Title: Devulcanization of Recycled Tire Rubber using Supercritical Carbon Dioxide

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Abstract

In this work, an extrusion process has been developed for the devulcanization of rubber crumb from recycled tires employing supercritical CO₂. For that purpose supercritical CO₂ has been injected in a twin screw extruder to swell the rubber crumb and to facilitate the otherwise impossible rubber extrusion process. As a consequence, waste rubber can be processed under mechanical shear and extensional forces at various operating conditions that may lead to different degrees of devulcanization.

Introduction

Recycling of automobile rubber tires is an important issue in the rubber industry due to significant environmental concerns and several methods of recycling waste rubber tires have been proposed for the various markets of scrap tires over the years (1). Since the early 1990s’, more attention is given to resources exploration, and the market that can constructively reuse, recycle or recover the value remained in scrap tires and waste rubber has been growing at relatively rapid rates(2,3). The reasons for this rapid growth include lower costs for tire-derived fuel and lower emission levels. The use of scrap tires also increased in civil engineering applications, fabricated products and size-reduced rubber products.

Ground rubber crumb is an important form in the rubber recycling industry and the market for ground rubber continues to grow. At present, ground rubber is mainly produced by reclaiming, ambient grinding, cryogenic grinding and wet or solution grinding. The ambient mechanical process uses a conventional high-powered rubber mill set at close nip. The vulcanized rubber is sheared and ground into small particles, and 10-30 mesh ground rubber is a very common product (4). The disadvantage of this processing method is that a significant amount of heat is generated in the rubber. Excess heat can degrade the rubber and it has the potential danger of combustion if not cooled properly. Cryogenic grinding usually begins with chips of a fine crumb, which is cooled with liquid nitrogen as the medium using a chiller or pre-cooler where it is sprayed with liquid nitrogen at −320°F or −195°C. This embrittles the rubber and makes it easier to grind to fine crumb (40 to 100 mesh). The frozen rubber is put through a high velocity impact type mill. Compared with ambient process, little or no heat is generated in this case, so less degradation occurs and the product has better flow characteristic than ambiently ground rubber. Finally, several studies have been done to compare the properties of rubber powder produced by these two (5-11). Numerous studies have addressed the incorporation of ground rubber crumb into compounds. However, untreated crumb only can be added in a small amount before the properties of the blend start to degrade. Once the ground rubber is already vulcanized, it is difficult to blend it with other existing polymers because there is little interfacial bonding between the rubber powder and the matrix. Therefore, a variety of technologies have been developed for
DEVULCANIZATION OF RECYCLED TIRE RUBBER USING SUPERCRITICAL CARBON DIOXIDE
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The goal of this research work (12,13) was to study the use of supercritical CO₂ (sc CO₂) in the development of a devulcanization process for recycled tire rubber crumb in a twin-screw extruder. More specifically, the objectives of this work were: (i) to determine if recycled rubber powder of various particle sizes could be extruded in a twin-screw extruder
without supercritical CO$_2$ (traditionally, vulcanized rubbers cannot be re-extruded due to crosslinking), (ii) to investigate the effect of scCO$_2$ in facilitating the extrusion of recycled tire rubber powder, (iii) to study the effect of processing conditions (rubber flow rate, CO$_2$ concentration, screw speed, screw configuration, and temperature) on the viscosity of devulcanized rubber, (iv) to study the chemical changes occurring during devulcanization and the effect of processing conditions on the degree of devulcanization, and (v) to evaluate some mechanical properties of the devulcanized rubber after compounding with curing agents.

**Experimental**

**Materials**

The materials used in these experiments were rubber crumbs from recycled truck tires supplied by S.O.T.A. Environmental Research Group Inc. This company has developed a cryogenic grinding system capable of producing 5000 lbs/hour with mesh sizes ranging from 40 mesh to 100 mesh minus. Three different sizes (40 mesh, 80 mesh and 4080 mix) of styrene-butadiene rubber (SBR) crumb were tested under various processing conditions.

**Equipment**

The extruder used for this project was a Leistritz LSM 30.34 twin screw model. This is a co-rotating and fully intermeshing extruder having a 34 mm screw diameter and an L/D=30. Barrel pressure measurements were performed through a commercial data acquisition system (OPTO22) interfaced with a personal computer to handle as many pressure transducer signals as required. The pressures were measured by Dynisco pressure transducers, connected to the OPTO control chassis by lengths of cable fitted with Bendix-type connectors. One pressure transducer (PT462E-5M-6/18) is mounted in the eighth section of the barrel to measure the barrel pressure, and other three (PT462E-10M-6/18, PT462E-7.5M-6/18 and PT462E-5M-6/18) are installed in the wedge die for calculating the viscosity changes. The eighth barrel section is also equipped with a gas injection port for CO$_2$ injection using a syringe pump. A wedge die was attached to the extruder head, and a secondary die is attached to the end of the wedge die. By controlling the opening area of the secondary die, the level of pressure in the die and barrel was manipulated. The temperature of the rubber/CO$_2$ mixtures was measured using a fiber optic melt transducer (Dynisco MTS 922-6/24) at the end of the wedge die. Rubber crumb was fed by a K-Tron feeder (LWFD5-200). A schematic of the experimental setup is shown in Figure 1.

**Procedures and Characterization**

Compared to plastics, crosslinked rubber powder is a thermosetting material and it can not be re-extruded without supercritical CO$_2$. Initial screening experiments were performed in order to determine the conditions at which the powder could be extruded. First, without CO$_2$ injection, after the crumb was fed into the barrel at a screw speed of 40 rpm, the rubber powder of 40 mesh was not able to be extruded through the twin-screw extruder at 250°C in the range of feed rate from 15 g/min to 40 g/min. The machine shut down automatically due to the overload of the motor. When the screw was extracted, it was found that the solid powder had filled the empty space between the screw and barrel without softening. This showed that the rubber powder was still vulcanized and crosslinked and it was impossible to be extruded at these conditions. Later, when CO$_2$ was injected into the extruder barrel, successful extrusion of the rubber powder was accomplished and continuous soft, sticky and elastic strands were produced. Extrusion is feasible with scCO$_2$ under certain conditions of feeding flow rate,
screw speed, temperature, screw configuration and time of CO₂ injection. In this work, the extrusion temperature was varied between 200 and 250 °C while two screw speeds (25 and 50 rpm) were used. Two rubber crumb flow rates (15 and 30 g/min) were employed under various CO₂ concentrations.

Soxhlet extraction was used to separate the soluble fraction from the gel in all samples collected. First, acetone was used to remove the low molecular weight substances. 20g of extrudate was placed in the thimble in the extraction tube. 250ml acetone was heated to boiling point (about 56°C). The vapor was condensed down to the tube by the condenser with cold water circulation. The experiment was run for 5 hours. Second, after the sample was distilled and dried in the fumehood and weighed, 250ml toluene was used as solvent to separate the sol from the gel in the residue by following the same procedure for 8 hours. The residue swelled in toluene. After distillation and drying, the sol part dissolved in toluene was extracted. The weight of the sol and gel fractions was determined by a balance.

FTIR analysis was used in order to elucidate the chemical bond changes during processing. For that purpose, thin films of the separated soluble fractions were formed and at a resolution of 4 cm⁻¹.

After extrusion, the products were very sticky. 5g extrudate was molded in the hot press at 210°C and 10,000 pounds for 2 hours producing an elastic and homogeneous sample with smooth appearance. That indicated that the rubber powder had been devulcanized after the extrusion and became moldable. Thus, re-activation yields rubber that can be reshaped and re-vulcanized to give new products. For the purpose of measuring mechanical properties, compounded specimens were prepared according to a typical curing recipe. The ingredients were mixed following the ASTM3182 standard. A Haake Rheocord90 mixer was used for compounding at 77 rpm, temperature 80°C in each zone, running for 10 minutes. The compound was molded in the hot press at 20,000 pounds and 190°C for 45 minutes. The molded rubber sheet had a very smooth surface and specimens were cut out for the measurement of tensile strength, elongation at break and yield stress.

The shear viscosity of the devulcanized rubber was: (i) calculated from the pressure drop measurements along the wedge die and (ii) measured with a Kayeness Galaxy V capillary rheometer.

Results and Discussion

Although different mesh sizes were tested, the discussion will focus on selected results from the 40 and 80 mesh crumb due to limited text space. Results from the rest of the materials and tests will be discussed during the oral presentation.

Figure 2 shows the effect of flow rate and CO₂ concentration on the degree of devulcanization of the 40 mesh crumb for two different screw configurations. More specifically, it can be seen that extrusion with scCO₂ resulted in an increase of the soluble fraction from 8% in the starting rubber crumb to about 26% in the devulcanized material. Also, it can be seen that the extrusion conditions (rubber flow rate and CO₂ concentration) did not have any significant effect on the soluble fraction of the devulcanized rubber. Furthermore, it may be seen that the soluble part is mainly consisting of the sol resulting from devulcanization (about 17%) and that the low molecular weight fraction (about 9%) is not considerably different from that of the starting material. Finally, it can be seen that the effect of the screw configuration was rather marginal with the exception of the 2 wt% CO₂ concentration.

The effect of processing temperature and screw speed on the degree of devulcanization is shown in Figure 3. This figure shows that increasing screw speed increased the weight percent of soluble part, sol part and low molecular weight part of devulcanized 80mesh crumb at 200°C, 250°C and 300°C respectively. Increasing screw speed leads to increased shearing and therefore increased devulcanization. At 300°C, CO₂ injection does not seem to affect the amount of sol and low molecular
weight. At that temperature, it appears that CO₂ is simply facilitating the extrusion process and that devulcanization is mainly through a thermal mechanism.

The effect of temperature on the devulcanization may be seen from Figure 4. It can be seen that increasing temperature resulted in increased weight percent of the soluble part. At 25 rpm, there is a change of 13.6% from 14.3% at 250°C to 27.9% at 300°C compared to the change of 5% from 9.3% at 200°C to 14.3% at 250°C. At 50 rpm, the soluble part increased from 17.7% at 250°C to 30.4% at 300°C for sol fraction.

The FTIR spectra of samples produced under various conditions are presented in Figure 5. It can be seen that there are clear differences between the starting material and the devulcanized ones; however, no clear effects of the screw configuration, temperature and screw speed could be observed. The changes of spectra between virgin SBR powder and devulcanized powder in the region from ca 1900 cm⁻¹ to ca 700 cm⁻¹ may be clearly seen. For SBR rubber crumb, the peaks were characterized by carboxylate group (−COO−) at ca 1706, ca 1537 cm⁻¹ and ca 1397 cm⁻¹ as well as C-H scissoring vibration in the methyl group at ca 1457 cm⁻¹. Meanwhile, bands at 1601 and 969 cm⁻¹ were typically assigned to out of plane bending vibrations of C-H bonds from the trans-methylene portion of butadiene-based chains (14). For devulcanized SBR, specific structural changes in this region were indicated in the spectra. Most bands in the spectra of SBR rubber powder disappeared, but the characterized band of butadiene-base chain, ca 967 cm⁻¹ increased after devulcanization.

**Concluding remarks**

Several kinds of recycled rubber crumb have been extruded and the effects of the following parameters have been evaluated. The feeding flow rate of rubber powder to the extruder was found to affect the extent of devulcanization, and have an impact on the product viscosity and processability. Although CO₂ concentration was a very important factor for the flow ability and extrusion, it was found to have little influence on the degree of devulcanization. In addition, the type of screw configuration employed affected significantly the rheological properties of the de-vulcanized rubber due to the varying amount of deformation that it imparts on the rubber crumb. Finally, the screw speed and the processing temperature also affected the viscosity behavior of the devulcanized rubber powder. Soxhlet extraction was used to evaluate the degree of devulcanization under various conditions and FTIR analysis indicated that significant changes occurred on the chemical structure of recycled rubber crumb due to the formation of new double bonds and scission of carbon-carbon bonds and carbon-sulfur bonds.

**References**

Figure 1. Experimental setup
Figure 2. Degree of devulcanization at 250 °C
Figure 3. Devulcanization degree for 80mesh crumb at different temperatures (15 g/min, 2wt% CO₂ concentration, screw 1)
Figure 4. Devulcanization degree for 80mesh crumb at different screw speeds (15 g/min, 2wt% CO$_2$ Concentration, screw 1)
Figure 5. FTIR for devulcanized 40mesh crumb at different extrusion conditions (250°C, screw 1)