

Structural changes in rubber during mechanochemical processing

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The reuse of end of life tires is increasing – shredded tire crumb is used in various applications such as improvement of bitumen properties, providing effective soil drainage systems, etc. However, production of processed rubber, which could be viably used as a partial substitute for virgin material, has not yet become widespread [1]. Although characterization of processed rubber still relies on extraction, additional analysis might be very beneficial. In this study truck tire buffings were processed mechanochemically and their sulfur cross-link density (CLD) values were measured as described [2]. During processing rubber's structure is altered both macroscopically (granulometric composition) and intramolecularly. The change in rubber's CLD values as a function of processing intensity has been observed and could be divided into two segments – the initial reduction of CLD value (segment A) and its subsequent rise (segment B), see Fig. 1.

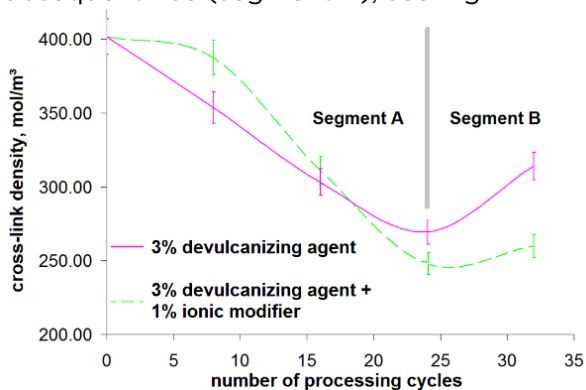


Fig. 1. Dependence of cross-link density (CLD) on intensity of rubber mechanochemical processing.

When rubber is exposed to higher processing intensities it changes its shape dramatically – rubber powder or sponge-like crumbs turn into a sheet. XPS analysis using XPS *VersaProbe* III (Physical Electronics) was performed on the rubber sample, after it had been processed for 32 cycles with 3% devulcanizing agent [3], extracted with acetone and dried [2]. The data showed the formation of sulfur – oxygen bonds in the outer-most layer of the rubber sample, see Fig. 2. The formation

of such bonds suggests that oxygen plays an important role in mechanochemical processing of rubber at higher processing intensities: it reacts with active sulfur species generated during cleavage of sulfide bonds and could be responsible for reestablishment of cross-links in the rubber matrix. Gas cluster ion beam sputtering showed that the amount of sulfur-oxygen bonds decreased by more than 1/3 inside the rubber.

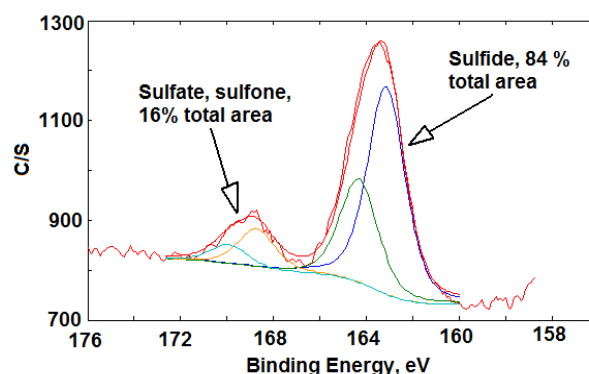


Fig. 2. XPS and peak deconvolution of outermost layers of processed rubber without sputtering

XPS analysis and CLD determination suggest that mechanochemical treatment of rubber is a surface targeted process with sulfide cross-links being the active reaction sites. Density of sulfur cross-links is increasing when going from the surface into the bulk of the rubber matrix. This needs to be appropriately considered when developing rubber recycling technologies.

Literature

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3. S. Asadauskas, A. Jukna "Devulcanizing agent for production of reclaim rubber powder" WO2014062043A1.

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