

IMPROVED CONTROL ON THE MICROWAVE DEVULCANIZING OF GROUND TIRE RUBBER BY MEANS OF SULPHUR GAS SENSORS

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Abstract. The success of a Ground-Tire Rubber (GTR) devulcanization process relies on the elimination of the sulphur atoms that are crosslinking the rubber polymer. From the chemical point of view, this requires providing enough energy to break the sulphur bonds while preserving the carbon bonds, to ensure a high quality devulcanized GTR for being of interest to the rubber manufacturing industry. GTR is very responsive to microwaves due to the presence of Carbon Black (CB) in its composition, so the radiant energy is absorbed quickly in the form of thermal energy. When its temperature reaches 140°C, the breakage of sulphur bonds may happen under an exothermic reaction, but also some new links might be built under that condition. Therefore, from the physical point of view, the released sulphur in the gaseous form of SO₂, H₂S, and/or CS₂ must be promoted to abandon the reactor to avoid its recombination. In this work, microwave devulcanization is monitored by detecting the concentration of sulphurous gases at the exhaust of the reactor. These sensors are very effective especially when pyrometer readings are degraded because of the gaseous layer on the GTR during the process.

Keywords: Microwave, Industrial applications, Measurement technology, Processing, Residue/Side-stream, Material interaction

1. Introduction

The management of the disposal of end-of-life tires (ELTs), also known as GTR, is a today's environmental worldwide challenge. Therefore, searching for new and pro-ecological reutilization methods of used tires and other waste rubbers is one of the biggest challenges of the 21st century waste management [1]. Regarding environmental impact, the energy recovering from landfill accumulation or combustion processes is a much worse solution than the recycling process, due to the toxic gas emissions and the residue powder, which pollutes the soil [2].

Nevertheless, the consideration of GTR as a valuable rubber feedstock for the manufacturing industry, relies on its ability of being processed to produce thermoplastic elastomers and blends in composite materials, and the most suitable way is through its devulcanization [1]. This process consists of a selective crosslink cleaving i.e., the elimination of the sulphur from the crosslinked rubber polymer while preventing the damage of the elastomeric chain. Thereby, it is necessary to apply enough energy to break up the sulphur bonds [3] formed during vulcanization while preserving the carbon bonds in order to ensure a high quality devulcanized GTR.

The devulcanization process is related to the transformation of waste tire rubber using a physical (thermal, mechanical, microwave, ultrasonic), biological, or chemical energy. In terms of devulcanization uniformity, it should be considered that only the microwave and ultrasonic methods act in the GTR particle's core, while the others do it on the surface. In addition, microwave devulcanization also offers the possibility of high productivity [4], and the regulation of microwave energy density (kJ/kg) acting on GTR, by controlling

power and time settings, thereby allowing selective breakage of the cross-linking bonds with minimum degradation of the main polymeric chains [5].

It is true that some types of rubber do not perform a good dielectric heating when exposed to microwaves. However, GTR heats adequately given the presence of CB in its composition [6], which absorbs the microwave energy that is turned into thermal energy [5]. This energy transduction may increase with the rising of the temperature, which could lead to a thermal runaway breaking the sulphur bonds but also the carbon ones that should be preserved. Consequently, parameters involved are to be thoroughly controlled to avoid degradation of the material due to excessive processing temperatures or uneven devulcanization degrees.

The ultimate temperature reached by the material is the primary parameter responsible of the success of the devulcanization process, according to [7]. Depending on the final temperature, different types of sulphur bonds can be broken. The amount of energy needed to break the poly-sulphur bonds is smaller than that required to break the di-sulphur ones. Hence energy required to break the di-sulphur links, in turn, is smaller than that required to break the mono-sulphur ones [8]. Thus, the structure of the rubber changes to be composed by mono-sulphur bonds. When breaking such bonds, some main chains can be also broken, leading to the formation of hydrogen sulphide (H_2S), sulphur dioxide (SO_2) and carbon disulphide (CS_2) [9]. These gases may blind the temperature monitoring system when pyrometers are employed.

Since some difficulties are found to make an adequate temperature monitoring and control subsystem on a laboratory scale [10], the gaseous products formed during devulcanization can be considered as parameters to control the process. Song et al. [11] deduced that the proportion of H_2S , which comes from the sulphur links in the vulcanized rubber structure, is useful to know the sulphur migrating degree to gaseous products. Hence gaseous products can be useful to control the microwave exposure time, which is mandatory in order to obtain a regenerated material with suitable properties [12].

In this work, funded by the 870000 VALUE RUBBER UE project, the H_2S , SO_2 and CS_2 concentration evolution are monitored during microwave devulcanization, and this is compared to the GTR surface temperature by using an infrared pyrometer. The gases concentration evolution can be useful to control the process, specially when certain gases are present, since they can cause temperature measurement errors, as stated in [13].

2. Materials and Methods

2.1 Materials

The material was crumb rubber from ELTs (GTR) kindly provided by Synthelast (Spain). The GTR had a granulate size range of [0.5, 1] mm, and an average density of 400 kg/m^3 . The holder used for the samples was a quartz dish. The dish had a cylindrical shape with an inner diameter of 18.5 mm (outer 19.1 mm), and a height of 88 mm. The samples had 300 g of GTR and a volume around 750 cm^3 .

2.2 Methods

The configuration schema is depicted in figure 1. Three 1.6-cm diameter hollow metal tubes on the top of the microwave oven act as cut-off cylindrical waveguides and allow the usage of several devices inside the microwave cavity without leakage. The leftmost tube is used to introduce nitrogen inside the cavity, thus producing an inert atmosphere. To achieve a GTR temperature as homogeneous as possible, a PTFE stirrer is used, whose axis is introduced through the central cut-off waveguide. The motor gear of the microwave oven was extracted and placed above the central tube. In this way, it forced the rotational

movement of the PTFE stirrer. A pyrometer was placed on the far-right tube. A fan on the left wall of the oven extracted the gases from the cavity pushing them through a pipeline, so that the sulphur gas concentration values were measured at the end of the pipeline.

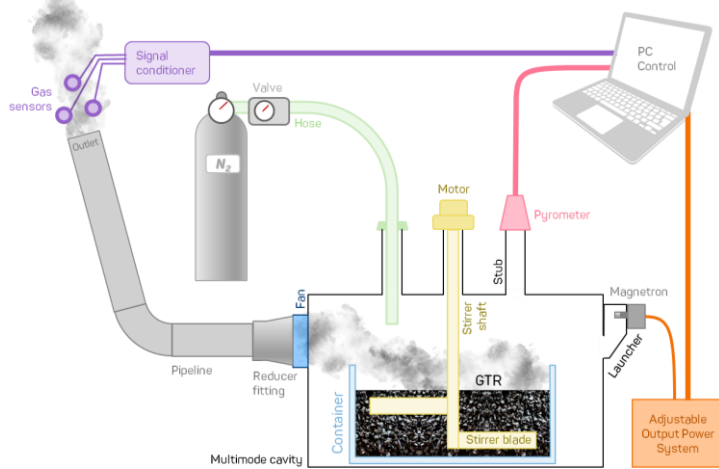


Fig. 1. Scheme of a microwave devulcanizing reactor with temperature and gas sensors

The sample mass was 300 grams, and the microwave power for heating the GTR was adjusted using a Dipolar Magdrive power source. The surface temperature of the GTR was monitored using an Optris LT CF2 infrared thermometer, with an accuracy of ± 1 °C (for temperatures up to 100 °C) or ± 1 % (for temperatures over 100 °C). To monitor the sulphur gases concentration during the process, three electrochemical sensors from Membrapor were used. Their resolution for measuring H₂S, SO₂ and CS₂, in parts per million (ppm), was 1, 0.5 and 0.5 ppm, respectively. Figure 2 shows the implemented configuration based on the scheme introduced in figure 1.

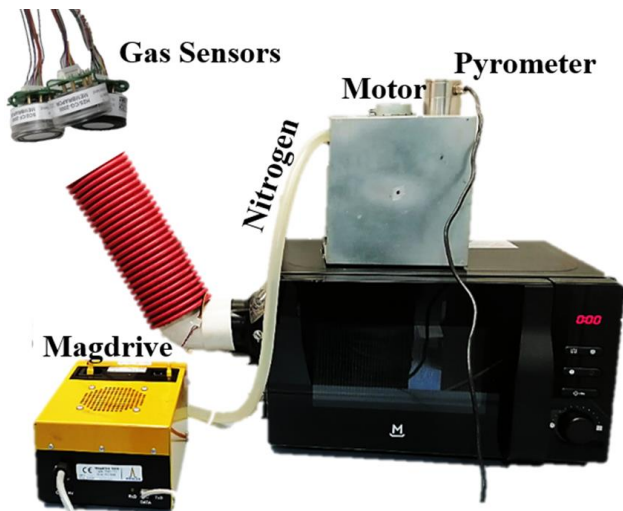


Fig. 2. Microwave devulcanizing reactor on a laboratory scale

Two different kind of power profiles were implemented in order to analyse the gases concentration evolution. First, a PID was used to control the power delivered so that a

constant temperature was kept at 120 °C. In the second test, a constant microwave power was continuously delivered to the cavity (270 W).

3. Results

Figure 3 shows the GTR surface temperature and the power profiles for the two tests. It must be remarked that temperature and power curves have been smoothed to enhance their visual quality. Given that power profiles were quite similar during the first twenty minutes, temperature profiles were similar as well. However, temperature value for the test using a PID increases at the 23rd minute and so the power was decreased in order to keep the desired temperature. From that point, that temperature value was near the desired value (120°C).

On the other hand, temperature values for test delivering a constant power value were smaller than those for the test using a PID, from the 23rd to the 41st minute. This fact is explained later, once sulphur gases have been shown. In the minutes thereafter, temperature values when using a constant power were quite higher.

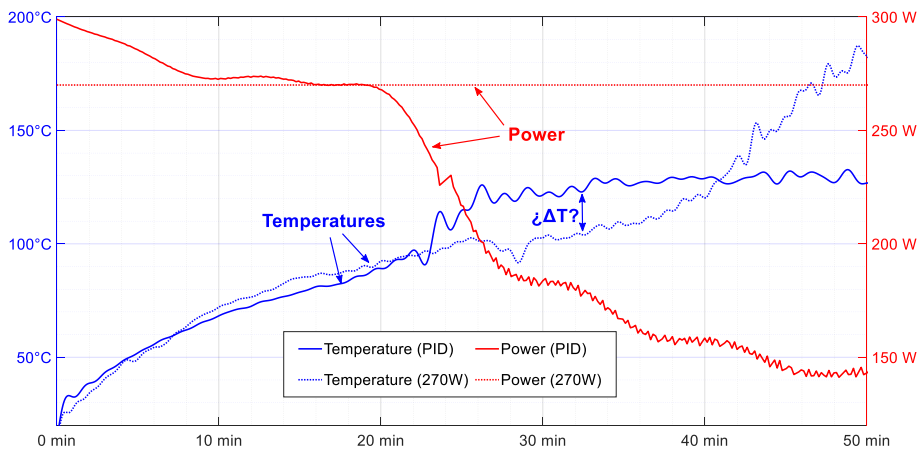


Fig. 3. Surface temperature and power profiles during the devulcanization tests

The concentration of the three sulphur gases monitored during the tests can be observed in Figure 4. Gases are detected at the 23rd and the 28th minutes, for the test using a PID and the test delivering a constant power, respectively. After the 28th minute, gases concentration was considerably higher for the test delivering a constant power. As a general trend, the gases behaviour is quite similar to each other's. Nevertheless, some differences are found for CS₂ during the test delivering a constant power i.e., its concentration value increases gradually from the 35th minute to the end, whereas those of the H₂S and SO₂ are diminishing in that period.

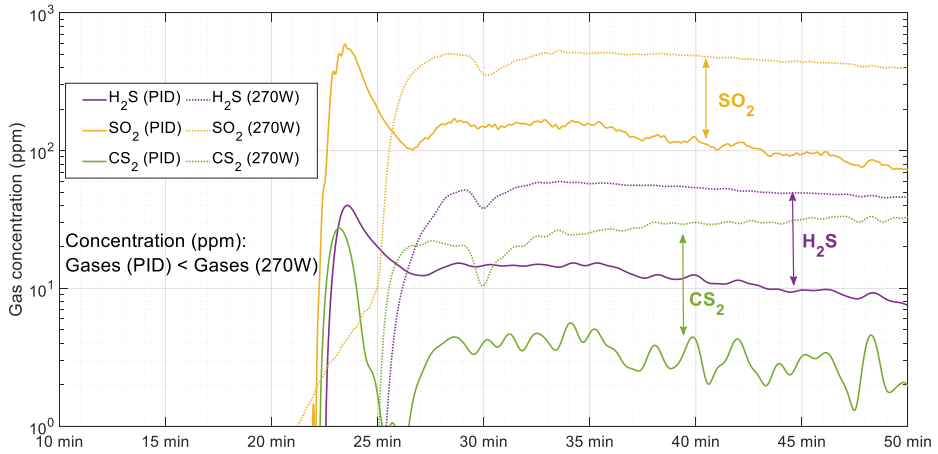


Fig. 4. H₂S, SO₂ and CS₂ gases concentration during the devulcanization tests

4. Discussion

The comparison between the temperatures for both tests was shown in figure 3. It is noticeable that the GTR temperature values when devulcanizing process starts (95~100°C) are smaller than expected ones (140°C) for both tests. The reason for this is that pyrometer is measuring the surface temperature of the GTR, which is constantly cooled because of the nitrogen. Moreover, figure 3 also emphasizes the pyrometer readings degradation as a consequence of the gaseous layer on the GTR during the process. Such degradation can be easily noted at the time the sulphur gases are released.

Figure 5 shows the temperature curves and the SO₂ gas concentration for both tests. The pyrometer was more obstructed for the test delivering a constant power, as higher gases concentration values are registered for that test.

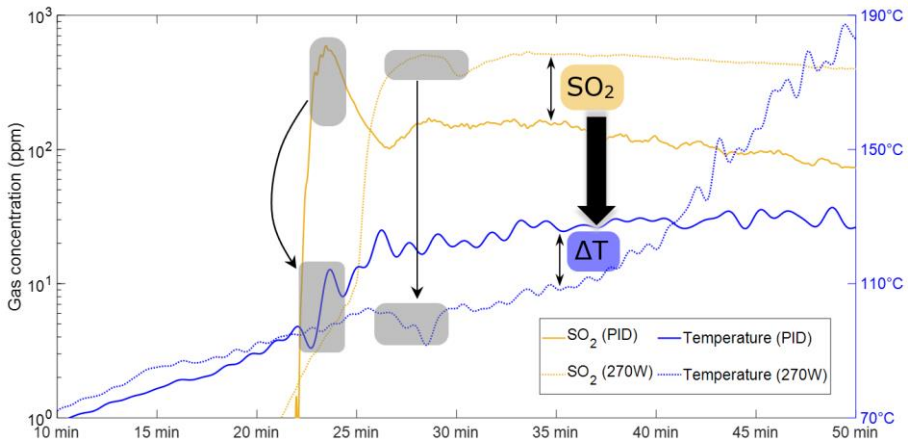


Fig. 5. SO₂ gas concentration and temperature profiles during the devulcanization tests

During the tests, it became clear that the higher the gases concentration values, the more blinded the pyrometer. In spite of the pyrometer was obstructed, higher temperature values are shown from the 42nd minute to the end for the test delivering a constant power. This fact can be explained by considering that the pyrometer is partially obstructed i.e., it is registering temperature values of the gases and the GTR surface. For the test delivering a

constant power, GTR seems to have a much higher surface temperature value. This fits perfectly with the delivered power shown in figure 3. The more delivered power, the more energy is absorbed by the GTR, that is, the GTR heats more.

Hence, it is advisable to extract the gases when devulcanizing, thus avoiding the gases obstruct the temperature monitoring and the recombination of the released sulphur or acquiring indirect temperature readings on the quartz container surface.

The comparison between the three gas concentration values for both tests shown in Figure 4 indicates that the sulphur gases are very useful to determine the beginning of the devulcanization process. Furthermore, they might be also useful to establish the end of the process, since the gases concentration behaviour is related to the amount of sulphur released from the GTR.

The relationship between the CS₂ gas concentration behaviour and temperature is shown in figures 6 and 7, for the test using a PID and the test delivering a constant power, respectively.

Figure 6 shows that temperature barely increases from the beginning of the devulcanization process (23rd minute) to the end. CS₂ concentration values are near zero throughout the whole test, entailing that the polymer was not degraded. In fact, there is potential for CS₂ concentration values were due to some kind of cross-interference with the SO₂ as they show very similar behaviours.

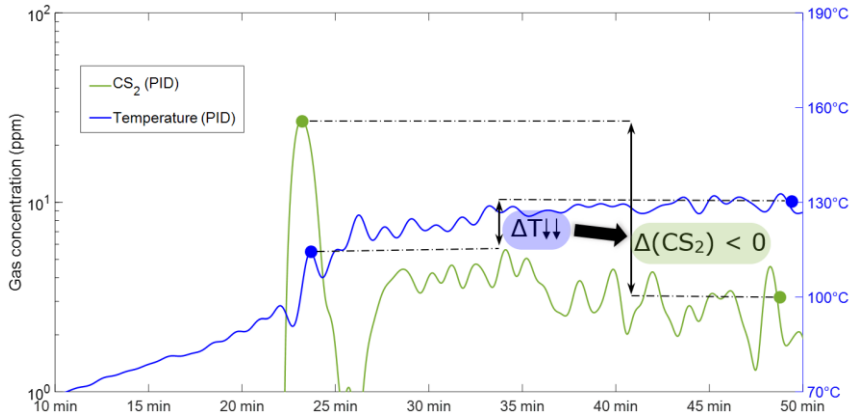


Fig. 6. CS₂ gas concentration and temperature profiles during the test using a PID

Figure 7 shows that temperature strongly increases from the beginning of the devulcanization process (28th minute) to the end. As a consequence, CS₂ gas concentration values not only are quite higher than those shown in figure 6 but also are higher at the end of the process, entailing that the polymer was degraded. In spite of CS₂ concentration values might be due to some kind of interference with the SO₂, its behaviour is different from that of the SO₂ for this test. Hence, one can conclude that some main chains were also broken, leading to the formation of the CS₂.

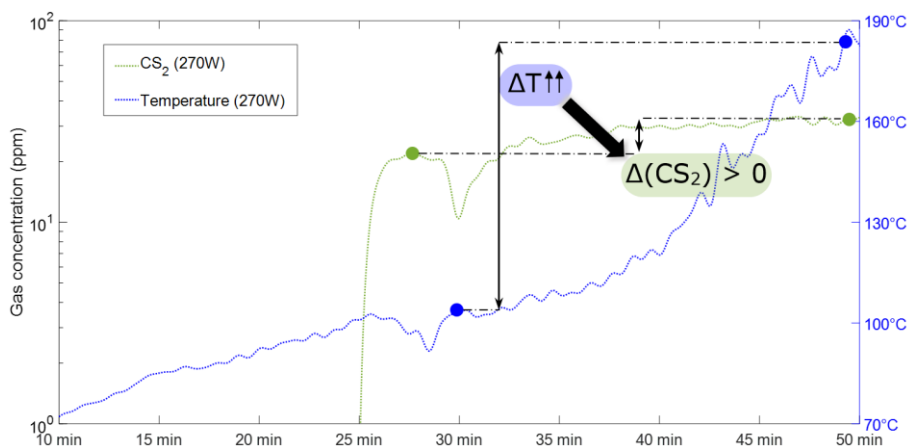


Fig. 7. CS₂ gas concentration and temperature profiles during the test delivering a constant microwave power

To sum up, CS₂ makes it possible to approach the polymer degradation, given that it is formed by the cleavage of the C-C bonds. Consequently, special attention must be paid to CS₂ in order to avoid the destruction of polymeric chains during microwave devulcanization.

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6. References

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