

Prozess zur Herstellung von hochqualitativen Regeneraten auf Basis von Schwefelvulkanisiertem SBR

Pathway for High-Quality Reclaim from Sulphur-Vulcanized SBR

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Abstract

The general problem of reclaiming of rubber is the fact that besides crosslinks also polymer chains are broken in this process, and this influences the properties and reduces the quality of the recycled material. An efficient devulcanization is needed in order to achieve a high-quality recycled rubber.

Within this study, the breakdown of sulfur-cured SBR (Styrene Butadiene Rubber) in a thermal de-vulcanization process is investigated under various conditions: The temperature range for the de-vulcanization is varied from 180 °C to 300 °C, and the treatments are done in air and in nitrogen under oxygen exclusion. Depending on the parameters used, the sol fraction increased as expected, crosslink density first decreased, but increased again above a temperature threshold of 220 °C. The reason for this increase in crosslink density is a complicated intramolecular rearrangement of chain fragments due to uncontrolled degradation and oxidation effects. Preventing oxidation during thermal treatment reduces the degree of rearrangement and results in significantly improved SBR devulcanize properties.

Introduction

Enabling recycling loops for used passenger car tires is a challenge and an opportunity: The challenge lies in the presence of SBR as the main elastomer in this type of tires, which makes this material difficult to reclaim due to the tendency of the elastomer chain fragments to recombine. The opportunity lies in the wide availability of the material and in the fact that passenger car tires form a huge potential market for recycled rubber.

There have been many attempts to recycle SBR rubber. However, de-vulcanization of SBR is difficult due to the specific structure of the elastomer. The reaction mechanisms of SBR de-vulcanization are not very well documented. In the SBR de-vulcanization process, a considerable amount of main chain scission takes place, which is outbalanced by an excessive recombination of molecular fragments as the de-vulcanization process proceeds, resulting in progressive hardening of the elastomer¹.

In the present paper, special attention will be devoted to the network breakdown and re-formation of sulfur-cured SBR in a thermal de-vulcanization process. The investigations were done under various conditions: The temperature range for the experiments was from 180 °C to 300 °C, and the treatments were done in air and under nitrogen.

The mechanical properties of various de-vulcanized SBR vulcanizates are compared. Finally, an application study for re-utilization of the de-vulcanizate in a blend with a virgin compound is performed.

Experimental

Mixing and vulcanization.– The SBR was first compounded using a Brabender Plasticorder 350S mixer with a mixing chamber volume of 350 cm³. The compounding formulation was according to ASTM D3185-99 as shown in Table 1, but excluding the carbon black for the material that is to be de-vulcanized.

Ingredient	phr
SBR 1723	100
Zinc oxide	3
Stearic acid	1
Sulfur	1.75
Accelerator (TBBS ^a)	1.38
Carbon black (N375)	68.5

a. N-tert-butyl-2-benzothiazyl sulfenamide

Tab. 1: Formulation of the SBR compound

Grinding.– The vulcanized SBR sheets were subsequently ground in a Fritsch Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

De-vulcanization.– The thermal de-vulcanization was performed in a batch process in an internal mixer Brabender Plasticorder PL-2000. The treatment temperature was varied from 180 °C to 300 °C, and the treatments were done in air and under nitrogen. After de-vulcanization, the material was taken out of the internal mixer under 2 different conditions, into atmospheric air and into liquid nitrogen. The following variations of the experimental conditions are compared in this study:

TT: thermal treatment without exclusion of oxygen;

TL: thermal treatment and quenching in liquid nitrogen after de-vulcanization;

TN: thermal treatment under nitrogen atmosphere and quenching in liquid nitrogen after de-vulcanization.

Rubber soluble fraction.– The soluble (Sol) and insoluble (Gel) fractions of the reclaimed materials were determined by extraction in a Soxhlet apparatus. The vulcanized and de-vulcanized SBR samples were extracted in acetone and THF. The extraction was followed by drying the

samples in a vacuum oven at 40 °C and determining the weight loss until constant weight. The sol fraction was defined as the sum of the soluble fractions in acetone and THF. The correction for the oil contained in the original SBR has been made. The gel fraction was calculated by the following equation:

$$\text{Gel fraction} = 1 - \frac{\text{weight of rubber dissolved in solvents}}{\text{weight of pure rubber in compound}}$$

Crosslink density.– The extracted SBR samples were swollen in toluene for 72 hours at room temperature. The weight of the swollen vulcanizates was measured after removal of surface liquid with absorption paper. The crosslink density was calculated according to the Flory-Rehner equation².

Viscosity.– Complex viscosity values were analyzed via dynamic viscoelastic measurements performed with the RPA 2000. The oscillation frequency was set in the range of 0.01-33 Hz at a constant strain of 0.56%. The storage (G') and loss (G'') shear modulus were measured. The complex viscosities, η^* , were then calculated by the following equations:

$$(\eta^*)^2 = (\eta')^2 + (\eta'')^2$$

where

$$\eta' = G' / \omega$$

$$\eta'' = G'' / \omega$$

Thermogravimetric analysis (TGA).– The thermal decomposition behavior of vulcanized and de-vulcanized SBR was analyzed by thermogravimetric analysis (TGA) using a TGA7 from Perkin Elmer. The samples were heated with a heating rate of 10 °C/minutes in nitrogen atmosphere.

Re-vulcanization.– Selected de-vulcanizates, which were processed at 220 °C, were blended with a virgin SBR compound at a blending ratio of 50/50. The formulation was according to ASTM D3185-99 as shown in Table 1. In this case carbon black was included. The mechanical properties of the blends were tested.

Results and discussion

Sol fraction.– The sol fractions of the TT, TL and TN de-vulcanizates as a function of the devulcanization temperature are depicted in Figure 1. Thermal treatment of sulfur-cured SBR at 180 °C exhibits a sol fraction similar to the sol fraction of untreated SBR. This is an indication that at this temperature the rubber network is still fully intact. The soluble fraction then increases with increasing devulcanization temperature up to 220 °C: The increase of the rubber sol fraction indicates the extent to which the rubber network is broken. Above this temperature, the sol fractions decrease again. This may be attributed to a more extensive generation of reactive radicals and to the complex chemical transformations taking place at higher devulcanization temperatures. These chemical transformations are main chain scission, breakup of poly-, di- and

monosulfidic crosslinks, transformation of sulfidic crosslinks into cyclic sulfidic structures on the elastomer backbone, and transformation of polysulfidic crosslinks into di- and monosulfidic crosslinks⁴. Prominence of these phenomena with increasing de-vulcanization temperature leads to formation of new inter- and intramolecular bonds⁵ resulting in a decrease of the rubber sol fraction above a certain temperature threshold.

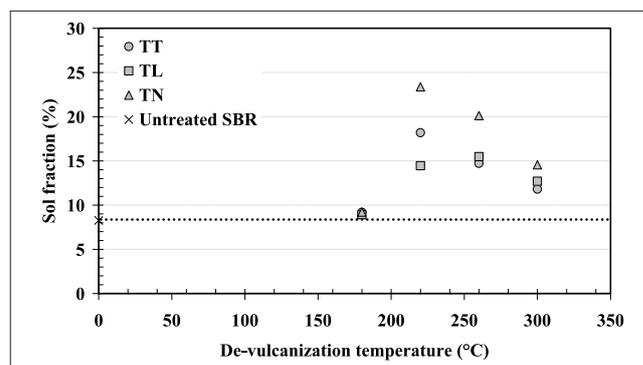


Fig. 1: Sol fraction as a function of the de-vulcanization temperature for de-vulcanized SBR compared to untreated vulcanized SBR (dotted line).

Additionally, it can be seen that the sol fraction increases with exclusion of oxygen in de-vulcanization process. The TN sample, treatment under nitrogen atmosphere, shows the highest rubber sol fractions for all temperatures. Exclusion of oxygen, or in other words, an inert de-vulcanization atmosphere leads to suppression of the generation of reactive radicals followed by reduction of the complex chemical transformations. With increasing temperature, the difference in sol fraction between the samples is reduced: breakdown of the polymer chains and reformation of bonds is mainly governed by temperature and less by the presence of oxygen. At temperatures from 250 °C onwards, the sol fractions of the two samples without nitrogen atmosphere, TL and TT, are almost equal and significantly lower than the sol fraction of the TN sample. This emphasizes the importance of an oxygen-free atmosphere during devulcanization.

Viscosity.– Plots of complex viscosity versus oscillating frequency of the 220 °C de-vulcanized SBR materials are shown in Figure 2. The viscosity levels of the de-vulcanized SBR samples are significantly lower than the levels of untreated SBR, mainly due to the cleavage of the three-dimensional rubber networks during de-vulcanization by both main-chain and crosslink scission. The viscosity curve of the de-vulcanized materials treated under nitrogen atmosphere and quenched in liquid nitrogen is the lowest. The trend of the viscosity curves corresponds well with the trend of the extracted rubber sol fraction (Fig. 1). This indicates that the generation of small molecular chains during de-vulcanization which are extracted in the rubber sol fraction measurement, is also explicitly demonstrated in the low viscosity of the material.

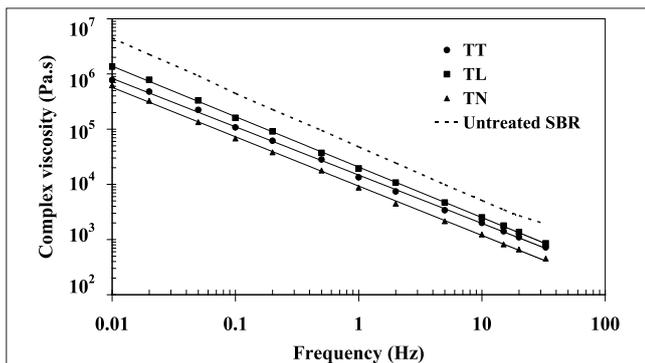


Fig. 2: Complex viscosity as a function of frequency of de-vulcanized SBR

Crosslink density.– The crosslink densities of the three de-vulcanized SBR samples, TT, TL and TN, are shown in Figure 3 as a function of de-vulcanization temperature. Increase of the de-vulcanization temperature up to 220 °C results in a decrease of the crosslink density. There is a slight difference between the 3 samples to the benefit of TN. At temperatures above 220 °C, a significant influence of the de-vulcanization condition on the crosslink density is observed. Within this temperature range, the crosslink density first decreases, but increases again at higher temperature. This effect occurs under all de-vulcanization conditions and is most pronounced for the thermal treatment without exclusion of oxygen: TT. This is in accordance with the trend found for the sol fraction. Therefore, the nitrogen blanket prevents to a large extent the increase in crosslink density due to the presence of air or oxygen.

The detrimental effect of the presence of oxygen in the de-vulcanization process causes inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is even higher than that of the untreated vulcanized one.

Thus, it must be concluded that working under exclusion of oxygen during and after de-vulcanization is a requirement for an efficient de-vulcanization process of SBR, and the temperature of 220 °C is the optimum for de-vulcanization.

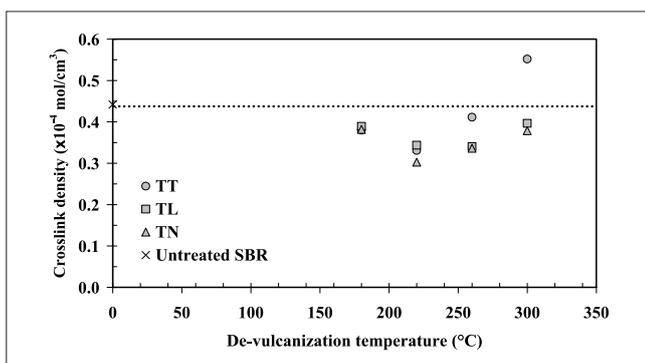


Fig. 3: Crosslink density as a function of de-vulcanization temperature for de-vulcanized SBR, compared to untreated vulcanized SBR (dotted line)

Mechanical properties.– The tensile strength and elongation at break values of the different materials are depicted in Figure 4. It is clearly seen that the tensile strength of the blends is lower than the strength of the original vulcanized SBR. Such a decrease in tensile strength with addition of de-vulcanized SBR is reported by many researchers⁶⁻¹⁰, and explanations given for the decrease in strength are:

- Flaws in the structure of the blend interface between original and reclaimed material, as co-vulcanization between the two phases in general is poor;
- An abrupt modulus change from the original compound, the continuous phase, to the reclaim particles, the discontinuous phase, resulting in inhomogeneities in stress distribution.

Figure 5 illustrates this effect: the modulus is approximately doubled and the hardness significantly increased for the 50/50 blend of de-vulcanized material with virgin SBR, compared to the original SBR rubber. This mismatch in properties can significantly reduce the strength of the material. The stress accumulates on the interface between the de-vulcanized particles and the matrix and fracture starts from this point¹⁰. Elongation at break values of the blends are also lower than the values of the original rubber, and they follow the same trend as the tensile strength values.

Typically, the mechanical properties of a blend of virgin and de-vulcanized rubber are affected by many factors¹⁰ such as:

- presence of gel in the reclaim;
- bonding between reclaim and matrix;
- particle size of the reclaim;
- sulfur distribution between the matrix and reclaim;
- crosslink density and distribution.

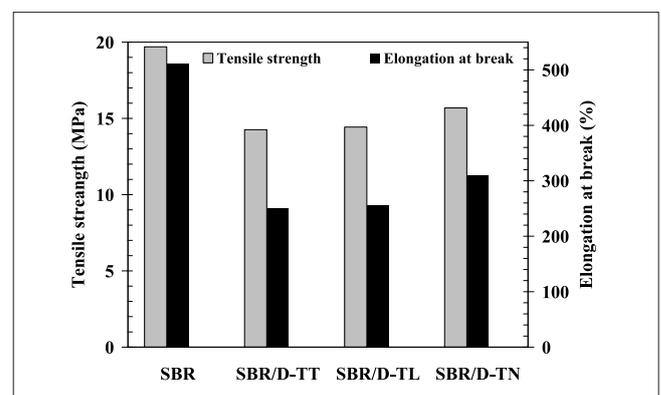


Fig. 4: Tensile strength and elongation at break of vulcanized SBR and SBR/de-vulcanized rubber blends (50/50 wt%).

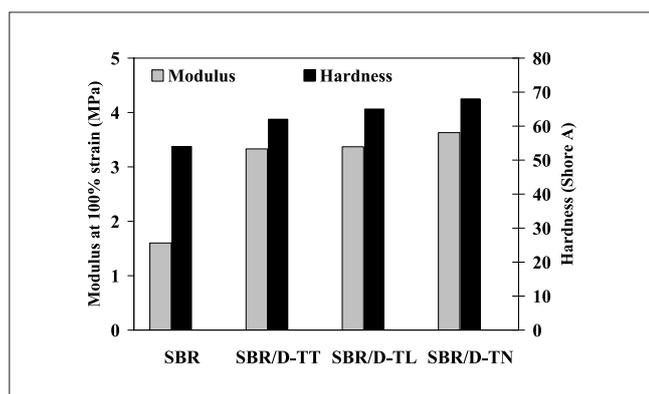


Fig. 5: Modulus at 100% strain and hardness of vulcanized SBR and SBR/de-vulcanized rubber blends (50/50 wt%).

As can be seen from Figure 4, the re-vulcanized SBR/TT blend suffers a 28% decrease in tensile strength and a roughly 50% decrease in elongation at break in comparison to the virgin vulcanized SBR. However, the influence on tensile strength and elongation at break is less when the de-vulcanization process is performed in a nitrogen atmosphere. The best tensile properties are obtained for the SBR/TN blend, which exhibits a 20% decrease in tensile strength and 40% decrease in elongation at break in comparison to the virgin vulcanized SBR for 50% of de-vulcanized rubber added. This improvement of tensile strength and elongation at break is clearly due to the suppressed damage of the polymer during de-vulcanization under exclusion of oxygen.

Under normal industrial compounding operations, the increase in hardness and modulus values would have been corrected by adjustment of the compound recipe. The most probable cause is a higher crosslink density in the blends, as the de-vulcanized rubber is only partially de-vulcanized and still contains reactive curatives. The use of less vulcanization ingredients would most probably have compensated for the hardness increase and brought the tensile properties more close to those for the virgin SBR vulcanizates.

Conclusions

In thermal de-vulcanization of sulfur-cured SBR, intramolecular rearrangements of chain fragments due to uncontrolled degradation and oxidation affect the properties of the material. Interestingly, an increase of the de-vulcanization temperature results in a decrease of the crosslink density in first instance, but it increases again above a temperature threshold of 220 °C. This effect occurs independently of the presence of oxygen during the de-vulcanization process, but it is most pronounced for a thermal treatment without exclusion of oxygen. Optimal properties of de-vulcanized SBR are achieved by working at an optimized temperature of 220 °C and in a nitrogen oxygen-free atmosphere.

The 50/50 w% blend compounds of virgin SBR with material de-vulcanized at low temperature and under nitrogen, showed better mechanical properties than the blend with mere thermally treated material in presence of oxygen. It exhibited a 20% decrease in tensile strength in comparison with virgin vulcanized SBR, while the addition of de-vulcanizate in presence of oxygen resulted in a reduction of almost 30%.

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