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ARTICLE

Comparative Study Between Calcination and Thermogravimetry Techniques in the Quantification of Carbon Black Content in Polymeric Resins

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In the characterization laboratory involving polymeric resins from the petrochemical industry, the carbon black content in polymeric resins is analyzed using two techniques: calcination and thermogravimetric analysis (TGA). The objective of this study is to verify whether there is a significant difference between the results obtained by these two methods, with the aim of reducing response times for customers while maintaining the same level of quality and accuracy and improving Health and Safety Environment (HSE) matters, such as reducing analysts' exposure to the high temperatures used in microwave oven for calcination. In the experimental conditions, the calcination technique obtained a higher uncertainty value compared to TGA, but the results showed precision and accuracy in both techniques. Furthermore, the method developed by TGA provided a 175% increase in productivity and advancement for the analysts safety involved in carrying out the activities as it has low risks when compared to calcination.

Keywords: calcination, TGA, carbon black, HSE, HDPE

INTRODUCTION

Carbon black is a commercial product manufactured by thermal decomposition (detonation or by incomplete combustion of carbon hydrogen compounds – oil or natural gas). According to IUPAC, it is an

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industrially manufactured colloidal carbon material in the form of spheres and of their fused aggregates, with sizes below 1000 nm.[1] Different categories of carbon black are available including furnace black (the most representative one), channel black, thermal black, acetylene black and lamp black.[2] From the technological point of view, carbon black is an additive incorporated into the polymer with the purpose of protecting against photooxidation, increasing the life cycle of the polymer exposed to the sun, acting as a radical inhibitor and as a bridge between molecules. Empirically it was found that an amount of 2 to 3% of carbon black prevents degradation and makes the polymer more resistant.[3]

The quantification of carbon black in polymeric materials has been investigated using calcination techniques, thermogravimetric analysis (TGA) and dispersion measurements. Examples of carbon black quantification by other techniques involve, for example, transmittance electron microscopy (TEM) through the quantification of structural parameters (on a nanometric scale),[4] physical quantification of interfacial interactions with polymer matrices[5] or laser welding.[6] In the petrochemical industry, the determination of carbon black content in polymeric resins is performed using gravimetric and TGA methods based on ASTM and ISO standards. The determinations aim to quantify and demonstrate the real concentration of carbon black present in polymeric resins, ensuring the specification, quality and life cycle of the polymer exposed to the sun.[7-9] The experimental conditions vary between the two methodologies: in the case of calcination analysis, 2 g of sample are used per duplicate, with a limitation of 2 analyses/day with manual steps due to the weighing, heating and cooling time of the microwave oven, while the TGA analysis uses 20 mg of sample per duplicate and has an average of 11 analyses/day that were performed automatically. The sample masses were defined through previous internal studies based on standards.[9] Thus, evaluating the process as a whole, the increase in productivity is evident, in addition to the simplification of the process and agility in terms of response time.

Therefore, the present study aimed to evaluate the potential differences between carbon black in polymeric matrix quantification by calcination and TGA measurements, seeking to reduce the response time of results for customers with the same quality, accuracy and improvements in terms of Health, Safety and Environment (HSE).[3] It is worth remarking that the fundamental responsibility of each company and employee is to minimize the environmental impact where one operates, focusing on the HSE and well-being in the workplace.

MATERIALS AND METHODS

Samples

A more common Braskem high-density polyethylene (HDPE) resin was selected and collected with a specification of 2.0 to 2.5% carbon black and, to carry out this study, the composition of the master used to additive the resins contains 48% carbon black.

Calcination

The technique is based on mass difference, where a sample is subjected to microwaves (CEM-PHOENIX, 2450 MHz and 122 mm band) in a compressed air atmosphere typical of an industrial plant and the energy is absorbed by the sample molecules, increasing the kinetic energy of the sample and causing internal heating and differentiated polarization, which expands, agitates and heats the material.[10] In this case, the carbon black content is determined from the degradation that occurs with the formation of volatiles, causing mass loss in the sample subjected to temperatures of 600 °C and 800 °C, with an average of 2 analyses/day.[8-10]

Thermogravimetric analysis (TGA)

This technique was performed on a TA TGA Q500 thermal analyzer (TA Instruments, New Castle, US). HDPE samples weighing 10.0 ± 2.0 mg were heated from room temperature to 500 °C at 10 °C min^{-1} under N_2. The inert gas N_2 ensures samples stability whithout the possibility of samples degradation (carbon black releasing) between the range of 500 and 600 °C. The percentage of carbon black is determined from the mass loss curve after changing gases from N_2 to O_2, with an average of 11 analyses/day.[8-11]

Method validation

Both methods were evaluated in terms of the following parameters:

Precision

It is the proximity among several readings carried out on the same sample, and is usually expressed by the standard deviation, variance or coefficient of variation (CV) of replicates, with ≤ 5% being considered appropriate, determined via Excel for the calculations.[12-14]

Repeatability (r)

It is the degree of agreement between the results of successive measurements of the same sample carried out under the same measurement conditions.[12-14]

Reproducibility (R)

It is the degree of agreement between the results of successive measurements of the same sample carried out under different measurement conditions, in this case, by a different analyst.[12-14]

Gage Repeatability and Reproducibility (Gage R&R)

It is the statistical tool that measures the amount of variation in the measurement system resulting from the measuring device and the people making the measurement, with ≤ 5% being considered adequate, determined by Excel for the calculations.[12-14]

Uncertainty

It is the expression of statistical dispersion of the values assigned to a measured quantity. All measurements are subject to uncertainty and a measurement result is only complete when it is accompanied by a statement of the associated uncertainty, such as the standard deviation, determined via Excel.[12-14]

Statistical tests

Complementary *t* and Grubbs' tests have been employed. The latter has been employed aiming at checking the presence of extreme values in sample observations. Extreme values can be considered as manifests of the random variability inherent in the data, or just an error in the calculation during data collection and even a hasty note by the operator, determined by minitab software for the calculations.[12-14] Expanded coefficient of variation (CVE) is the acceptance criterion for a quantitative analysis carried out with more than one route. It is the repeatability limit, i.e. the maximum value admitted for a given analysis, with acceptance criteria in the laboratory of ≤ 5%, determined via Excel calculations.[12-14] Statistical analyses were also performed using analysis of variance (ANOVA) using SPSS (IBM). A value of $P < 0.05$ was considered statistically significant.

RESULTS AND DISCUSSIONS

Analytical results

The sample was evaluated on five different days in triplicate by two analysts, totaling 15 repetitions per analyst, with the aim of testing homogeneity and amplitude. The results can be found in Table I.[12-14]

It is observed through the reference values present in Table I that the results obtained are within the sample specification range, therefore, it is considered that the HDPE sample is homogeneous and stable. It can also be seen that, using the TGA technique, the standard deviation found is smaller than that using calcination.[10-14]

Table I. Quantification results by calcination and TGA

Repetition	Calcination Results		TGA Results	
	Analyst 1 (%)	Analyst 2 (%)	Analyst 1 (%)	Analyst 2 (%)
1	2.3	2.1	2.2	2.1
2	2.2	2.1	2.2	2.2
3	2.2	2.0	2.2	2.2
4	2.1	2.1	2.2	2.2
5	2.1	2.2	2.2	2.2
6	2.1	2.2	2.1	2.2
7	2.1	2.2	2.1	2.2
8	2.1	2.2	2.2	2.2
9	2.1	2.1	2.1	2.2
10	2.2	2.2	2.1	2.2
11	2.3	2.2	2.1	2.2
12	2.2	2.2	2.2	2.2
13	2.1	2.0	2.1	2.2
14	2.1	2.0	2.2	2.2
15	2.2	2.0	2.0	2.2
Average	2.2	2.1	2.1	2.2
Reference value (% Carbon Black)	2.1 ± 0.10		2.2 ± 0.04	

A typical thermogram is shown in Figure 1a and presents two stages of mass loss. In an inert atmosphere (N_2), the first stage, close to 500 °C, corresponds to the mass loss (TG) related to the decomposition of the polymer (HDPE). Subsequently, the atmosphere is changed from inert (N_2) to oxidizing (oxygen) close to 500 °C and the second stage of mass loss refers to the carbon black, which is oxidized and released in the form of carbon dioxide (CO_2). The maximum temperatures of polymer decomposition and carbon black oxidation can be obtained from the DTG curve. In the case of HDPE (Figure 1b), we observed the absence of the signal related to the degradation of carbon black between 500 and 600 °C at the decomposition of the polymer (HDPE) close to 450 °C. By comparing Figure 1a with Figure 1b, it is possible to observe the difference in initial temperature of the polymer decomposition (HDPE) and relate it to the thermal stability characteristic of carbon black.[2,8,11]

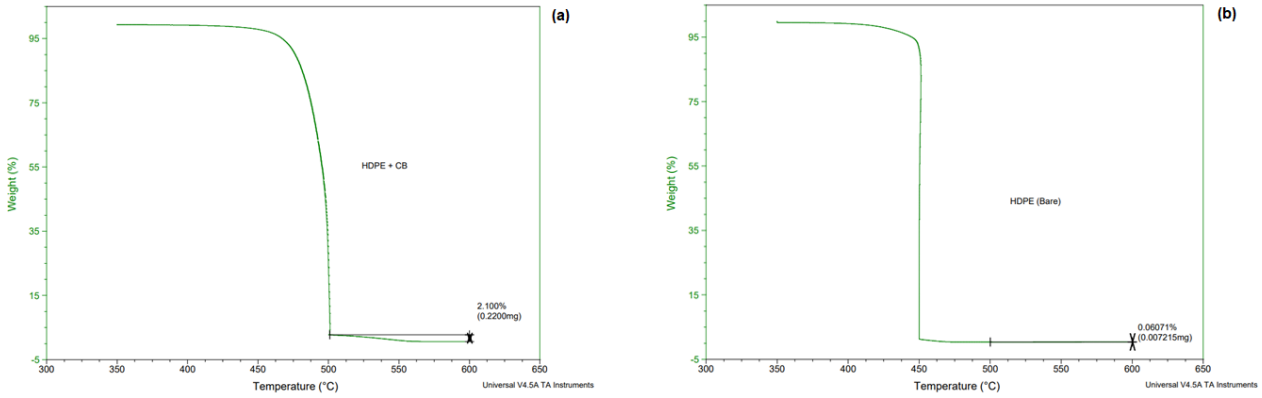

Figure 1. Typical TGA thermogram of (a) HDPE containing CB; (b) HDPE (bare).

Precision / Repeatability and Reproducibility

Repeatability and reproducibility were calculated according to laboratory results acceptance criteria standards (it is worth noting that internal control was performed and verified by Braskem's quality management through control charts and is based on standards cited in references),[12-13] using the data available in Table I. From these values, repeatability and reproducibility calculations were performed, as shown in Table II.[12-14]

Table II. Calcination and TGA results from the Repeatability and Reproducibility assessment

Assessment	Calcination Results (%)	TGA Results (%)	Conclusion
CV R&R	2.1	1.2	Adequate
CV REPE	1.63	1.07	Adequate
CV REPRO	1.25	0.59	Adequate
Max CV Analyst 1	2.8	2.7	Adequate
Max CV Analyst 2	2.7	4.8	Adequate

Where, %CV ≤ 5 is adequate; 5 < %CV ≤ 15 may be appropriate depending on the importance of the application, the cost of the instrument, the maintenance cost, etc.; %CV > 15 % is inadequate, measurement system needs improvements.

Through the values obtained by the Repeatability and Reproducibility calculations, the results of the calcination and TGA techniques are considered adequate, i.e., the coefficient of variation values are equal to or less than 5%, in accordance with specific laboratory standards.[12-14]

Uncertainty calculation

The data present in Table I were used to calculate and generate uncertainties, with the calcination method presenting an uncertainty of 4.3% and the TGA method 2.6%. Combined uncertainty was used, where the square root of the squared deviation results is taken according to results acceptance criteria standards.[12-14]

Expanded coefficient of variation (CVE)

The CVE for the TGA analysis is 3% and for the calcination method 4.7%, determined based on the repeatability limit over the analysts' average multiplying by 100, in accordance with results acceptance criteria standards.[12-14]

Statistical tests

Two-Way ANOVA was conducted to determine to what extent analytical technique and technician have an effect on income. The statistical analysis revealed that there was not a statistically significant interaction between both effects ($F(2, 57) = 1.4172$, $p = 0.251$).

The results obtained in Table I were also subjected to the Grubbs Test to verify whether there is significant variation between the two techniques and the presence of outliers (anomalous results). (Figure 2)

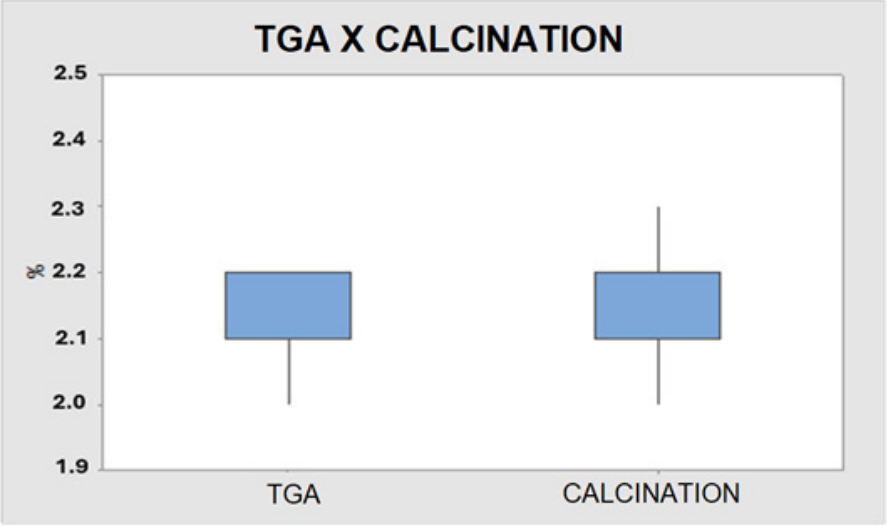

Figure 2. Grubbs test results between TGA x calcination techniques.

Through the Grubbs test it was possible to verify that the TGA results presented precision and accuracy, as well as the calcination results. Furthermore, it can be observed that there is no presence of outliers.

FINAL REMARKS

It was possible to observe that the calcination technique achieved a higher uncertainty value compared to TGA, which was already expected as it has more steps during the execution of the analysis (use of analytical balance, microwave oven, desiccators and handling) that may influence. The TGA technique is automated, having an internal scale system, which results in a reduction in analytical errors. Thus, with the help of statistical tools, after determining the analytical uncertainty of the techniques and correlating the data obtained in this study, it is concluded that the TGA technique presents precision and accuracy as much as the absolute calcination technique, being able to correlate the proximity to the real value of the samples with their dispersion in a series of measurements.

Furthermore, considering the number of daily analyses possible through calcination (2 analyses) compared to TGA (11 analyses), a 175% increase in productivity was obtained, as well as an improvement in the safety of the analysts involved in the execution of the activities, since the calcination technique required exposure to high temperatures, around 800 °C, and for each sample, this exposure was repeated 4 times. While using the TGA technique, the existing risk is considered low, where there is also heating to high temperatures, but the analyst does not have contact with the heated region.

Thus, through this study, it was possible to understand the process improvements resulting in increased safety, health and environment (HSE), as well as the importance of using statistical calculations as problem solutions, as each tool has its own importance, however the use of them in combination associated with correct interpretation is fundamental, thus allowing opportunities for growth and development.

Conflicts of interest

The authors declare to have no conflicts of interest.

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