

CHLOROPRENE RUBBER DEVULCANIZATION BY USING MICROWAVE PHYSICAL PROCESS

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Abstract - The chloroprene rubber is used to make several artefacts, such as diving and gymnastics outfits, cables coating, special pneumatic automobile tires, and in the shoe industry, among others. In spite of its benefits, a great problem nowadays is to recycle these used or with their lifetime expired galvanized articles, aiming to preserve the environment. The devulcanization of these products may be carried out by biological, chemical and physical processes. The main target of this work was to study the chloroprene recycling/re-use (DuPont - Neoprene®), by the physical microwave process. For this purpose, a basic formulation was done with this kind of rubber, to be used in the automobile industry. The samples irradiations were performed in a microwave generator equipment, developed at the CQMA of the IPEN, which operates with a frequency of 2,450MHz and power of 1,000W to 3,000W. The analyses of the samples irradiated with microwave and with those not irradiated were done by means of hardness, density, permanent deformation and compression, tesile strenght and reometry assays. The results showed that the chloroprene rubber irradiated with microwave presented a trend to vulcanize again and may substitute some unused rubber parts in formulations, without causing considerable losses in the phisical-chemical properties.

Introduction

Rubber is a part of the three great polymer types, that still include plastics and fibres. It is an engineering material as well as metals, fibres, concrete, wood, plastics and glasses. It presents diverse types and due to its physical properties and versatility, it has a great application in several industries: automotive, chemical, pharmaceutical, footwear, electrotechnical, petrochemical, construction and so on.

The chloroprene rubber is used to make several artifacts, such as diving and gymnastics outfits, cables coating, special pneumatic automobile tires and in the shoe industry, among others [1].

Among the elastomers, the chloroprene rubber (generic name - DuPont Neoprene®) is, probably, the one that possess better performance, being the most used until the current days. It presents physical properties, such as: high breaking stretching, tearing, and elongation; excellent resiliency; great resistance to the abrasion; low permanent deformation to the compression; good resistance to oils and solvents, oxygen, ozone, bad weather and flame [2].

The virgin rubber (elastomer), either natural or synthetic, must be processed before the use, that is, must be submitted to mixtures, molding and vulcanization (usually), to get the desired properties. The vulcanization is the conversion of rubber molecules inside a net, for formation of crosslinks. The vulcanization agents are necessary for the formation of

these links, in which the made up of rubber compounds changes from the thermoplastic form to the elastic form.

However, although all the benefits obtained from the vulcanization of rubber (discovered by Goodyear), one of the several problems faced currently are that after the rubber article was used or its depleted useful life, it is difficult to devulcanize it and to produce a useful material again. Therefore, the reversible process of rubber vulcanization, called «devulcanization», has been widely studied, with the objective to break the crosslinked carbon-sulphur (C-S) and sulphur-sulphur (S-S) bonds [3, 4, 5, 6]

Microwave energy has been used world-wide, also, as an important tool in the rubber devulcanization obtaning high temperatures. The processing with microwaves consists of the conversion of the electromagnetic energy in thermal energy, for its incidence in polar molecules of some rubbers. When the electromagnetic radiations penetrate the material, a part of the energy is absorbed by it and converted into heat, consequently increasing its temperature, in such way that the inner parts are hotter than the surface. It occurs because there is a greater heat exchange around it. With this characteristic, it is possible to heat great volumes of materials uniformly. The main associated advantages to this process are the fast heating, with economy of energy in relation to the conventional heating, fast beginning and stop, with the use of small spaces [3, 7].

In Brazil, it is intended to use this technique as an alternative in the recycling/reuse (devulcanization) of the chloroprene rubber, aiming at the preservation of the environment. The objective is to obtain products that allow a new reticulation (or vulcanization), with equivalent properties to the original composition, due to the breaking of tridimensional net of the reticulation, without causing rubber depolymerization. In this case the recycled one returns as active load (component) and not as an inert load.

Experimental

2.1 Samples

Polychloroprene (CR) samples had been prepared (for use in the automobile industry) for microwave interaction studies with this type of rubber, solvent and greases resistant. In these preparations, a composition with carbon black (CB) was used, from a known formulation.

The mixtures were prepared in a coil cylinder (Copé), according to ASTM (American Society for Testing and Materials) D 3182 standard, between 50°C and 60°C.

The chloroprene masterbatches were cut in pieces of approximately 1cm x 1cm, with total weight of 250g, to be later irradiated, as can be seen in figure 1.



Figure 1 – Model of chloroprene masterbatch obtained from a coil cylinder, before and after cutting.

2.2 Irradiations

The previously cited samples were irradiated in the unit of microwave generation, projected, manufactured and assembled at IPEN. This equipment operates with frequency of 2,450MHz and powers of 1,000W up to 3,000W. It possess an exit of residual gases and material collection system, beyond automatic control of irradiation time. The samples temperature were monitored by a thermocouple connected to a measuring device. The irradiations were carried out by time and power varying, according to Table 1.

Table 1 – Irradiation data of CR samples.

Sample	Time (s)	Power (W)
A1	43	1,000
A2	150	1,000
A3	180	1,000
A4	60	1,000
A5	60	1,000
A6	60	2,000
A7	15	3,000
A8	30	3,000

2.3 Processing and Characterization Samples

All the assays were carried out in accordance to ASTM standards. In these controls, the following properties were verified: tensile strength (S) and elongation (E), hardness (H), density (D), permanent deformation and compression (DPC), ashes (A) and rheometry (t_{90}).

The standard test specimens for these assays were prepared by agreement to ASTM D 2240 standard, in a *Luxor* press. They were vulcanizate at 160°C, for 20min.

The assays of tensile strength and elongation were carried out in a dynamometer, ZR 60/300 model (*Otto Wolpert-Werk*), according to ASTM D 412 standard, at room temperature.

The determination of the rheometric parameters was made in rheometer of oscillatory disk, 100 S model (*Monsanto*), in accordance to ASTM D 2084 standard. The evaluated parameters of vulcanization were: minimum (ML) and maximum (MH) torques, besides 90% vulcanization time (t_{90}), with temperature of 160°C and time of 12 min.

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

The analysis of the density was carried out in analytical balance (*Marte*), with device for solid density, according to ASTM D-297 standard, at room temperature.

For the ashes test, a muffle (*Quimis*) in temperature of 600°C was used, during 4h, according to ASTM D-297 standard.

The test of permanent deformation and compression was carried through in agreement ASTM D 395 standard, B method, in the following conditions: temperature of 100°C, for 22h, in greenhouse of circulating air, 315 IF model (*Fanem*).

All the irradiated samples were passed again in the coil cylinder, to evaluate if it was possible to confection the respective masterbatches and specimen tests. In some of them, the obtained masses presented deformed

aspect (scaled or sticky) or odor of burning, indicating that devulcanization or degradation occurred. Therefore, it was not possible to carry out this procedure.

Results and Discussion

In table 2, the results of the characterizations of the irradiated and not irradiated samples of CR (original mass - A0 sample) are shown.

Table 2 – Characterization of the irradiated and the original mass CR samples.

Sample	H (ShoreA)	D (g/cm ³)	S (psi)	E (%)	A (%)
A0	57	1.40	1,428	500	14.09
A1	48	1.35	891	780	12.20
A2	45	1.38	688	700	12.50
A3	54	1.17	700	620	15.52
A4	-	-	1,270	480	11.26
A5	-	-	-	-	14.18
A6	-	-	-	-	14.87
A7	-	-	1,890	460	14.22
A8	-	-	-	-	13.85

The A5 sample was the stickiest and did not have burnt rubber characteristic odour, being, therefore the one chosen as starting point to carry out tests of loading mixture, assuming that it had not been degraded but otherwise devulcanized. On the other hand, in those where it was possible to carry out the confection of the masterbatches with more homogeneous aspect and to mold the standard test specimens, one could deduce that they were still vulcanized. As it can be seen in table 2, it was not possible to perform the DPC tests, because it was not feasible to prepare the standard test specimens.

After that, this same sample (in the granulated form) was used as raw material in the formularization of the chloroprene, in two distinct devulcanized rubber parts: Mass 1 (M1) - three parts and Mass 2 (M2) - five parts. In both, the acceleration of the initial formularization was maintained. The two masses were vulcanized (160°C for 15 min) in the press (*Luxor*), according to ASTM D 2240 standard, then preparing the standard test specimens for assay. Later, the obtained masses were passed in the coil cylinder for confection of the masterbatches and standard test specimens for assay were characterized soon after. The gotten results are shown in table 3.

Comparing the results of the original mass (A0) with masses 1 and 2, it was observed that the last one, that possesses 95% of virgin rubber, presented a longer time of cure (5.53 min). As the acceleration of the composition was not modified, this mass was submitted to a new rheometric curve, at temperature of

170°C. The t_{90} value was of 4.82 min, similar to the one of the original mass (4.3min).

Table 3 – Masses of CR characterization.

Sample	H (shoreA)	D (g/cm ³)	S (psi)	E (%)	A (%)	DPC (%)	t_{90} (min)
A0	57	1.40	1,428	500	14.09	20.46	4.3
M1	64	1.39	1,929	500	12.08	3.85	5.45
M2	60	1.36	1,417	600	11.62	7.65	5.53

Conclusions

All the assays indicated that the samples of chloroprene had alterations in their physical and chemical properties, that is, the processing with microwaves provoked negative (degradation) and positive (devulcanization) effects in this type of rubber.

According to the results of this work, one can conclude that the masses here obtained, after the mixtures of the parts with rubber irradiated with microwaves, had a tendency to vulcanize again, since small adjustments are made in the original formulation, or either, the devulcanized composition could be replaced in some parts by the virgin rubber in formulations, without provoking great losses in the physical and chemical properties.

The tests must have continuity, they are promising in relation to this rubber. Great expectations for its reuse exist, in the manufacture of some devices used in the automobile industry.

A comment that must be detached is that the recovery compounds are obtained without the use of any chemical additive, that in the future it will be of utmost importance in the preservation of the environment.

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