Chapter 8

CONCLUSIONS

This chapter provides a glimpse of the conclusions drawn from the research work carried out on natural rubber vulcanizates prepared using safe accelerators and the scope for the future work on non-regulated accelerators incorporated synthetic rubber vulcanizates. The primary objective of the study was to develop safe binary accelerators incorporated natural rubber vulcanizates with mechanical properties comparable to that of the NR vulcanizates prepared using conventional regulated nitrosamine generating accelerators. The results of MTT assay show that tertiarybutyl benzothiazolesulfenamide (TBBS) and tetrabenzyl thiuramdisulfide (TBzTD) are safe (non-carcinogenic) substitutes for N-oxydiethylene 2-benzothiazolesulfenamide (MBS) and tetramethyl thiuramdisulfide (TMTD) in natural rubber based formulations.

Safe natural rubber vulcanizates can be prepared using N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS) too. Though the vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD are non-cytotoxic, the mechanical properties are inferior compared to the vulcanizates prepared using TBBS and TBzTD. So for the further studies TBBS and TBzTD were chosen as the safe accelerators.

Commercial applications of rubbers require the use of particulate fillers such as carbon black, silica, etc. Natural rubber vulcanizates with desired mechanical properties could be obtained by mixing carbon black.

The addition of carbon black improved the tensile strength, tear strength and abrasion resistance. Swelling studies in toluene show that the addition of carbon black decreases the diffusion, permeation and sorption coefficients in NR vulcanizates. Rubber-filler interactions of the carbon black-filled NR compounds were confirmed through bound rubber content and strain-sweep analysis. SEM images confirmed the proper dispersion of the filler in the vulcanizates. Thermogravimetric analysis results show better thermal stability of the carbon black-filled NR vulcanizates compared to the gum vulcanizate. Non-cytotoxic nature of the carbon black-filled NR vulcanizate was proved by the MTT assay. The safe black-filled vulcanizate containing 40 phr filler shows optimum mechanical properties.

One of the non-black reinforcing fillers with reinforcing properties closer to carbon black is precipitated silica. The natural rubber compounds containing silica filler show more scorch safety compared to the gum compound, but require longer cure times. Incorporation of silica to the natural rubber compound improved the tensile strength, modulus at 300 % elongation, tear strength and hardness. Abrasion resistance increased as the dosage of silica increased. Optimum properties were obtained with 15 phr of precipitated silica. Swelling studies in toluene show reduction in diffusion coefficient, sorption coefficient and permeation coefficient with increase in silica content. Incorporation of silica in NR compounds improved the fluid resistance of the vulcanizates in diesel and lube oil. The MTT assay results confirmed the non-cytotoxicity of the silica-filled natural rubber vulcanizates.

For a filler to be effective in rubber as a reinforcing agent it has to be well dispersed. Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on

to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction. Conventionally silica-reinforced rubber vulcanizates are prepared by mechanical mixing of rubber and silica with silane coupling agent (Si69), which provides a chemical link between silica and rubber. A promising alternative method for proper dispersion of silica in the natural rubber matrix is the incorporation of small dosages of epoxidised natural rubber (ENR). Evaluation of epoxidised natural rubber as a reinforcement modifier in precipitated silica-filled NR was made and compared with silane modified silica-filled NR. Presence of ENR in the rubber matrix during mixing of silica has improved the distribution of silica in the rubber matrix. The mechanical properties of the ENR modified silica-filled vulcanizates were compared with that of the Si69 modified silica-filled vulcanizates. The results of mechanical properties indicate that ENR has a coupling effect in silica-filled rubber vulcanizates.

Relatively good distribution of silica-filler with less number of agglomerates in the NR was observed in the SEM photomicrograph of the vulcanizates prepared using silane coupling agent and ENR. Addition of the silane coupling agent and ENR enhanced the bound rubber content of the compounds and improved the fluid resistance of the vulcanizates. Addition of silane coupling agent and ENR results in low rolling resistance in the safe silica-filled NR vulcanizates. It is observed that the ENR modified silica-filled NR vulcanizates give reinforcement equivalent to that of silane modified silica-filled NR vulcanizate at dosages of ENR more than double that of Si69. ENR can be considered as an alternative to the expensive silane coupling agent. From the MTT assay it is observed that the silica-filled natural rubber vulcanizates modified with silane and ENR are found to be mildly cytotoxic,

but safe to use. The repeated exposures through careless handling or misuse of the vulcanizates may increase the risk of adverse effects.

The mechanical properties of the vulcanizates prepared using commercial TQ (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline) or high pure grade TQ, i.e. HPG (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline with dimer as the predominant constituent) as antioxidant were compared with that of the vulcanizate prepared using N-(1,3-dimethyl buty1)-N'-pheny1-p-phenylenediamine (6PPD) as control antioxidant. The vulcanizates containing 6PPD show better mechanical properties compared to that containing TQ and HPG. The vulcanizate prepared using HPG show slightly high tensile strength and tear strength compared to that prepared using commercial TQ. All the vulcanizates show improved tensile strength after ageing at 70 °C and 100 °C for 24 hours and retained the tensile strength even after ageing at 70 °C for 96 hours. Thermogravimetric analysis of the vulcanizates containing 6PPD and HPG establishes better efficiency of these materials as antioxidants compared to the commercial TQ. The MTT assay results show that the natural rubber vulcanizates containing TQ and HPG produce mild cytotoxicity and the vulcanizate containing 6PPD is non-cytotoxic.

Suggestions for future work

Future prospects of these studies include:

- Preparation of safe vulcanizates by incorporating nitrosamine-safe accelerators (TBBS and TBzTD) into synthetic rubbers such as styrene butadiene rubber (SBR), nitrile rubber (NBR) and ethylene-propylene-diene monomer rubbers (EPDM).

- Use of zincdibenzyl dithiocarbamate (ZBEC) - a nitrosamine safe accelerator - for the preparation of vulcanizates based on synthetic rubbers (SBR, Butyl rubber (IIR), EPDM) and also on NR and SBR lattices.
- Evaluation of the mechanical properties and cytotoxicity of the proposed safe accelerator incorporated vulcanizates.