MICROWAVE ENERGY APPLIED TO CHLOROPRENE/SILICA COMPOUND DEVULCANIZATION

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Abstract. Among vulcanized elastomers, the chloroprene rubber (DuPont Neoprene® - generic name) shows a good performance, being considered one of the most used up to current days. However, in end life time products contribute in damaging the environment whether not reprocessed or recycled. A method that has been used worldwide as an important tool in rubber de-vulcanization is the microwave energy process by employing the use of high temperatures. Elastomer wastes may be de-vulcanized without de-polymerization and allows a new vulcanization into a product presenting physical properties essentially equivalent to that original vulcanized rubber. In this present work chloroprene rubber formulated with silica was irradiated in a microwave generator equipment at 2.450MHz (frequency) and within 1.000W to 3.000W (power). Characterization of post irradiated samples (according to ASTM standards) showed distinct physical properties.; these samples tested as a part of rubber content in formulations presented similar properties to those ones from original rubber compounds.

Introduction

As polymeric materials do not easily decompose, the disposal of their wastes has being presenting a serious environmental problem. In case of rubber residues, especially tires, a lot of them are discarded and disposed in landfills. In other situations, they are used as fuel, further incinerated for yielding power. Besides, costs are very high. So, recycling and recovering are considered the best management options. Due to this, various process have being developed worldwide toward the reuse and recovering of these materials. They consist in the conversion from a thermosetting polymer to a thermoplastic one, easier to be processed and prone to be vulcanized, exhibiting properties similar to those ones showed by natural rubber [1]. There are various types of rubber which are comprehensively used in following sectors: automotive industry, hospitals, toys, rubbery clothes, shoes and insulants, among others. It can be concluded from its large employment, that rubber transformed into a vital item in human being routine [2].

Among all types Chloroprene – CR (Neoprene® - DuPont), the first synthetic elastomer commercialized (1932), deserves a special mention. It is very versatile and able to be vulcanized with sulfur or organic peroxides, exhibiting following and special characteristics, such as: isothermal protection, good elasticity, lightness, exudation, resistance to oil, solvents, climate, heat, oxygen, ozone, solar rays, high temperatures, flame and tensile strength[3], increase in tearing, tensile strength and abrasion resistance.

However, although all benefits obtained from rubber vulcanization (discovered by Goodyear), one of several problems currently faced is that after the use or depletion useful life of a rubber good the de-vulcanization is difficult and almost impossible to produce an useful material again.

Therefore, the reversible process of rubber vulcanization, called «de-vulcanization», has been widely studied, aiming to a break in crosslinked carbon-sulphur (C-S) and sulphur-sulphur (S-S) bonds [3,4,5, 6]

Microwave energy has been used worldwide, also, as an important tool in rubber de-vulcanization at high temperatures. The process with microwaves consists in conversion of electromagnetic energy to thermal energy, by its incidence in polar molecules of some rubbers. When electromagnetic radiations penetrate in the material, a part of energy is absorbed and converted into heat, and consequently increasing temperature, that inner parts are hotter than surface ones. This occurs because there is a great heat exchange around it. Due to this characteristic, it is possible to warm homogeneously a great volume of materials. Main advantages to this process is the fast heating with a reduced energy consumption in relation to the conventional heating associated to a fast start-up and stop, using small spaces [3, 7].

The objective is to obtain products that allow a further crosslinking (or vulcanization), maintaining equivalent properties to those ones exhibited by original composition, due to the breaking of crosslinking tridimensional net without causing rubber de-polymerization. This way, recycled material will be used as active load (component) and not as an inert load.

Experimental

Samples

Formulation used was based in rules applied to automotive industry [8] and material employed was Chloroprene type W, using silica dioxide (SiO_2) as filler reinforcement, as shown in TABLE 1. Incorporation of particulate fillers, such as SiO_2, improves mechanical performance of vulcanized elastomers. A practical reinforcement consequence is a raise in rubber goods utile life. Fillers contribute too for a raise in elastic modulus and are often used toward this purpose [9].

Table1. Chloroprene Formulation

Ingredientes	**phr**
Neoprene W	100,0
Magnesium Oxide	4,0
Stearic Acid	0,8
Calcium Carbonate	20,0
Silica Dioxide	25
Anti-ozone 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

Admixtures were prepared in a coil cylinder (Copé), according to ASTM (American Society for Testing and Materials) D 3182 Standard, within 50º C and 60º C range.

Irradiations

Samples previously mentioned were irradiated in microwave-generation unit, projected, manufactured and assembled in IPEN. This equipment operates under a 2,450MHz frequency and 1,000W up to 3,000W power. It is provided with an exit for residual gases and material collection system, besides automatic control of irradiation time, as shown in Figure 1.

Figure 1- Removable unit for microwave-generation power

Temperature samples were monitored by using a thermocouple connected to a measuring device. Irradiations were carried out by varying time and power, according to Table 2.

Table 2 – Irradiation data for CR samples.

Sample	Time (s)	Power (W)
1	90	1000
2	120	1000
3	150	1000
4	180	1000
5	210	1000
6	240	1000
7	60	2000
8	90	2000

Processing and Characterization Samples

All assays were performed in accordance with ASTM standards. From these controls, there were verified following properties: tensile strength and elongation, hardness, compression (DPC) and swelling.

Standard test specimens were prepared according to ASTM D 2240 standard, in a *Luxor* press. They were vulcanized at 160ºC, for 20min.

Tensile strength and elongation tests were performed in a dynamometer, ZR 60/300 model (*Otto Wolpert-Werk*), according to ASTM D 412 standard, at room temperature.

Hardness test was carried out according to ASTM D 2240 standard, in «Shore A» durometer (*Bareiss*).

Permanent deformation and compression essays were performed according to ASTM D 395 standard, B method, by using following conditions: 100ºC temperature, for 22h, in a greenhouse under circulating air, 315 IF model (*Fanem*).

Swelling tests were accomplished dipping samples in toluene, as solvent (*Merck*). For these analyses it was employed ASTM D-3616 method. Samples were weighed in the same balance used for density measurements, with 10^{-4} mg accuracy (*Marte)*, kept in the solvent within 16 hours period and further completely cleaned and re-weighed.

Swelling degree was calculated in accordance with Equation 1:

$$Q = \frac{m - m_0}{m_0} \qquad (1)$$

Where: m_0 is sample initial mass (g) and m final sample mass (g) [10].

All irradiated samples were treated again in the coil cylinder, in order to evaluate whether it was possible to prepare respective masterbatches and specimen tests.

Results and Discussion

In table 3 are shown results for irradiated and non irradiated CR samples characterizations (original mass - CR sample)

Table 3 – Characterization of irradiated and original mass CR samples.

Sample	Strength (MPa)	Elongation (%)	DPC (%)	Swelling (Q)
CR	6,5	1000	26,54	4,23
1	3,4	420	3,41	1,83
2	6,5	1000	2,79	2,60
3	4,1	420	22,80	2,68
4	6,7	800	5,28	1,82
5	2,3	320	25,09	1,82
6	6,8	660	4,47	2,57
7	7,6	1000	17,34	2,57
8	3,4	400	2,67	1,90

Results obtained for tensile strength and elongation are presented in Figure 2.

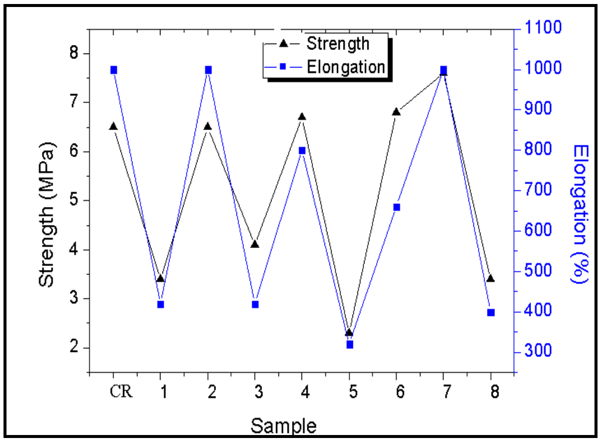

Figure 2- Tensile strength / elongation variation for CR compound.

Irradiated samples were further processed in a roll-mill. It was possible to prepare specimens for all obtained mixtures. Results were not those expected ones, once a raise in power and irradiation time imparted to the samples failures in their physical properties; a few samples showed a distorted appearance, fragile and sticky when touched, indicating the occurrence of degradation or elasticity loss. In many cases it was observed a change in standard color (from beige to black or dark-brown), according shown in Figure 3.

Figure 3 – CR specimens, standard color modified in function of irradiation.

Degradation of some samples is demonstrated in hardness and tensile/elongation resistance parameters variations. It was accomplished too swelling test for determining crosslink branching density, observing for original sample (CR) a higher swelling when compared to irradiated samples (Figure 4), indicating that 2 and 3 samples are apparently degraded.

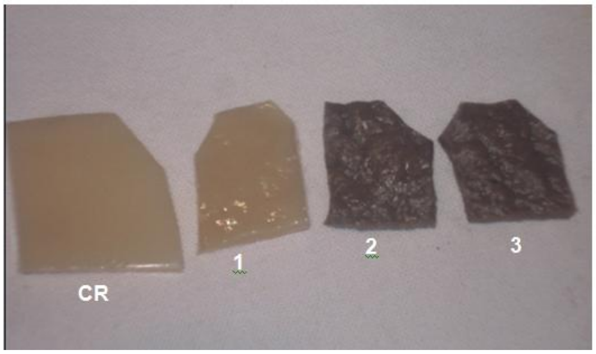

Figure 4. CR compound sample after immersion in the solvent.

Swelling indexes variation is shown in Figure 5. As previously mentioned, the higher the swelling the lower the number of crosslinkings. So, lesser values presented by irradiated samples indicate a higher crosslinking density. This effect is more evident in compounds with silica which have treated surface, showing that free-radicals from irradiation are able to increase crosslinking density, probably due to their recombination in filler load surface.

These interactions are prone to modify macromolecular mobility that influences crystallization behavior.[11]

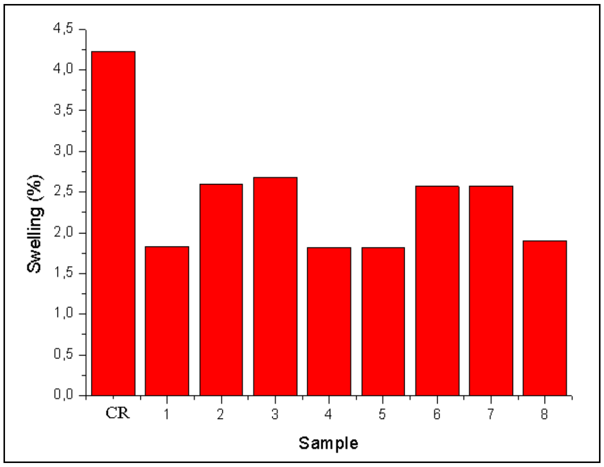

Figure 5- Variation in swelling indexes for CR compound with SiO2.

Obtained results were eventually prejudiced due to the difficulty of incorporation and dispersion oof precipitated silica in the compound (particle size and low apparent density). Other particular characteristic exhibited for silica is particles superficial porosity that shows a tendency to partially extract accelerators, causing unbalance in cure system [11].

Conclusion

All accomplished tests in this work were fundamental to point physical and chemical modifications in Chloroprene samples after irradiation.

The apparent crosslink density increases with irradiation dose, being this sensitivity to irradiation much stronger in presence of silica filler.

It is well known that this kind of filler improves mechanical properties of elastomers, as indicated by a raise in modulus, hardness and wear resistance. In summary, these interactions between filler and polymer chains affect the mobility and crystallization behavior.

Aknowledgements

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