

Preliminary analysis to BIIR recovery using the microwave process

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Abstract

This paper shows the results of preliminary assessment to devulcanize and recover the bromobutyl rubber (BIIR) using the microwave process. In this work, a heat generating system with high microwave frequency (2.45 GHz) was used. Samples of BIIR (about 0.250 kg) such as rubber caps production leftovers and materials that had not been approved in the quality tests were irradiated, at powers of 1000 W, 2000 W and 3000 W. Various heating times were used: 540 s (9 min) up to 1500 s (25 min). The standard test specimens of non-irradiated and irradiated samples were characterized by rheometric analysis, Shore A hardness measurement and ash test. The best operation conditions were obtained at 780 s and 2000 W. The results showed that the microwave process caused an expressive effect in the BIIR recovery. Some samples presented the tendency to vulcanize again, hence there is a great expectancy for reusing and recycling the devulcanized BIIR, without using any chemical agent in the microwave process.

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1. Introduction

The industrial and urban residues have become one of the most serious concerns that the modern society must deal with and their inadequate disposal causes environmental degradation.

Nowadays, some of these residues such as papers, wood, glasses and metals are recycled using well-established techniques reducing the waste and the raw material bulk and the consumption of power supply, thereby improving the citizen's quality of life. Other materials such as polymers are more difficult to reclaim (usually the degradation time is more than one hundred years) and several recycling processes are still in development [1].

Their waste disposal management is an important worldwide concern, especially because they do not decompose easily as papers and metals.

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In the case of polymers, they are usually classified into two main groups: thermoplastics and thermosetting materials. When thermoplastic materials are heated, they soften and may be molded and cooled at room temperature to obtain the desired shape. This process may be repeated several times to produce scrap granules. Only a reversible physical change by heating the resins (above its processing temperature) is necessary to recycle them with less troubles. Also the remanufacturing technology is well established and economical. Thus a recycled thermoplastic material competes directly with the virgin polymer and its commercial viability depends on the relation between performance and cost benefit of the finished product.

Concerning recycling of thermoplastics, these recovered materials are used along with virgin resins and fresh additives in the formulation to obtain desired properties in the product. Although the physical properties of recycled plastics undergo reduction in this process, they still retain an acceptable fraction of virgin resin properties.

Regarding thermosetting materials like rubbers, they cannot be softened or remolded by heating due to crosslinked bonds formed during processing and molding. The recycling of these materials is not easy because their three-dimensional net must be broken down. This process is much more severe and the finished products are entirely different from the starting thermosetting material or even its precursor thermoplastic materials. In the meantime, the recycling technology of thermosetting polymers including rubbers is complex, costly and less economically viable.

Although reprocessing of thermosetting materials is difficult, the use of reclaimed thermosetting resins as fillers, in new polymer formulations, is found with some influence on flow and deformation characteristics during processing [2].

Rubber is an elastic hydrocarbon polymer which can occur in nature in the sap of some species of plants (latex whose commercial source is the *Hevea brasiliensis* tree) or can also be produced synthetically (polymerization of several monomers to produce polymers).

Usually, uncured natural rubber smells in a few days when it starts to perish. The process of perishing partly consists of the large rubber molecules breaking up by oxidation. In 1839, Goodyear and Hayward discovered the vulcanization process that greatly facilitated experimental investigations. In this technique, crosslinked bonds are formed in the

polymer chains, normally done by addition of sulphur or other chemical agents as peroxides.

The number of sulphur atoms in a vulcanized polymer has a strong influence on its physical and chemical properties. When rubber is vulcanized it changes from plastic characteristic to elastic characteristic allowing flexible movements [3].

In 2001, the annual consumption of natural rubber was more than 15 million tons and the output of rubber products was more than 31 million tons worldwide.

With the development of rubber industry, a lot of waste rubber is produced in the world every year. The main recycling source of this material is discarded rubber products, such as tires, pipes, hoses, belts, shoes, scraps and waste products which are produced in rubber process. At the same time, many recycling techniques for waste rubber are in development around the world [4].

Reclamation of these materials, therefore, is the most desirable approach to solve the disposal problem. This can be done by the conversion of a three-dimensionally interlinked, insoluble and infusible strong thermosetting polymer to two-dimensional and thermoplastic products simulating many of the properties of virgin rubber. Many attempts have been made for reclaiming of scrap rubber products. However, reclaiming process may be broadly classified into two groups: chemical processes and physical processes.

The majority of reclaiming rubber industries use chemical agents for recovering rubbers. These are generally organic disulfides or mercaptans which are exclusively used during mechanical working at elevated temperature. Based on these chemicals many processes have been developed. Also a few inorganic compounds have been tried as reclaiming agents.

In a physical reclaiming process the rubber can be recovered with the help of external energy. Thus in this process, the three-dimensional network of crosslinked rubber breaks down in the presence of different energy sources. Due to the breaking of network structure, macromolecular rubber chain is transformed into small molecular weight fragments so that it can be easily miscible with the virgin rubber during compounding. So reclaim rubber produced by physical reclaiming process may be used as a non-reinforcing filler. But if in this process a specific amount of energy is used which is sufficient to cleave only the crosslinked bonds, then it may be reclaimed rubbers with good quality. Also these products might be compared with virgin rubber

properties. The different kinds of physical reclaiming processes are mechanical, thermo-mechanical, cryo-mechanical, ultrasonic and microwave.

Among the previously mentioned processes, the microwave technique has been studied all over the world to identify (qualitatively and quantitatively) and define the mechanism of microwave-material interaction, in rubbers devulcanization [2].

In Brazil, the application of this process is a very recent field and has been studied as a new tool in materials processing, which uses high temperatures.

Thus, the goal of this work was to make the preliminary assays of vulcanized bromobutyl rubber recovery, using leftover caps of pharmaceutical industry, trying to devulcanize them through microwave technology. In Brazil, the knowledge of this technology is important to begin the development process in industrial scale and consequently in reducing the environmental pollution caused by these kinds of residues.

2. Experimental

2.1. Microwave process

Microwaves are a form of electromagnetic energy in the frequency band from 300 MHz to 300 GHz. Microwave-radiation is not an ionizing radiation and is therefore not hazardous for human tissue. Industrial microwave processing is usually accomplished at a frequency of 2.45 GHz (which corresponds to a wavelength of 12.24 cm) to avoid interference with telecommunication and cellular phone frequencies.

Materials react differently when an electric field, such as can be generated by microwave energy, interacts with them: in conductor materials (such as metals) electrons move freely and they tend to reflect them; some non-polar compounds (for example, many plastics) are transparent to microwaves; and materials that respond to them are polar molecules (e.g., water and some kinds of rubbers), free ions or conductive compounds that create a momentum of dipole which results in the volumetric heating throughout the mass of the material. Therefore, these molecules vibrate at high frequency tending to reorient and align themselves with the frequency of the microwave field. Heat is generated via interaction of the material with microwave energy. These are called dielectric materials. The ability to convert microwave energy to thermal energy depends on the dielectric constant and dielectric

loss associated with the material. Greater effects are observed when the material involved has a greater dielectric constant at a given microwave frequency and power.

Microwave processing offers numerous advantages in relation to conventional heating methods (convection or conduction), where the material's surface heats first and then the heat moves inward. One of the most important characteristic is saving energy. It happens due to the fact that the material absorbs microwaves readily (the heat is generated from the inner parts to the surface of the material) reducing the processing time. Also the selective energy absorption allows heating in specific points of the material. This process is environmentally clean because it reduces pollutant emission. Finally, the microwave heating does not require an appreciable amount of time to effect temperature changes such as the conventional methods and when the microwave device is turned off the effect of these electromagnetic waves is instantaneously interrupted [5].

In this work, a microwave generating system was developed and installed by IPEN-CNEN/SP with high frequency (2.45 GHz) and RF valves (maximum 3000 W). It consists of a wave generator, wave guides, and a cavity to be filled with the material to be irradiated (Fig. 1), which has a residual gas outlet. Also, a digital control panel was projected, manufactured and installed that permits remote and automatic monitoring and handling of irradiation time and power applied to the material.

2.2. Materials

Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene. The primary attributes of this kind of rubber are excellent impermeability/air retention and good flex properties, resulting from low levels of insaturation between long polyisobutylene segments.

The other important properties are high heat, climatic conditions and aging resistances, which explain its use in steam hoses, impermeabilization of terraces and watertank and anti-corrosion coverings. It is also used in the manufacturing of products to electrical and pharmaceutical industries. The butyl rubber presents as inconvenience its incompatibility with other rubbers that can be solved with the manufacturing of chlorinated and brominated polymers. Bromine is added to conventional butyl rubber in order to obtain faster curing.



Fig. 1. Heat generating system.

In this work, samples of bromobutyl rubber (BIIR) were used. The related samples are rubber caps production leftovers (of pharmaceutical industries) or materials that had not been approved in the quality tests. Fig. 2 shows the received samples. First of all, they were selected and weighed (sample mass around 0.250 kg, each one) in a scale model AS 5500C (Marte Balanças e Equipamentos), then they were irradiated using the microwave system.

The main idea is using the recovery rubber for manufacturing the same product or another (depending on the results of *in vivo* and *in vitro* toxic tests, made by those industries), once the production leftovers are high and the quality control is rigorous.

The BIIR basic formulation includes bromobutyl $\times 2$ rubber, starter substance, mineral load, polyethylene wax and accelerator.

2.3. Irradiations

The samples of BIIR were irradiated using the microwave system previously cited, at powers of 1000 W, 2000 W and 3000 W. The microwave system power was monitored by a multimeter (Fluke 189) and a current clamp (Fluke i410). Various heating



Fig. 2. Samples of bromobutyl rubber (BIIR).

times were used: 9 min (540 s) up to 25 min (1500 s) and the temperatures of the samples were monitored by a thermocouple. In Table 1, the data of the irradiated samples are shown.

Table 1
Data of the irradiated BIIR samples

Sample	Weight (g)	Time (min)	Power (kW)
S1	250	15	1
S2	225	15	1
S3	250	13	2
S4	250	9	3
S5	250	15	3
S6	250	20	1
S7	250	20	2
S8	250	20	3
S9	250	25	3
S10	250	20	1

2.4. Characterization of the samples

After being irradiated, the BIIR samples were put in a roll open mixer (cylinder – *Copé*), to homogenize the material and take the rubber straps. Some parts of these samples were pressed at 150 °C during 15 min to make masterbatches (Luxor press). Then they were used to manufacture the standard test specimens which were characterized by rheometric analysis, Shore A hardness measurement and ash test, according to the ASTM standards (American Society for Testing and Materials) D-2084, D-2240 and D-297, respectively.

Rheology can be defined as the study of the flow and deformation of materials. The relationship between stress and deformation is a property of the material. Rheometer is a mechanical spectrometer that is capable of subjecting a sample to either a dynamic (sinusoidal) or steady (linear) shear strain

(deformation). Different geometries can be used for measurements. In this work, the samples were sheared between two circular plates (the inferior one – heated with a set up temperature; the superior one – put in motion) separated by a determined distance. Two important measurements are torque versus time and Tc-90 (time to 90% torque increase). The rheometer tests (R-100 rheometer, *Monsanto*) were carried out to verify their vulcanization curve – 160 °C during 12 min.

The hardness is the resistance measurement imposed to penetration of one surface, by using an instrument with specific dimensions and weight. Shore Hardness, using either the Shore A or Shore D scale, is the preferred method for rubbers/elastomers. The Shore A scale is used for ‘softer’ rubbers while the Shore D scale is used for ‘harder’ ones. The scale results are given in a value between 0 and 100, with higher values indicating a harder material. The tests were carried out by using a durometer Shore A (*Bareiss*).

The ash test provides a measure of the distribution of fillers (residue – inorganic material present) within a material such as rubber or plastic. The specimens were ignited and burned under high heat, by using a muffle furnace (*Quimis*), 600 °C during 4 h. All resulting left over residue matter (ash) was recovered and the percentage of recovered ash was calculated.

Also standard test specimen of BIIR non-irradiated sample was prepared to be characterized. The results were compared between both kinds of samples (irradiated and non-irradiated).

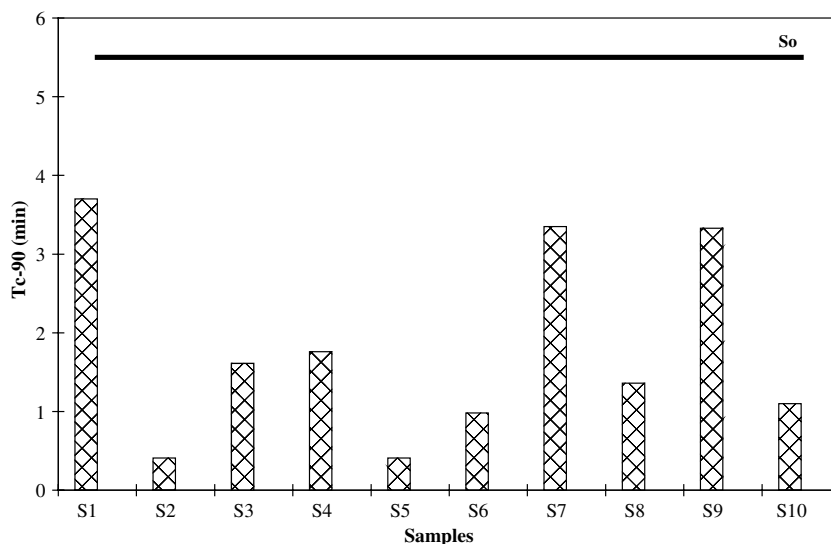


Fig. 3. Rheometric tests results (Tc-90).

3. Results and discussions

The preliminary tests were made to evaluate the microwave equipment and performance of the technique in the BIIR recovery. All the results of the irradiated samples were compared with those obtained for the non-irradiated sample (S0).

According to the measurement of the temperatures of the samples, before and at the end of the irradiations, they were about 25 °C (room temperature) up to 550 °C, respectively.

Regarding the rheometric analysis, the obtained curves showed that some samples tended to vulcanize again. The results of the tests (Fig. 3) showed that the Tc-90 losses were very high, denoting that

some samples were degraded instead of being devulcanized.

Concerning the hardness measurement, all the samples presented losses in their hardness values (Fig. 4), but only in some of them the microwave caused a suitable effect such as the S3 sample.

According to the deterioration by heat – ashes tests – (Fig. 5), in general the results showed a little increase in the ashes grade or kept the same value, suggesting that there was not expressive loss of organic materials under microwave irradiation.

Considering all the tests, including the visual analysis of the test specimen obtained with the rheometric analysis, the S3 sample presented the most suitable results to be applied in this research. This

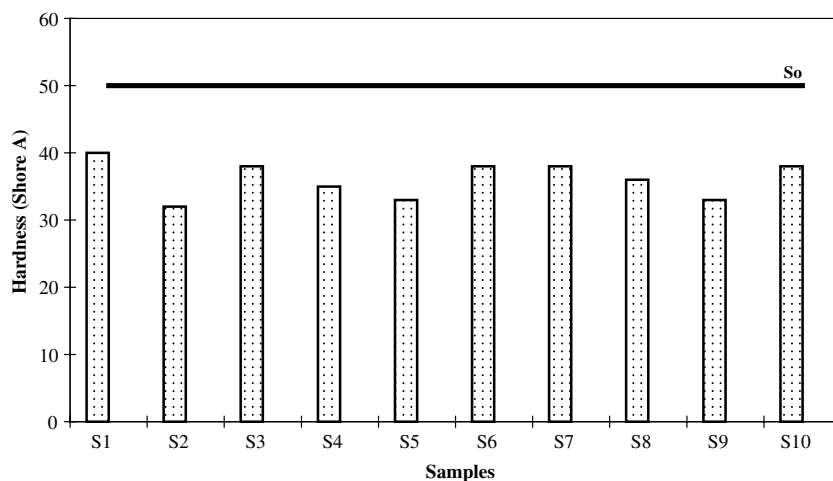


Fig. 4. Hardness tests results.

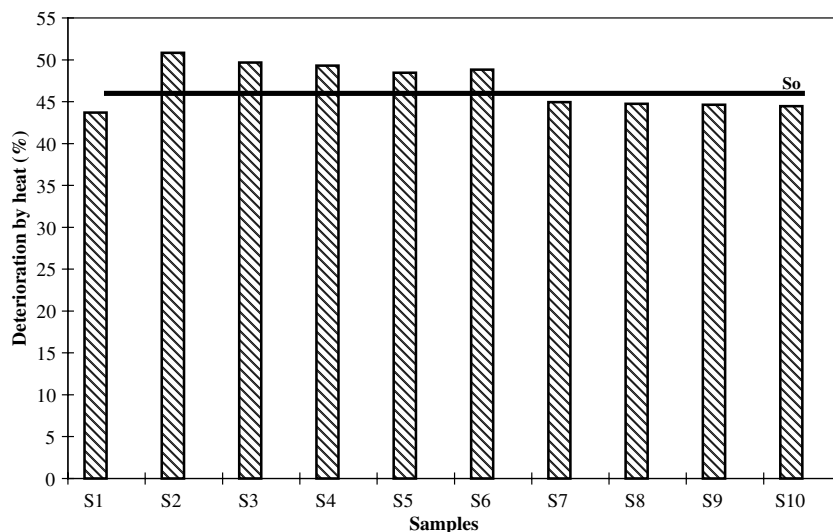


Fig. 5. Deterioration by heat – ash tests results.

suggested the possibility to modify some characteristics such as Tc-90 and texture (a homogeneous mass).

To do that, some parts of virgin (crude) rubber were mixed with this sample. Then the mixture was processed in the roll open mixer and the characterization tests were done. The test result for Tc-90 was around 3.8 min (so value was about 5.5 min) and the sample vulcanized again without losing the elasticity and homogeneity.

As this sample presented good properties in the characterization, it may be considered as an useful parameter to be followed in the improvement of other processes, adding different proportions of virgin rubber.

4. Conclusions

All the performed tests were important because the results showed that the microwave process caused an expressive effect in the BIIR recovery.

Some samples presented the tendency to vulcanize again, hence there is great expectancy for reusing and recycling the devulcanized BIIR. 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.

Also the microwave technique has proved promising for this kind of rubber. The flexibility of this technique allows the improvement and studies in order to attend to the specific necessity according to the determined applications.

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