EVALUATION OF THE THERMAL PROPERTIES OF CHLOROBUTYL RUBBER SUBMITTED TO DEGRADATION CONDITIONS IN A PIGMENT

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Abstract: The pigment industry uses rubber as chemical protection in equipment that operates in a corrosive environment. These rubbers can suffer degradation reducing their useful life. This work compared the thermal properties of two samples of chlorobutyl rubbers (CIIR) submitted to degradation conditions. One sample (BCu) was taken from equipment that operated for about 15 years, the other not yet used (BCn). Thermal events were analyzed using thermogravimetry (TGA) and differential scanning calorimetry (DSC) and it was found that the thermal stability of the samples in use is lower. The degradation conditions in the laboratory did not influence the thermal properties despite observing a superficial degradation in the micrographs of the samples.

Keywords: Rubber; degradation; thermal properties.

AVALIAÇÃO DAS PROPRIEDADES TÉRMICAS DE BORRACHAS CLOROBUTÍLICAS SUBMETIDAS A CONDIÇÕES DE DEGRADAÇÃO EM UMA INDÚSTRIA DE PIGMENTOS.

Resumo: A indústria de pigmentos utiliza a borracha como proteção química em equipamentos que operam em meio corrosivo. Estas borrachas podem sofrer degradação reduzindo sua vida útil. Este trabalho comparou as propriedades térmicas de duas amostras de borrachas clorobutílicas (CIIR) submetidas a condições de degradação. Uma amostra (BCu) foi retirada de um equipamento que operou por cerca de 15 anos, a outra ainda não utilizada (BCn). Analisou-se os eventos térmicos através da termogravimetria (TGA) e calorimetria exploratória diferencial (DSC) e verificou-se que a estabilidade térmica das amostras em uso é inferior. As condições de degradação em laboratório não influenciaram nas propriedades térmicas apesar de se observar uma degradação superficial nas micrografias das amostras.

Palavras-chave: Borracha; degradação; propriedades térmicas.

1. INTRODUCTION

Rubbers are widely used as chemical protection of the carbon steel substrate in the pigment industry, which are responsible for the production of TiO_2, in many equipment that operate in a corrosive medium containing solutions based on H_2SO_4.

Among the rubbers that have good characteristics for this application is chlorobutyl, as it has a high vulcanization rate, low permanent deformation and compatibility with other rubbers [1]. The presence of a chlorine atom in the chemical structure of this material increases the polarity of the elastomer allowing the formation of new cross-links, improving vulcanization and adhesion. This improvement in adhesion is essential so that CIIR can be applied as an internal lining on equipment, tires, etc. [2-3].

In this work, the properties of two CIIR samples used as protection in equipment of a pigment production industry were evaluated. In this application, the rubber is placed in the form of a 4 mm sheet together with an adhesive, immediately after anticorrosive surface treatment of the carbon steel substrate (sandblasting and painting). Figure 1 below shows an example of applying a rubber lining to the side of a tank, typical configuration of equipment in the pigment industry.

Figure 1-. Example of application of chlorobutyl rubber lining on the side (or body) of a TiO_2 processing tank.

Source: Author

This lining is immersed or in contact with a corrosive medium which can degrade the rubber, causing CIIR to detach and deteriorate, reducing its performance, service life and increasing the number of premature failures. Thus, the thermal properties of two types of samples of chlorobutyl rubbers were analyzed. Through thermogravimetry it was possible to verify the variation of the thermal stability of the materials and the differential exploratory calorimetry gave us information about changes in the temperatures of thermal transitions of the polymers and the occurrence of thermal events that can contribute to the degradation of the samples [4].

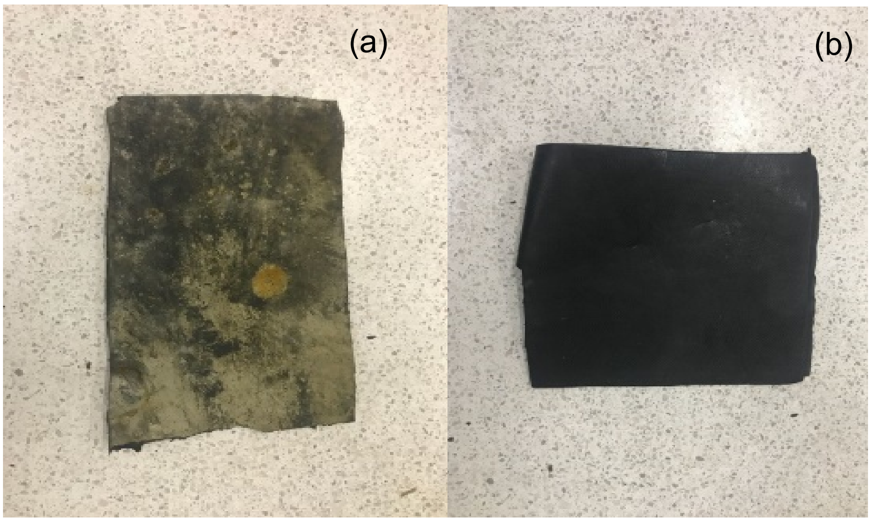
2. METHODOLOGY

2.1 Materials

In this study the analyzed rubbers are of the chlorobutyl type from the same manufacturer. They have a hardness of 65 Shore A, operating temperature ranging between 60 - 110 ºC and density 1.23 g / cm³. These rubbers are widely used as chemical protection for the carbon steel substrate in the pigment industry (TiO_2 production) in many equipment, such as tanks and pipes.

In order to evaluate the influence of the sample condition on the thermal properties of the rubbers, when subjected to degrading environments, two samples were selected, one called BCu and another called BCn (Figure 1). BCu was removed from equipment that operated for about 15 years in a corrosive medium (30% H_2SO_4 solution), this rubber was vulcanized in the field using saturated steam. BCn was vulcanized in the manufacturer's calendering process and has not yet been applied as protection in industrial equipment.

Figure 2. Rubber samples: (a) BCu and (b) BCn.



2.2 Simulation of degradation conditions

In order to simulate industrial conditions, the rubber samples were fixed on stainless steel metal walls and subjected to a temperature of 60 ° C, where a fluid called “clarified liquor” was transported and handled for 1000 hours. The clarified liquor is fluid with about 30% H_2SO_4, very common in the pigment industry (TiO_2 production), which has a corrosive fluid characteristic and a composition with titanium, sulfur and iron as its main components. This situation simulates, with relevant similarity, the rubber applied in the lining of tanks and pipes.

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2.3 Thermal characterization

The thermal properties of the rubbers, before and after subjected to degradation conditions, were evaluated using thermogravimetry (TGA) and differential exploratory calorimetry (DSC) tests. The TGA test was performed on a TA Instruments Q10 thermobalance, with a heating rate of 10 ° C / min and heating up to 1000 ° C. The DSC was performed on a TA Instruments Q10 equipment, with a heating rate of 10 ° C / min between -90 ° C to 200 ° C. These tests were carried out in an atmosphere of ultra-dry synthetic air (80% N^2 and 20% O^2) with a flow rate of 20 ml / min.

2.4 Morphology

For a better identification of the surface aspect provided by the action of the fluid, the surface of the rubbers was analyzed looking for evidence of the degradation process, such as localized loss of mass, crack opening, craters or islands. For this, scanning electron microscopy (SEM) was performed and a Jeol microscope and model JSM-6510 LV was used.

3. RESULTS AND DISCUSSION

The results found for the TGA / DTG are shown in Figure 3 and the stages of mass loss detailed in Table 1.

Figure 3. Thermogravimetric curves of samples of chlorobutyl rubbers.

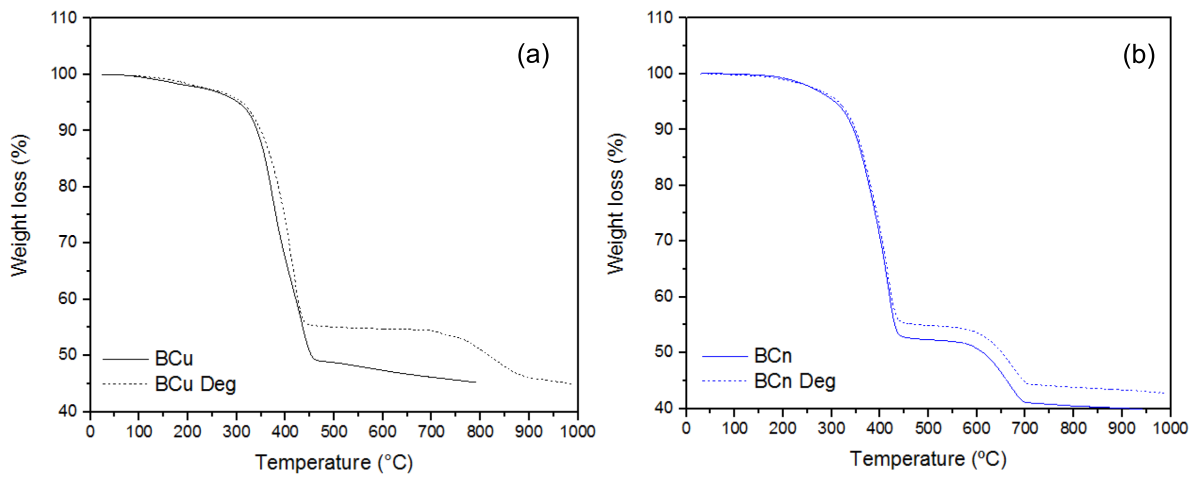

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Table1. Stages of mass loss of samples of chlorobutyl rubbers.

	Stage	T1 – T2 (°C)	Δm (%)	Losses (%)
BCu	I	95,30 – 433,08	54,14	45,26
BCu Deg	I	97,12 – 414,27	44,81	44,94
	II	711,47 – 849,98	9,67	
BCn	I	136,67 – 415,42	47,67	39,36
	II	576,12 – 666,82	11,84	
BCn Deg	I	135,43 – 414,27	45,14	42,73
	II	575,92 – 679,19	11,13	

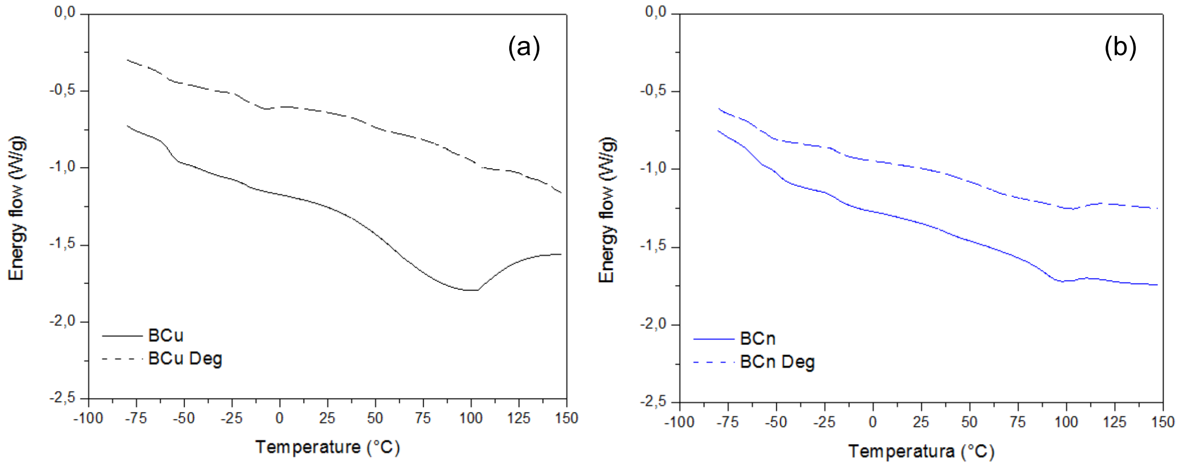
The literature indicates that chlorobutyl rubber has high thermal stability [1], this behavior can also be observed in the results obtained in this work. All samples show a peak of thermal degradation around 415 ° C, which corroborates with other studies [2,5].

The samples of the rubbers called BCu showed similar thermal stability, starting mass loss at approximately 95 ° C. These samples have a thermogravimetric profile different from BCn rubber, which presents greater stability, starting mass loss around 135 °. Ç. This behavior is due to the time of use of BCu which possibly caused degradation in the material.

The thermal decomposition profile of chlorobutyl rubbers consists of an initial loss of volatiles, followed by the pyrolysis of the polymeric component, this step is responsible for the greatest loss of mass. It is observed in this type of rubber the formation of carbon black in pyrolysis, adding the amount of the same additive used in the formulation of the rubber, resulting in a high residue content that is composed of ashes, fillers and other inorganic additives [5].

The temperature of thermal transitions of the samples were determined using the DSC. Figure 4 shows the rubber thermograms and a change of baseline around -60 ° C is observed in all samples, characteristic of the glass transition temperature (Tg) due to the amorphous nature of these materials, this temperature being characteristic of a chlorobutyl rubber. There is also an endothermic peak at approximately 100 ° C related to moisture loss [6]. It was not possible to evidence significant changes in thermal events in the analyzed samples.

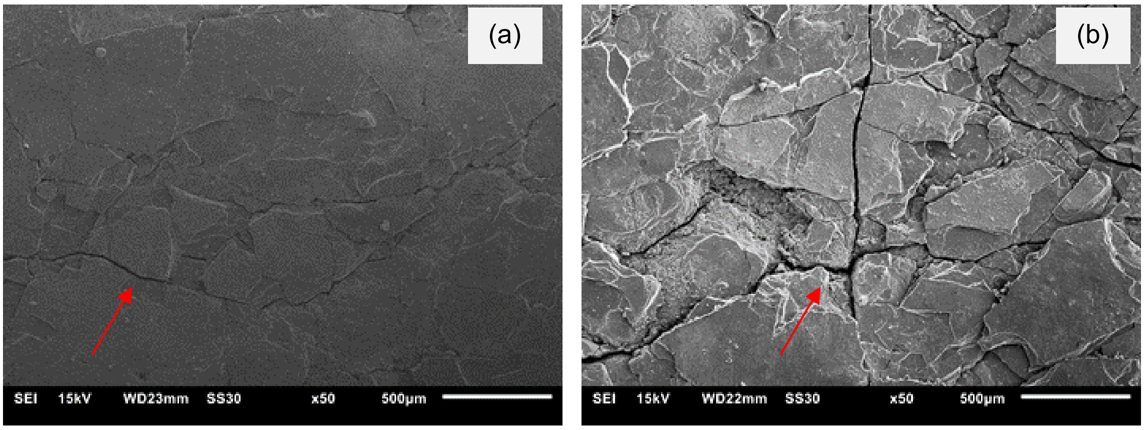
Figure 4. Calorimetric curves of chlorobutyl rubbers.



The morphologies of the rubbers were analyzed through Scanning Electron Microscopy (SEM), before and after simulation of degradation in the laboratory and it can be seen, in the two samples analyzed (BCu and BCn), that there was superficial degradation characterized by the formation of small cracks.

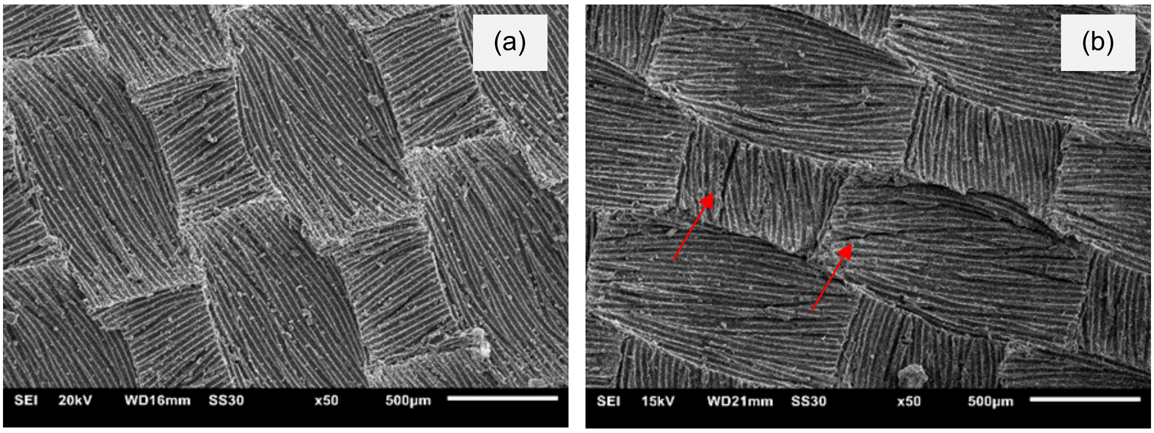
Due to the time of use of the sample in an industrial environment, small cracks are observed in the BCu sample even before degradation in the laboratory (Figure 5a), these failures are accentuated after the simulation (Figure 5b) resulting in loss of mass and reduced stability as seen in the TGA results.

Figure 5. Micrograph of BCu samples. (a) without degradation; (b) with degradation in the laboratory.



There is a difference between the morphologies of the samples (BCu and BCn) that can be associated with the time of use and type of vulcanization. The BCn rubber sample also showed small surface flaws after degradation in the laboratory (Figure 6b). However, according to the results of TGA and DSC, the failures did not influence the thermal properties of this rubber.

Figure 6. Micrograph of BCn samples. (a) without degradation; (b) with degradation in the laboratory.



4. CONCLUSION

CIIR rubbers used as lining for corrosion protection of carbon steel show a reduction in thermal stability with time of use and vulcanization in the field. The characterized rubbers have a high residue content from carbon black. The glass transition temperatures of BCu and BCn samples are similar and have not been altered with the degradation simulation process in the laboratory.

Through the morphology, it was verified that the simulated conditions for degradation caused superficial failures in the samples, however the failures do not alter the analyzed thermal properties.

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