Abstract

Devulcanization of vulcanized elastomer is very difficult, due to their three dimensional chemical network structure, which makes the material insoluble, infusible and non-melting. Mechano-chemical process is a novel method for devulcanization study. From which it is possible to de-vulcanize the vulcanized natural rubber from waste rubber (namely aged natural rubber vulcanizate) through the application of mechanical shearing (by open two-roll cracker cum mixing mill), temperature and de-vulcanizing agent simultaneously. The whole thesis reports the findings of the investigation on devulcanization of aged rubber vulcanizte, assessment of extent of devulcanizing agent and compared the properties of revulcanized rubber with the original rubber vulcanizate. Five different devulcanizing agents taken to devulcanize the vulcanized elastomer (both gum rubber vulcanizte containing three different sulfur accelerator ratio and aged tyre) are diallyl disulfide, diaryl disulfide, thio acid, diphenyl disulfide and dibenzyl disulfide. The devulcanization of vulcanized rubber was done with the help of open two roll cracker cum mixing mill in both absence and presence of devulcanizing agent at around 90°C to 120°C temperature. The de-vulcanized rubber was vulcanized again with the addition of proportionate amount of sulfur, CBS and retarder at 150°C up to the optimum cure time with the help of compression molding to get revulcanized rubber. The mechanical, dynamic mechanical, thermal, morphological, spectral and cure properties of original rubber vulcanizate and revulcanized rubber were investigated.

Rheomertic study shows that there is decrease in maximum rheometric torque and scorch time for revulcanized rubber. This is due to the revulcanized rubber

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contain less gel compared to original rubber vulcanizate. The rate of cure is more for revulcanized rubber containing devulcanizing agent and increased with increasing the concentration of devulcanizing agent. This is due to increase in concentration of devulcanizing agent; it breaks the crosslink bond more and creates more cross-link side for next revulcanization. For aged tyre rheometric study, it shows that the devulcanizing agent containing rubber has minimum rheometric torque and it decreases with increasing the concentration of disulfide. These results suggested that the devulcanizing agent breaks the cross-links bonds and decreases the viscosity.

The mechanical properties of revulcanized rubber mostly depended on the concentration of devulcanizing agent used in the devulcanization step and the type of devulcanizing agent. Mechanical properties of re-vulcanized rubber obtained by devulcanization in presence of devulcanizing agent were higher than in their absence. Enhance of these mechanical properties manifests itself by a sharp increase in cross-link density and gel fraction. This was due to the fact that devulcanizing agent breaks the sulfur cross-link of the vulcanized rubber, which on re-vulcanization with sulfur and CBS forms more new cross-links. By adopting this de-vulcanization technique more than 70% mechanical property of vulcanized natural rubber was retained.

From FTIR spectral analysis studies it was cleared that all the vulcanizates (both vulcanized and revulcanized rubber) have a typical poly-isoprene peak. It also revealed that an increase in devulcanizing agent, the peak at 1540cm⁻¹ was diminished. This suggests that the mechanical properties of revulcanized rubber increased with concentration of disulfide. Another important observation was that for revulcanized **rubber** there was no peak at 1730 cm⁻¹ (carbonyl stretching frequency), which indicates that the main polymeric chain did not oxidize at the time of milling with the help of open two-roll cracker-cum mixing mill at high temperature, which also increase the mechanical properties of revulcanized rubber. A brief look into the

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mechanism of de-vulcanization and the influence of de-vulcanizing agent on mechanical properties of re-vulcanized rubber are presented.

From the thermo-gravimetric analysis (TGA), it was found that the thermal stability of revulcanized rubber enhanced with increasing the concentration of devulcanizing agent. The temperatures where the maximum degradation occurs of revulcanized rubber containing devulcanizing agent was higher. This may be due to the re-vulcanized rubber has more cross-link density. Cross-linking increases the rigidity of the system, which in turn increased the thermal stability.

DMA analysis revealed that below the glass transition temperature the storage modulus of revulcanized rubber was higher than original rubber vulcanizate. At above ambient temperature the storage modulus of ruvelcanized rubber was higher than original rubber vulcanizate. The increase in storage modulus again suggests that the degree of cross-linking of the re-vulcanized rubber significantly improved. The SEM study suggested the change in failure mechanism as influenced by the type of cross-linking present and the devulcanizing agent used.

Key Words: Mechanochemical devulcanization Process, natural rubber, aged tyre, diallyl disulfide, diaryl disulfide, dibenzyl disulfide, thio acid, diphenyl disulfide, devulcanization, devulcanized rubber, revulcanized rubber, mechanical properties, cross-link density, devulcanization mechanism, FTIR study, TG analysis, DMA study, morphology.