Research Article

Effects of Posttreatments on the Storage Stability of Reclaimed Rubber

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Reclaimed rubber should be considered a source of new material with an economic impact, so the recycling of waste rubber is especially important. In this paper, sulfur-cured waste tire rubber powder is successfully devulcanized in a normal-pressure continuous regeneration system under the application of an activator and aromatic oil. Then, the reclaimed rubber was subjected to further mechanical shearing using a two-roll mill, rubber extruder, and rubber strainer. The effects of the storage time at room temperature on the properties and structure of reclaimed rubber were examined by sol fraction measurement, Mooney viscosity measurement, crosslink density measurement, tensile property testing, and Rubber Process Analyzer (RPA) measurement. The results under the test conditions indicated that different postprocessing operations were not making much difference to the properties of the reclaimed rubber. But the effect of storage time is more significant; the Mooney viscosity value increased from 65 to 90 when the storage period increases to 60 days, the sol fraction decreased, and the crosslink and density storage modulus also increased with increasing storage time due to the slow recombination and aggregation of the molecular fragments with free radicals happening in the reclaimed rubber during the storage.

1. Introduction

Due to its specific rubber properties at room temperature, vulcanized rubber is widely used in transportation, aerospace, and other fields. However, the three-dimensional crosslinked structure of vulcanized rubber cannot be reprocessed easily or undergo biodegradation by microorganisms; thus, how to reuse waste rubber is a great challenge in the rubber industry, especially for waste tires. According to available statistics, there were, for instance, about 283 million waste tires generated in China in 2013, which is more than 10.8 million tons. To solve this problem, waste rubber products have been disposed of in many ways, such as waste rubber powder [1], reclaimed rubber [2], direct use, and pyrolysis [3, 4]. In order to fully utilize available resources and protect the environment, reclaiming rubber is one of the most important methods to treat scrap rubber.

The reclamation of waste rubber has long been investigated with great effort. In general, scrap rubber can be reclaimed by breaking the existing crosslinks in the vulcanized rubber or by main-chain scission of the rubber or a combination of both processes, which means the reclaiming process involves partial or complete cleavage of S-S crosslinks which were formed during vulcanization [5, 6]. The reclamation can be performed by mechanical or chemical methods using reclaiming agents [7, 8], microwaves [9, 10], ultrasonics [11, 12], and supercritical carbon dioxide methods [13, 14]. De et al. [15] studied the reclamation of ground rubber tires using tetramethylthiuram disulfide (TMTD) as the reclaiming agent and evaluated the cure and mechanical properties of the various blends of natural rubber (NR) and the reclaimed rubber produced. Given the circumstances, environmentally friendly reclaiming agents have generally been used, such as the Renewable Resource Material (RRM) reclaiming agent [16, 17] and shea butter softener from the nuts of African shea trees [18]. De et al. [16, 17] studied the reclamation of sulfur-cured NR with a vegetable product and diallyl disulfide under various reclaiming conditions. The progress of reclaiming was monitored by determining the sol content, molecular weight of sol, and
Mooney viscosity of the reclaimed rubber produced. Tensile properties and swelling characteristics of the revulcanized reclaimed rubber were also studied. Xu et al. [18] studied the effect of softeners such as the shea butter softener and wood tar softener on the reclamation of GTR using a torque rheometer.

Based on previous studies, the chemical reactions occurring in the rubber during the regeneration process are complex and not well understood; many researchers have speculated the possible mechanism of the devulcanization, as shown in Figure 1 [19]. The essential component of the activator 450 is a polymeric phenyl disulfide with the chemical structure shown in Figure 1(a). During the regeneration process, the waste tire powder is milled with the activator 450 and aromatic oil at a temperature of ~180°C. Under the heating and mechanical shearing of the rubber-activator mixture, the following chemical reactions are possible: the disulfide bonds in the activator can break, resulting in sulfenyl radicals (Figure 1(a)), and the S-S crosslinks and C-C bonds in the rubber can cleave, resulting in molecular segments with radicals (Figure 1(b)), even though the C-C bond cleavage may occur in substantial amount only above a temperature of 300°C. The radical species on the molecular fragments can get neutralized by coupling with each other or with the sulfenyl radicals produced by the activator compound; the molecular fragments (neutralized or unneutralized) constitute the sol component of the reclaimed rubber. The unneutralized radical species present in the reclaimed rubber may recombine during the storage of the reclaimed rubber to increase its Mooney viscosity, affecting its processability.

Therefore, reclaimed rubber should have a high sol fraction and a proper Mooney viscosity, thus having excellent performance and good processability. And maintaining a low and stable Mooney viscosity is critical for the successful application of the reclaimed rubber in new rubber products.

Both the sol fraction and Mooney viscosity can be influenced by the regeneration methods, agents, temperature, time, and shear force in mechanical regeneration. There are many researchers that have studied the structure and properties of reclaimed rubber, such as the crosslink density of gel, number average molecular weight ($M_n$) of sol, Mooney viscosity, and mechanical properties of the reclaimed rubber [20–22]. But we know of no research on the storage stability of reclaimed rubber and the mechanism of its changes during storage, which is the aim of this paper. We described the changes of structure and mechanical properties of reclaimed rubber samples during storage at room temperature in air. The reclaimed rubber of this study was obtained by reclaiming waste tire rubber powder with an activator and aromatic oil using a proprietary normal-pressure continuous regeneration system. The reclaimed rubber was subjected to further mechanical shearing using a two-roll mill, rubber extruder, and rubber strainer to see the effects of these different postprocessing operations on the storage stability of the reclaimed rubber.

2. Experimental

2.1. Materials. Tire rubber powder (40 meshes) from entire tires removed of their skeleton materials was provided by China Rubber Resource Regeneration (Qingdao) Co., Ltd., China. The regeneration activator (activator 450) and other rubber ingredients, such as zinc oxide (ZnO), stearic acid (SA), sulfur, N-t-butylbenzothiazole-2-sulfenamide (TBBS), and aromatic oil, were commercial grade materials obtained in China.

The chemical component of the waste tire rubber powder includes the natural rubber, butadiene styrene rubber, butadiene rubber, rubber reinforcing filler such as carbon black, rubber aging inhibitor, and vulcanizing agents such as ZnO, SA, and sulfur, and the physical type is powder.

Reclaimed rubber powder has the same chemical compositions as the waste tire rubber powder, and it can be made into a sheet structure.

2.2. Sample Preparation. The reclaimed rubber was produced from tire rubber powder by a normal-pressure continuous regeneration system at China Rubber Resource Regeneration (Qingdao) Co., Ltd. During the regeneration process, the waste tire powder was milled with a regeneration activator (activator 450) and aromatic oil; the formulation used was as follows: waste tire powder (100 phr), regeneration activator (1 phr), and aromatic oil (15 phr). The reclaimed rubber obtained after the process was further processed in three different ways to study the effects of three different postprocessing operations on the physicomechanical properties of the reclaimed rubber: the #1 reclaimed rubber was masticated on a two-roll mill 18 times; the #2 reclaimed rubber was extruded by an extrusion machine and then masticated on a two-roll mill twice; and the #3 reclaimed rubber was passed through a rubber filter at 70°C. The different reclaimed rubbers (#1, #2, and #3) thus obtained were stored at room temperature for 60 days, and their Mooney viscosity and mechanical properties of the vulcanizates were tested at various intervals during the storage. The contrast revulcanization was prepared after 8 hours of storage of the reclaimed rubbers. The recipe for the revulcanization compounds is shown in Table 1, and the compounding was carried out on a two-roll mill (X(SK)-160, Shuangyi Rubber & Plastic Machinery Co., Ltd., China) at a temperature of 50–60°C by thin passing 18 times. The compounds were then pressed into 2 mm thick sheets under a pressure of 10 MPa at 145°C for 10 min. The vulcanized samples obtained from the different reclaimed rubber samples were designated as #1, #2, and #3.

2.3. Sol Fraction Measurement. The sol fraction of the reclaimed rubber was measured by Soxhlet extraction using toluene as solvent. The reclaimed rubber samples were refluxed in toluene for 12 h and then dried in a vacuum oven at 60°C for 6 h. The weight of the samples was recorded before and after the extraction, and the sol fraction of the reclaimed rubber was calculated as the total soluble fraction in toluene minus the fraction of the reclaiming agent and reclaiming oil added with the waste rubber powder during the reclaimation process.

2.4. Mooney Viscosity Measurement [23]. The Mooney viscosity [ML(1 + 4)100°C] values of the reclaimed rubbers
and their compounds prepared for revulcanization were measured using a Mooney Viscometer (EKT-2000M, Ektron Tek Co., Ltd., Taiwan).

2.5. Crosslink Density Measurement. The crosslink density of the reclaimed rubber samples was determined by the equilibrium swelling method in toluene for 72 hours. Low-molecular weight components were extracted by acetone (using a Soxhlet apparatus) before the swelling tests. The crosslink density was calculated according to the Flory-Rehner equation [24] for tetrafunctional networks by using the swelling data:

\[
Ve = \frac{\ln \left( 1 - Vr \right) + Vr + \chi Vr^2}{Vs \left( 0.5Vr - Vr^{1/3} \right)},
\]

where \( Vr, \chi, V_s, \) and \( Ve \) are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of the solvent, and molar crosslink density, respectively. Since tire rubber typically contains NR, BR, and a large amount of SBR, we assumed the value of \( \chi \) equal to 0.43 (cm³/mol) and the value of \( Vs \) equal to 106.4 (cm³/mol) for toluene [24].

2.6. Tensile Property Testing. The tensile properties of the revulcanized reclaimed rubber were measured according to the ASTM D412 standard. Dumbbell-shaped specimens forming to the Die C of the standard were punched out from the vulcanized sheets and tested using a universal testing machine (AI-7000M, Gotech Testing Machines Inc., Taiwan) at an extension speed of 500 mm/min at room temperature (23 ± 2 °C).

2.7. Rubber Process Analyzer (RPA) Measurement. The cure properties of the rubber compounds were measured using a cure rheometer (RPA 2000, Alpha Technologies Inc., USA) at the temperature of 145 °C, frequency of 1.0 Hz, and strain amplitude of 2.8%. The dynamic mechanical properties of the reclaimed rubber samples were also measured by the same instrument by doing dynamic strain sweep experiments at the temperature of 60 °C and frequency of 0.6 Hz with strain varying from 0 to 100%.
3. Results and Discussion

3.1. Mooney Viscosity. The Mooney viscometer is commonly used for measuring the flow properties of raw rubbers in the rubber industry. The Mooney viscosity or viscosity in Mooney units is defined as the torque required to rotate a rotor immersed in the rubber at 2 rpm (average shear rate of 1.6 s\(^{-1}\)) at a fixed temperature (100°C for NR) [25]. In the reclaimed rubber industry, the Mooney viscosity is one of the most important parameters to describe the degree of reclaimation of the waste rubber; the lower the Mooney viscosity of the reclaimed rubber, the higher the degree of reclaimation achieved.

The variation of the Mooney viscosity values of the three different reclaimed rubber samples with storage time is shown in Figure 2. As shown in the figure, the Mooney viscosity values of the reclaimed rubbers increase with increasing storage days but Mooney viscosity values are similar for different reclaimed rubber samples. It indicates that the effects of different postprocessing operations are not much different for the reclaimed rubbers. The Mooney viscosity of the reclaimed rubbers increases from a value of about 65 to about 90 when the storage period increases to 60 days. It means that substantial recombination and aggregation occur during storage for the molecular fragments formed in the reclaimed rubber by the reclaimation process and result in the increased Mooney viscosity during storage. During storage, the macromolecular chains containing radicals remain, from a thermodynamical point of view, in an unstable state;
the polymer chains tend to rearrange themselves, leading to a new configuration [26]. The schematics of the recombination of molecular fragments leading to larger network structures are shown in Figure 3.

The Mooney viscosity values of the reclaimed rubber compounds containing curing additives prepared for revulcanization are shown in Figure 4. The Mooney viscosity values of these compounds are significantly lower than that of the as-prepared reclaimed rubber samples, and their Mooney viscosity is less affected by the storage. The shearing happening during the two-roll compounding may have been the reason for the lower Mooney viscosity values of these compounds compared to the as-prepared reclaimed rubbers. The surprising Mooney viscosity stabilization effect seen for these compounds during storage may be due to the presence of curing ingredients (TBBS, ZnO, SA, and S) in the compounds, but the exact mechanism of this Mooney viscosity stabilization effect is not known.

Figure 7: The variation of the storage modulus and tan δ of the different reclaimed rubber samples with strain amplitude. The $G'$ values continuously decrease with increasing strain amplitude; $G''$ increases with increasing storage time.
3.2. Sol Fraction Analysis. The sol fraction and crosslink density of the reclaimed rubbers measured at different intervals during the 60-day storage at room temperature are shown in Figures 5 and 6, respectively. The sol fraction of the reclaimed rubber includes low-molecular weight fragments of the rubber molecules formed during the reclaiming process and additives such as the plasticizer and aromatic oil that were originally present in the waste rubber. The sol fraction of the reclaimed rubber decreased, and the crosslink density increased with increasing storage days. It indicates that some amount of the molecular fragments with radical sites undergoes recombination and produces larger insoluble structures during the storage period causing the sol fraction to decrease and crosslink density to increase with increasing storage time. In Figure 6, the #1 reclaimed rubber sample had a lower crosslink density than the other two samples, possibly indicating the higher effectiveness of the two-roll milling process in breaking down the crosslinks in the reclaimed rubber compared to the other two postprocessing operations, passing through an extruder (#2) and rubber strainer (#3).

3.3. Dynamic Mechanical Properties. The microstructural difference between the reclaimed rubbers can be reflected in their dynamic mechanical properties. Figure 7 shows the variation of the storage modulus (G') and tan δ of the different reclaimed rubber samples stored for various time periods with varying oscillatory strain. There is not much variation between the G' and tan δ values of the different reclaimed rubber samples with the same storage time when tested at constant strain amplitudes. But two clear trends can be seen in the variation of the G' values for each of the reclaimed rubber samples: (i) the G' values continuously decrease with increasing strain amplitude, and (ii) G' increases with increasing storage time. The first trend, the decreasing of G' with the increasing strain amplitude, is a common phenomenon for filled rubbers known as the Payne effect [27, 28]. This is attributed to microstructural changes happening to the filler polymer network or internal assembly of the filled rubber when it is subjected to the increasing amplitude of the dynamic straining. The second trend of having higher storage modulus for the reclaimed rubber with longer storage time arises as a result of the structural changes happening to the reclaimed rubber during storage. The polymer chain radicals in the reclaimed rubber that are not terminated by radical coupling or by coupling with sulfenyl radicals from the activators can undergo coupling with each other during the storage, as shown in Figure 3. The recombination and aggregation of the molecular fragments lead to increased crosslink density and lead to higher storage modulus for the reclaimed rubber with longer storage time.

3.4. Tensile Properties. The tensile strength values of the different reclaimed rubber samples vulcanized after different storage periods are shown in Figure 8. The tensile strength values of the vulcanizates do not vary much for the different reclaimed rubbers and with varying storage time of the reclaimed rubber. The elongation at break values of the revulcanized reclaimed rubber were less affected with storage time of the reclaimed rubber.
4. Conclusion

The Mooney viscosity of the reclaimed rubber vulcanizates was found to be increasing with increasing storage time. The sol fraction decreased, and the crosslink density increased for the reclaimed rubbers with increasing storage time. However, the different postprocessing operations used for the preparation of the different reclaimed rubber vulcanizates were not making much difference to their Mooney viscosity, sol fraction, and crosslink density values. The values of the dynamic mechanical properties such as the storage modulus and tan δ did not vary much for the different reclaimed rubber vulcanizates when the storage period and strain amplitude are constant. But for all reclaimed rubber vulcanizates, the storage modulus increased with increasing storage time. The increase in the Mooney viscosity, crosslink density, and storage modulus of the reclaimed rubber vulcanizates with storage time was attributed to the slow recombination and aggregation of the molecular fragments with free radicals happening in the reclaimed rubber during the storage. The Mooney viscosity values of the reclaimed rubber compounds prepared for revulcanization were significantly lower than that of the as-reclaimed rubbers and did not increase significantly with storage, indicating the Mooney viscosity stabilization effects of the curing agent compound. The tensile properties of the different reclaimed rubber vulcanizates stored for various storage time were not showing much difference; when the curing additives and their proportion as well as the compounding and vulcanization conditions are held constant, not much differences were expected on the network structure formed in the different reclaimed rubber vulcanizates upon revulcanization.

Data Availability

The data (Figures 1–9) used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


[19] V. V. Rajan, Devulcanization of NR based latex products for tyre applications, University of Twente, Enschede, 2005.