural parameters. Surprisingly, the effect of possible chains' modifications and their influence on properties is barely discussed. The reason of this fact can be that there are no established and reliable direct methods to identify and quantify the various modifications of the chains formed upon curing. In the present work we demonstrate that Dynamic Mechanical Analysis (DMA) and Positron Annihilation Lifetime Spectroscopy (PALS) techniques can serve for this purpose.

The aim of the investigation was to characterize the network microstructure of the elastomer samples, cured with use of various curatives. The subject of the study were sets of samples based on emulsion styrene–butadiene rubber (E–SBR) with 23.5% of bound styrene, crosslinked with the aid of various types of curing systems – rhombic sulfur (S_8) and accelerators, such as dibenzothiazyl disulfide (MBTS), 1,3-diphenylguanidine (DPG), N–cyclohexyl–1–benzothiazole sulfenamide (CBS), tetramethylthiuram disulfide (TMTD), zinc dialkyldithiophosphate (ZDT), which resulted in the formation of sulfide crosslinks of various structures (mono–, di– and polysulfide). Samples crosslinked with curatives without sulfur, such as TMTD and dicumyl peroxide (DCP) were also prepared to obtain shorter, uniform crosslinks. The samples were cured to obtain a broad range of crosslink density in every set, determined with use of equilibrium swelling in toluene and calculated on the basis of Flory – Rehner equation. The crosslinks' structure was investigated with the aid of thiol – amine analysis. Temperature sweep measurements, performed with DMA in the range of -80°C to 80°C, provided values of glass transition temperature (T_g), determined by the maximum of mechanical loss tangent (tan δ) and the maximum of loss modulus (E''). With the aid of *fast–fast* positron lifetime spectrometer, room-temperature PALS measurements were performed. The spectra were deconvoluted assuming three lifetime components, of which the longest-living (τ_3) of *ortho*-positronium (*o*-Ps) was ascribed to free volume size.

As investigated by DMA, for all systems the increase in crosslink density was followed by a rise in T_g, which effect is consistent with literature reports [3-4]. The crosslinks, being chemical linkages between the polymer chains, are topological constrains, which stiffen the chains and hinder the mobility of the polymer segments. However, it is evident that the influence of crosslink density on T_g exhibits significant differences for sets of samples crosslinked with various types of curatives. The change of T_g with increasing crosslink density is the lowest for DCP and TMTD cured samples. The formed crosslinks are in this case uniform, short, and the molecules of the curatives are small, hence their grafting on the polymer chains does not influence their flexibility and mobility. For the other curing systems, the increase in crosslink density is followed by larger changes in T_g. In the sets MBTS/S_8, DPG/S_8, CBS/S_8, TMTD/S_8 and ZDT/S_8, this pronounced effect can be ascribed to the presence of both rhombic sulfur and accelerators. Sulfur reactivity at elevated temperature is very complex; therefore the abundant intramolecular sulfur structures can be formed. Moreover, the contribution to the increase in T_g comes also from accelerators, which alone or in combination with sulfur can form various modifications of the polymer chains, resulting in hindering the movements of the chains and decreasing their flexibility. Since the largest change in T_g occurs for the sets cured with accelerators with the largest molecules and the most complex structures, namely ZDT/S_8 and MBTS/S_8, it can be concluded that most likely it is the effect of bulky moieties that affects stiffening of the polymer chains.

The PALS studies showed that the lifetime of *o*-Ps exhibits a downward trend as the crosslink density increases. For DCP and TMTD cured samples, the shortening of *o*-Ps lifetime is very little; this indicates on a small change of free volume size with increase in crosslink density. The molecules of these curatives have therefore negligible effect on the size of free volumes, formed by the surrounding polymer chains and crosslinks. The changes in the *o*-Ps lifetime are more evident for DPG/S_8, CBS/S_8 and TMTD/S_8 sets of samples, what shows that in case of accelerators combined with rhombic sulfur, the formed modifications reduce the size of the free volumes. The most rapid drop of the size of free volumes with increase in crosslink density was found for ZDT/S_8 and MBTS/ S_8 sets. The reason of this dependence is the fact that ZDT and MBTS accelerators characterize themselves with large structures, which are grafted on the polymer chains and located in the free volumes, occupying large areas and considerably shortening the *o*-Ps lifetimes. The PALS and DMA studies provide very coherent information, demonstrating that the parameters of network structure are strongly dependent on the kind of curatives used. The curatives exhibiting large structures, by formation of modifications, fill up the free volumes and decrease their size, at the same time hindering the movements of the polymer chains and causing their stiffening.

The present research aims at highlighting two points: (i) the significance of the type of curatives used for crosslinking and (ii) the consequent structures formed during curing process, other than intermolecular crosslinks, which modify the polymer chains and influence materials' properties. The DMA studies, based on following the T_g changes, provided information on stiffening of the chains, which comes not only from the density of effective crosslinks, but also modifications of the polymer chains by the curatives. The PALS study revealed that the observed changes in the DMA results are reflected by decrease in free volume sizes, which are filled up by molecules of curatives grafted on the polymer chains. Combined DMA and PALS studies provide complementary information on the effect of various types of curatives on structural parameters and network microstructure of crosslinked elastomers. Moreover, since the parameters are influenced to a large extend by the structure and size of the curatives' molecules, it allows to establish a basic structure – properties relation and serves to make the behaviour of crosslinked elastomers more "predictable".

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