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STUDY OF PROPERTIES OF CHLOROPRENE RUBBER DEVULCANIZATE BY RADIATION IN MICROWAVE

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ABSTRACT

Among the vulcanized elastomers, the chloroprene rubber (DuPont Neoprene® - generic name) possesses a good performance, being one of the most used in the current days. However, this kind of polymer causes a serious environmental problem if it is not reprocessed or recycled. A worldwide method that has been used and that is an important tool in the rubber devulcanization is microwave irradiation at high temperature Elastomer waste may be devulcanized without depolymerization and allows a new vulcanization into a product having physical properties essentially equivalent to the original vulcanized. In this work, the chloroprene samples were irradiated in microwave generator equipment with 2,450MHz (frequency) and 1,000W to 3,000W (power). The properties of samples (according to ASTM standards) were analyzed before and after irradiation. The degraded material after irradiation will be tested for re-use.

1. INTRODUCTION

Thermosetting materials like rubbers on processing and molding are crosslinked and therefore cannot be softened or remolding by heating process again. The three dimensional network of the thermoset polymer system must be broken down either through the cleavage of crosslink or through the carbon–carbon linkage of the chain backbone [1].

Generally, rubbers are used as tires, footwear, toys, clothing, etc. The wide use of these materials has lead to great generation of post-consumer waste. Recycling this waste is a environmental challenge and an economical - social problem. A reason for the interest in rubber recycling is that the rubber waste represents a source of significant raw material for the rubber industry [2].

Among all types of rubber the Chloroprene - CR (generic name of Neoprene ® - DuPont) is a prominent material. This rubber was the first market synthetic elastomer (1932) due to advantageous properties and has been investigated in the last years. It is very versatile and can be cured with sulfur or organic peroxides and has the following characteristics: good elasticity, allows perspiration, resistance to oil, solvents, weather ageing, heat, oxygen, ozone and flame [3]. However, this kind of polymer causes a serious environmental problem if it is not reprocessed or recycled [1].

The rubber waste is generated from objects that are not practical and discharged. The post-industrial waste is generated during the processing and molding elastomers in the production line and in some situations the amount of waste can be equivalent with the production [4].

The most appropriate way to reduce the volume of polymeric waste and minimize the environmental impact generated by them is improve recycle methods [4]. Currently, due to difficult on reprocessing techniques, the vulcanized rubbers are a big problem in the recycle field [1]. One of the main forms of discharge rubber is to apply as fuel to generate electricity and steam [5-6], this process is still in use but creates a new problem of air pollution and is also a low value to recovery process of the rubber waste [1].

Reclaiming of scrap rubber is, therefore, the most desirable approach to solve the problem. Reclaiming rubber is the conversion of the three-dimensional interlinked which is insoluble and infusible strong thermoset polymers into a two–dimensional interlinked with desirable properties like: soft, tackier, low modulus, processable and a thermoplastic product vulcanizable essentially. These properties are similar of the virgin rubber properties. Recovery and recycle of rubber from used and scrap rubber products can, therefore, save some precious petroleum resources as well as solve scrap/waste rubber disposal problems. However, reclaiming process may be broadly classified into two groups: physical reclaiming processes and chemical reclaiming processes. This technique is called devulcanization [5].

In a physical reclaiming process scrap/waste rubber products is reclaimed with the help of external energy. In this process three-dimensional network of crosslinked rubber breaks down in presence of different energy source. Due to this network structure break, the macromolecular rubber chain is transformed into small molecular weight fragments so that it can be easily miscible with the virgin rubber during compounding [7, 8]. In this process is necessary a specific amount of energy which is sufficient to cleave only the crosslink bonds. After this process a good quality product is obtained with some properties of the original rubber. Depending on the recycling process, the variation in mechanical and rheological properties can be observed [9, 10].

The devulcanization by microwave is a process that requires a high energy level to break carbon–sulfur and sulfur–sulfur bonds. Thus in this process the elastomer waste can be reclaimed without depolymerization into a material that has capacity of re-compounded and re-devulcanized and that keep the physical properties similar to the original vulcanized. This method is very useful because it provides an economical and ecologically method of reusing elastomeric waste to return it to the same process and products in which it was originally generated and it produces a similar product with equivalent physical properties. The devulcanized rubber is not degraded when the material being recycled which normally takes place in the usual commercial processes currently being practiced [1].

Microwave devulcanization process as a method of pollution controlled reclaiming of sulfur vulcanized elastomer containing polar groups. The waste material must be polar in order to the microwave energy creates the necessary heat to devulcanize the polymer. The microwave energy devulcanization device generates heat without contact and the process starts inside of material [11].

In this work were analyzed the hardness, the tensile strength, elongation at break properties and the vulcanization parameters of devulcanized chloroprene rubber (CR). The rubber was

submitted in a microwave energy with controlled dose at specify frequency and a sufficient energy level to break all crosslink bonds but not sufficient to degrade the polymer chain. The properties of devulcanized rubber and original rubber were compared.

2. MATERIALS AND METHODS

2.1. Material

To study the microwaves interactions with chloroprene rubber (CR - DuPont Neoprene® - generic name) was prepared a basic formulation, (Table 1), based on standards for the automotive industry. It was prepared in an open two-roll mixing mill (COPÉ) with 40 kg of capacity, at temperature between 50 ºC and 60 °C. For comparison, the non-irradiated sample (A0) and the irradiated samples were designated as A1, A2 and A3 according to the time and power of exposure to microwaves.

Table 1. Base formulation of CR.

Rubber Formulation	phr
Neoprene W	100.0
Magnesium Oxide	4.0
Stearic Acid	0.8
Calcium Carbonate	20.0
Carbon Black	40.0
Antiozonant Wax	3.0
Antioxidant	2.0
Polyethylene Wax	2.5
Aromatic Oil	20.0
Zinc Oxide	5.0
MBTS	0.4
NA 22	0.8

2.2. Irradiation

The samples were irradiated with microwave equipment (removable drive) to generate heat, operating at microwave high frequency, using magnetrons. This equipment was designed, manufactured and installed in IPEN [12], (Fig. 1). The operation was carried out with a frequency of 2,450MHz and power of 1,000W to 3,000W, with a system to gaseous waste removal and material collection and automatic control of irradiation time. The temperatures of the samples were monitored using thermocouple.

Figure 1. Removable drive to generate heat - Microwave (IPEN).

The irradiation was performed for each sample. The exposure time and power used in this work are demonstrated in Table 2.

Table 2. Irradiation conditions of CR samples.

Sample	Time (s)	Power (W)
A1	43	1000
A2	60	1000
A3	120	1000
A4	150	1000
A5	180	1000
A6	210	1000
A7	240	1000
A8	300	1000
A9	360	1000
A10	60	2000
A11	90	2000
A12	120	2000
A13	30	3000

2.3 Samples Characterization

The samples were prepared according to ASTM standards (Annual Book of ASTM Standards) applied on rubber and were analyzed before and after the irradiation. Rubber sheets were prepared with dimensions of 160 x 160 x 1.5 mm, as ASTM D-3182-96 [13], in press Luxor with table size 300/350mm. All samples were vulcanized at 160 °C for 15 min.

For irradiation process the chloroprene samples were cut in small pieces of about 1cm x 1cm, with total weight of 250g, (Fig. 2).

Figure 2. Sample cut into small pieces from prepared sheet.

Non irradiated and microwave irradiated CR was tested for Hardness (ASTM D-2240-96 [14], Durometer - Hardner Tester JIS, Resistance to Tensile Strength and Elongation (ASTM D-412-96) [15], Dynamometer ZR 60/300 - Otto Wolpert-Werk), determination of vulcanization parameters in the oscillating disk rheometer, model 100 S (Monsanto) according to ASTM D-2084-96 [16]. The parameters analyzed were: T_{S1} - minimum torque presented for each sample (lower point of the curve); T_{S2} - the pre-cure time; T_{90} - optimum time of vulcanization. The conditions used in the tests were: temperature of 160°C; arc of oscillation - 3 and time of 12 min. The curves were obtained by vulcanization torque (lbf.in) against time (min).

3. RESULTS AND DISCUSSIONS

All the irradiated samples were processed again, to prepare the specimens according to the standard method. It was not possible to obtain some samples because they showed a little inhomogeneous granular aspect and characteristic smell of burned rubber, (Fig 3). Therefore, it was not possible to characterize samples A10, A11, A12 and A13.

Figure 3. Specimens with aspect irregular.

The results of mechanical properties of non-irradiated (A0) and irradiated (A1 - A9) CR samples are shown in Table 3.

Table 3. Mechanical properties of non-irradiated (A0) and microwave irradiated (A1-A9) CR samples.

Sample	Hardness (shore A)	Tensile Strength (psi)	Elongation at break (%)
A0	57	1428	500
A1	48	891	780
A2	48	572	300
A3	48	690	700
A4	45	688	700
A5	50	700	100
A6	49	95	140
A7	47	102	140
A8	45	82	120
A9	52	97	100

Comparing the results of irradiated and not irradiated rubber, it was observed thatall properties: hardness, elongation at break and tensile strength decrease, when increase exposition time and energy power. The effects of irradiation cause degradation in some samples, because de elongation break of the samples depends upon the nature of the polymer as well as on degree of crosslink, which restricts the movement of the polymer chain against the applied force [17].

The Fig. 4 shows the parameters of vulcanization of irradiated and non irradiated rubber. The samples A6, A7, A8, A9, A10, A11, A12 and A13 were not analyzed because were partially degraded.

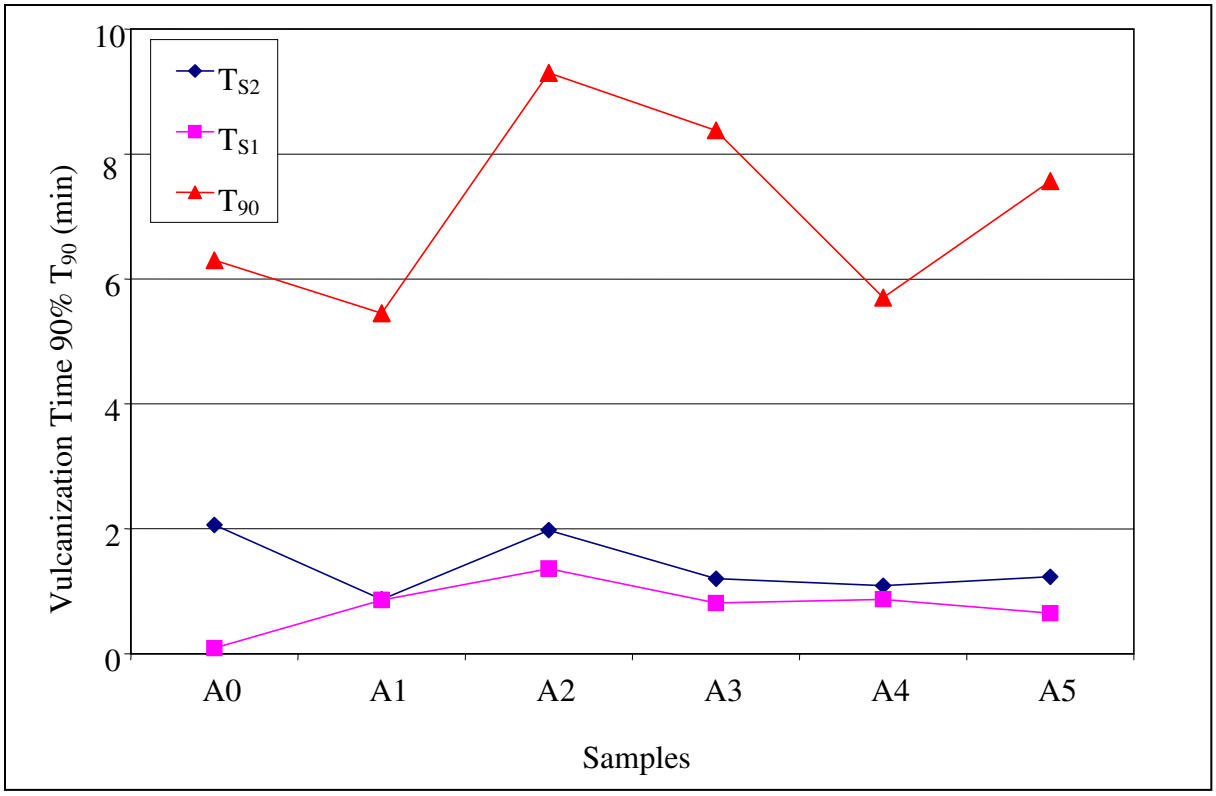

Figure 4. Vulcanization parameters of vulcanized and devulcanized CR.

Regarding the rheometric analysis, the curves showed that some samples tended to vulcanize again. The T_{90} parameter shown that all samples irradiated have a higher time to cure than the original rubber; this fact is possible due to the degradation process or the devulcanization process in the irradiated rubber

4. CONCLUSIONS

All tests indicated that microwave treatment caused some changes in the physical and chemical properties of CR, which can cause adverse effects (degradation) and positive (devulcanization). Among the properties, the emphasis is the possibility of recycle material and re-cured ability which shows a wide applicability of devulcanization rubber by microwave.

Some samples presented the tendency to vulcanize again; hence there is great expectancy for reusing and recycling the devulcanized CR. All these results were obtained without using any chemical agent. This is one aspect that must be pointed out because it is very important for environmental preservation.

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