

New Continuous Recycling Technology for Vulcanized Rubbers

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Continuous devulcanization technology using the modular screw type of reactor based on “Shear-flow Stage Reaction Control Technology” has been developed for sulfur-vulcanized EPDM. In this process, the breakages of crosslinking points occur selectively under the controls of shear stress, reaction temperature, internal pressure, and additives such as devulcanizing agent and process oil in the reactor. The obtained devulcanized rubber is found to be even mixture of two components. One is linear chain which is soluble in toluene and whose average molecular weight is nearly equal to that of the original raw rubber, and the other is very loosely crosslinking network whose crosslinking density is about one twentieth of that of the original vulcanized rubber. The devulcanized rubber can be re-vulcanized by conventional curing process with sulfur-accelerator vulcanizing system. The re-vulcanized rubber exhibits excellent mechanical properties and formability nearly equal to those of the original vulcanized rubber.

Introduction

There are strong calls for the recycling of rubbers in order to protect the environment and save resources. From the viewpoint of energy balances, material recycling is most desirable method. Most material recycling involves merely pulverizing the rubber and using it as filler; the chemical devulcanization is extremely rare. The mainstream devulcanization method is called “pan process” and it involves batch thermal process using an autoclave, however, this process needs long processing time (more than 5 hours). Recently, new material recycling technologies such as microwave devulcanization [1] and ultrasonic devulcanization [2] methods have been developed for shorter reaction times. However, the properties of devulcanized rubbers by these methods are not satisfactory.

For the vehicles, many rubber parts are used as wheather strips, hoses and miscellaneous parts except tires. Among rubbery polymers for these rubber parts, about half of them are made of ethylene-propylene-diene rubber (EPDM). In this study, a new continuous recycling technology has been developed for vulcanized EPDM in order to obtain the high-quality devulcanized rubber [3,4].

Materials and Methods

The newly developed continuous devulcanization was performed on the modular screw type of reactor based on “Shear-flow Stage Reaction Control Technology”. The screw used for this process is configured using a segment system, and the screw geometry and configuration can be designed as required in accordance with the application. In this experiment, the sulfur-vulcanized EPDM waste which was roughly crashed in the size of about 5mm was used.

Results and Discussion

Devulcanizing reaction process

The geometry and configuration of the screw type of the reactor is an important factor in the ability to devulcanize rubber continuously. Figure 1 shows the devulcanizing reaction process with the reactor which consists of two zones; the first zone in which the rubber is reduced to fine particles and heated to the devulcanizing reaction temperature, and the second zone in which the rubber devulcanizing reaction takes place. In the generation of fine particle zone, the coarsely crushed rubber loaded into the reactor is reduced to fine particle by the shear forces applied by the screw and compressed, heated quickly to the processing temperature, and fed into the devulcanizing reaction zone. In the devulcanizing reaction zone, the flow of the rubber is restrained and the fill factor inside the reaction zone increased; the rubber therefore becomes highly compressed and the hydrostatic pressure acting on it is increased. Using the reactor based on these concept, subjecting the rubber to high shear distortion under high pressure was found to accelerate the devulcanizing reaction. The devulcanized rubber was obtained continuously at the head of the reactor as the strand. The surface appearances of the devulcanized rubber depend on devulcanizing conditions as shown in Figure 2. When the conditions are not appropriate, the surface of strand is rough, but setting the appropriate conditions, devulcanization can be proceeded well, generating devulcanized rubber in strands with smooth surface.

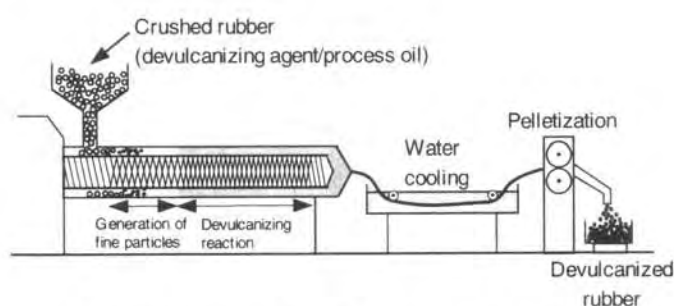


Fig.1 Continuous devulcanizing process for vulcanized rubber

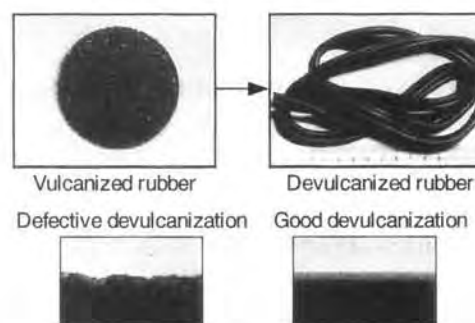


Fig.2 Surface appearance of devulcanized rubber

Mechanical properties of re-vulcanized rubber

The devulcanized rubber can be re-vulcanized by the same type of sulfur-accelerator vulcanizing system as is used to the original rubber. The curing properties were found to be the same as those of the original rubber. Figure 3 shows typical stress-strain curves of re-vulcanized rubbers for 100% devulcanized rubber obtained. The tensile properties of re-vulcanized rubber depend on the conditions of the devulcanizing reaction. Under the optimum conditions (conditions 1), the stress-strain curve of the re-vulcanized rubber was approximately the same as that of the original vulcanized rubber. Under conditions 2 and 3, the elastic modulus and tensile strength of the re-vulcanized rubber were lower, and its elongation at break was higher in comparison with those of re-vulcanized rubber obtained by conditions 1. It is confirmed from

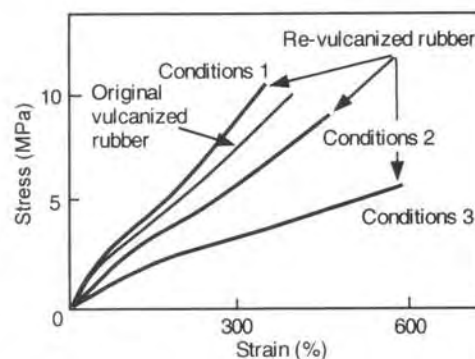


Fig.3 Tensile properties of re-vulcanized rubbers

these results that, in the devulcanizing reaction process with screw type of reactor, the mechanical properties of the re-vulcanized rubber can be controlled over a wide range by the conditions. By optimizing the conditions, it was found possible to obtain re-vulcanized rubber with mechanical properties almost comparable to those of the original vulcanized rubber. The devulcanized rubber also showed approximately the same hardness, heat aging resistance and durability, as the original vulcanized rubber.

Formability of the devulcanized rubber

Formed products obtained by molding, extrusion and extrusion foaming of devulcanized rubber are shown in Figure 4. In molding, the plasticity and other properties of the devulcanized rubber were found to be comparable to those of the original rubber. The surface of the formed product was smooth and of good condition. In the extrusion, the surface appearance of the product is also the same as the original rubber, although the die swell might be a little large. It was also found that the extrusion foaming by adding reagents is possible, and that the specific gravity of the foam can be appropriately controlled. Thus, it is confirmed that the devulcanized rubber can be applicable to the various forming processes in the similar manner to the original rubber.

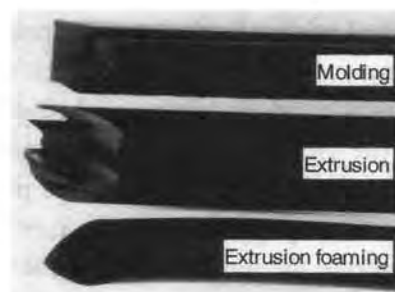


Fig.4 Formed properties of devulcanized rubber

Network structure of the devulcanized rubber

The network structure of the devulcanized rubber was analyzed by the measurements of its solubility and swelling degree in toluene. About half of the devulcanized rubber was insoluble in toluene. The swelling degree of the insoluble component is approximately three times that of the original vulcanized rubber, corresponding to that number of crosslinks had decreased. The crosslinking density as estimated from swelling degree was decreased to be approximately one twentieth of that of the original vulcanized rubber. This means that the insoluble component has a loosely network structure. The remaining half is the linear chain component which is soluble in toluene, and its molecular weight is comparable to that of the original raw rubber (Figure 5). These results may show that the crosslinks formed by vulcanization in the rubber are selectively broken in the devulcanizing reaction.

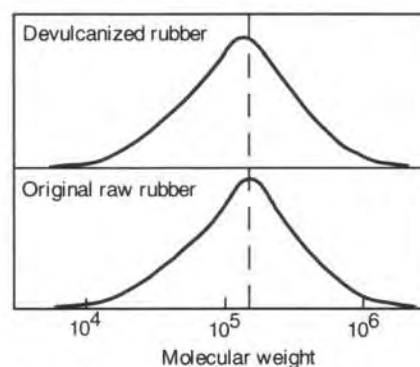


Fig.5 Molecular weight distribution of devulcanized rubber

Change in network structure during the devulcanizing reaction

The change in network structure during the devulcanizing reaction was analyzed by pulling out the screw through the reactor and examining the properties of the rubber at various positions along the screw. Figure 6 indicates the changes in the network structure of the insoluble component during the devulcanizing reaction process. The quantity of the insoluble component decreased as the devulcanizing reaction progressed, and eventually amounted to about 45% of the devulcanized rubber. The crosslinking density also decreased as the devulcanizing reaction

progressed, and the crosslinking structure in this component also became progressively looser. On the other hand, the quantity of the linear chain component which is soluble in toluene increased as the devulcanizing reaction progressed. The average molecular weight was almost the same as that of the original raw rubber. These results may show that the sulfur crosslinks are selectively broken during the devulcanization process, and the linear chain component with a molecular weight comparable to that of the original raw rubber gradually increases as the devulcanizing reaction progresses.

Behavior of crosslink breakage

In order to analyze how sulfur crosslink bonds in the rubber change during the devulcanizing reaction, we analyzed these bonds at various positions along the screw. The sulfur crosslink bonds in vulcanized rubber are of three types: mono-, di- and polysulfide bond. The proportions of these types of bond can be determined using the swelling method. Figure 7 shows the results of an analysis of the sulfur crosslink bonds at various positions along the screw. In the initial stages of the devulcanizing reaction, the numbers of polysulfide bond and disulfide bond decreased but the number of monosulfide bond increased. Then as the devulcanizing reaction progresses, the number of monosulfide bond decreased. In application of heat only in a nitrogen atmosphere, the numbers of polysulfide bond and disulfide bond decreased, but the number of monosulfide bond increased. It is considered from these results that during the devulcanizing reaction, firstly polysulfide bonds and disulfide bonds are converted to monosulfide bonds by heat, then the monosulfide bonds are eventually broken by the shear distortion applied by the screw.

Conclusion

We have developed a new continuous recycling technology for vulcanized EPDM with the modular screw type of the reactor. Furthermore, we have recently confirmed that this technology can be applied to the material recycling for various types of vulcanized rubber such as NR/SBR (material used for tire) and IIR (material used for tire tube), and other types of rubber are being investigated sequentially.

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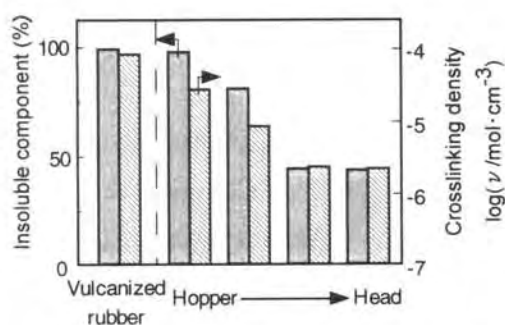


Fig.6 Changes in network structure during devulcanizing reaction

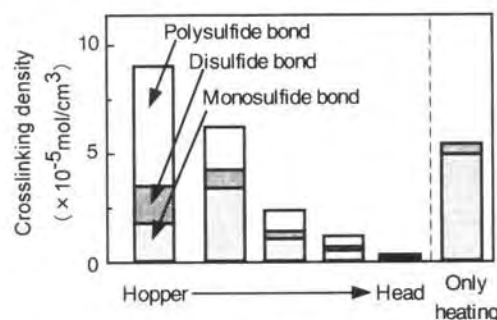


Fig.7 Changes in sulfur crosslink bonds during devulcanizing reaction