Mechanochemical reclaiming of ground rubber tire using a dual-functional reclaiming agent

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Disulfide chemicals act as a reclaiming agent during the mechanochemical reclaiming of ground rubber tire and can subsequently help to disperse silica filler into the revulcanizate.

The problems associated with the rapid accumulation of waste tires in recent decades have attracted an enormous amount of attention in the 21st century. Disposing of this waste material poses serious environmental threats. Among traditional disposal methods, energy recovery and pyrolysis (i.e., recovery of fuel or valuable chemicals) are economically undesirable because they discard valuable material that remains present in the waste rubber at the end of the tire’s service life. Reclamation (devulcanization) is therefore the most desirable approach. This method solves the disposal problem and also saves valuable petroleum (i.e., from which the polymeric material in tire is developed).

The reclamation of scrap rubber products is essentially a conversion: from a 3D, interlinked, insoluble, strong, and infusible thermoset polymer to a 2D, soft, plastic, tacky, low modulus, processable, and vulcanizable thermoplastic product that mimics many of the properties of virgin rubber. The reclaimed material can be used as a substitute for fresh rubber—either in combination with another material, or alone—in the manufacture of new rubber products, particularly for relatively light-duty applications (e.g., tire inner liners, inner tubes, automobile floor mats, animal mats, and insulation tiles). In the chemical reclaiming process, a large number of chemical reclaiming agents (e.g., different disulfides, monosulfides, and thiols) have been used for the treatment of scrap ground rubber crumbs or powders at an elevated temperature and under pressure. However, almost all disulfides and thiols have a very unpleasant smell and are hazardous, making their handling undesirable. In addition, they are expensive and as such their use may not be economical for reclaim-rubber production.

The mechanochemical devulcanization of natural rubber (NR), styrene butadiene rubber (SBR), guayule natural rubber (GNR), and ground rubber tire (GRT) can instead be carried out using bis(3-triethoxysilyl propyl) tetrasulfide (TESPT), i.e., a well-known coupling agent for the dispersion of silica filler into non-polar rubber...
compounds. The extent of reclamation can be monitored by measuring the crosslink density and Mooney viscosity of reclaimed rubber as a function of reclaiming time. In our process, we make use of this unique reclaiming agent, which is non-hazardous and can be handled safely. TESPT functions as a reclaiming agent during the reclamation process, and the ethoxy end group of the fragmented TESPT (which is attached to reclaimed rubber) forms a chemical bond with silica filler during its product application. Costly carbon black can therefore be replaced by comparatively inexpensive silica filler without a great reduction of mechanical properties in the resultant revulcanizate.

To reclaim GRT, we mixed 100g of GRT with 6mL TESPT and soaked it for 24 hours. We subsequently transferred the mixture to an open-roll mill, where we performed mechanical milling at a friction ratio of 1:1.25 for different time intervals. We thus prepared devulcanized GRT (DeVulcGRT) at around ~70°C for devulcanization times of 20, 30, 40, 50, and 60min to fabricate DeVulcGRT(20), DeVulcGRT(30), DeVulcGRT(40), DeVulcGRT(50), and DeVulcGRT(60), respectively.

Figure 2. Results of our experiments on the effect of reclaiming time on (a) the tensile strength and (b) elongation at break of ReVulcGRT/silicon dioxide (ReVulcGRT/SiO$_2$) and ReVulcGRT. ReVulcGRT: The product formed after vulcanization of compounded DeVulcGRT.

Figure 3. Scanning electron micrographs showing the tensile fracture surface of (a) ReVulcGRT(20), (b) ReVulcGRT(40), and (c) ReVulcGRT(60).

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We determined the crosslink density of our DeVulcGRT using the Flory-Rehner equation, the results of which are shown in Figure 1(a). We find that the crosslink density constantly decreases throughout the reclaiming process. During the mechanochemical reclamation of GRT in the presence of TESPT, the vulcanized rubber experiences tremendous mechanical shearing (resulting in a random polymer chain distribution and crosslink scission). This breaks the disulfide bonds of TESPT, leading to radical-mediated disulfide fragmentation. The fragmented TESPT then attaches to the broken crosslink bonds through a radical capping reaction, leading to a decrease in the crosslink density of GRT. Finally, the 3D rubber network is converted to a thermoplastic rubber material with a relatively low molecular weight. The bond energy of different crosslinks in the vulcanizates—monosulfide: 285kJ/mol; disulfide: 268kJ/mol; polysulfide: 195kJ/mol—are comparatively lower than that of the carbon–carbon bonds in the main chain (352kJ/mol). As such, the crosslink bonds are more susceptible to homolytic cleavage rather than main-chain scission.

We also confirmed capping by fragmented TESPT via sulfur analysis. We analyzed the sulfur content after acetone extraction (carried out for 72h to remove free sulfur) and found sulfur contents of 2.95, 3.12, 3.25, and 3.43% for GRT, DeVulcGRT(20), DeVulcGRT(40), and DeVulcGRT(60), respectively. Our results support the theory that attachment of the fragmented reclaiming agent to DeVulcGRTs occurs due to an increase in the combined sulfur content in the DeVulcGRT with reclaiming time. The effect of reclaiming time on the Mooney viscosity [ML(1+4) 100°C] of different DeVulcGRTs—as shown in Figure 1(b)—indicates a decrease in the Mooney viscosity with reclaiming time. This is because excessive mechanical degradation leads to the formation of a reclaim rubber with superior processing characteristics.

To test the performance of DeVulcGRT, we mixed the samples—i.e., DeVulcGRT(20)/(30)/(40)/(50)/(60)—with silica at a ratio of 30phr (parts per hundred rubber) and compounding ingredients (5phr zinc oxide, 1.2phr N-cyclohexyl-benzothiazyl-sulfenamide, and 1.8phr sulfur). We carried out this compounding for 25min at room temperature in an open two-roll mixing mill. The compounded DeVulcGRTs were then cured at 150°C and pressures applied (~35MPa) for the respective optimum cure time (i.e., \( t = 190 \)).

The mechanical properties, including tensile strength and elongation at break, of revulcanized GRT (ReVulcGRT)—i.e., vulcanized DeVulcGRT—are presented in Figure 2(a) and (b), respectively. Our results clearly show that for silica-loaded ReVulcGRTs, both the tensile strength and elongation at break increase with reclaiming time (up to 40min) and then stabilize. For ReVulcGRT without silica, however, the values continuously decrease for reclaiming times of up to 60min, which conclusively proves the reinforcement of ReVulcGRT/SiO\(_2\) vulcanizate. The mechanical performance of vulcanizates shows excellent agreement with the scanning electron micrographs (see Figure 3) of the tensile fracture surface. Figure 3(a) shows a significantly rougher surface and more matrix tear lines due to the presence of a higher proportion of gel rubber (18.5%), which leads to an increased resistance to crack propagation and a lower tensile strength compared to that of the ReVulcGRT(40) (gel content: 23.5%)—see Figure 3(b)—or ReVulcGRT(60) (gel content: 28.0%); see Figure 3(c). Moreover, the micrographs of the tensile fracture surface of DeVulcGRT/SiO\(_2\) vulcanizate showed a homogeneous structure with a uniform dispersion of silica filler within the rubber matrix.

In summary, we carried out mechanochemical reclaiming of GRT using TESPT, a unique dual-functional reclaiming agent. The evaluation of crosslink density and Mooney viscosity as a function of reclaiming time shows that good mechanical properties are achieved in the resultant ReVulcGRT. Sulfur analysis indicates that the fragmented reclaiming agent is attached to the reclaim rubber and, in turn, facilitates the dispersion of silica filler during its product application. Indeed, this result is evident from our mechanical property measurements and scanning electron micrographs. In our future work, we will further investigate the applications of reclaim rubber by incorporating silica as a reinforcing filler in natural rubber or styrene butadiene rubber without the use of a coupling agent.

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