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Determination of carbon black content in HDPE – purge gas buoyancy effect

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Abstract

Oxygen and air have been interchangeably used as the purge gas in the determination of carbon black content in polyethylene. This study shows that accuracy of the carbon black filler content is significantly affected by the choice of oxygen as the purge gas used to oxidise the carbon filler. It is believed that the difference in the density of the oxygen give rise to the buoyancy effect. Air, having closer density to the initial nitrogen purge gas in the analysis, is the better choice for purge gas for accuracy of analysis and reproducibility of results. © 1997 Elsevier Science B.V.

Keywords: Buoyancy; Carbon; Content; Gas; Purge

1. Introduction

Carbon black is one of the most common fillers used in rubber and thermoplastic materials. In rubber, it serves as an efficient reinforcement agent that control the key properties of the compound while in polyolefin materials, it acts as an effective thermal and ultraviolet stabiliser [1–4]. Thermogravimetric analysis technique is a common method to measure the carbon black content in these materials [5,6]. Maurer has reported on the factors that influence precision and accuracy of the analysis by this technique, giving due considerations to the experimental conditions [7].

The basic experimental procedure is quite simple; the sample is heated up at a constant rate in an atmosphere of nitrogen. After the polymer has been completely burnt off (e.g. at 550°C), oxygen or air is introduced. Subsequent weight loss will be exclusively due to the oxidation of the carbon black in the system.

Oxygen and air have been interchangeably used as the oxidising gas for carbon black determination and the applications have been reported in numerous established literature and technical reports [8–11]. It appears that the type of the purging gas is immaterial to the result of the analysis. In this study, we wish to show that the choice of gas, either air or oxygen do have significant effect on the accuracy of the carbon black quantification. It is suspected that at elevated temperature, the buoyancy effect due to the difference in density between the initial nitrogen purge gas and the subsequent oxygen introduced to the system, plays a significant role. This effect is particularly enhanced when the quantity of carbon black to be determined is very small.

In the case of carbon black incorporated in the high density polyethylene (HDPE) pipe, the stipulated content requirement in the standard is only 2.25% ± 0.25 [12]. Any small changes that affect

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the weighing of the sample will be reflected in the subsequent analysis of the level of carbon black. It is also believed that this buoyancy effect is further aggravated by the design of the thermogravimetric analyser, that is, one with a vertical weighing/furnace system which is susceptible to the influence of the purge gas. Since the analysis forms the basis for decision on acceptance or rejection of the HDPE resins for pipe water application, this variation has to be resolved technically during the thermogravimetric analysis for the filler content.

2. Experimental

Three HDPE resin samples, namely, Sample A, B and C were analysed for their carbon black content. The analysis were performed using the Mettler TG50 thermobalance utilising the M3 microbalance with a vertical weighing/furnace system. The sample was placed in an alumina crucible (with lid) and was scanned from 30 to 550°C at a heating rate of 20°C/min, in an atmosphere of nitrogen. At 550°C, oxygen was introduced and the heating continues till 800°C. The analysis was repeated using air instead of oxygen as the oxidising gas. The carbon black level was calculated using STEP analysis available in the Mettler *Graphware* data evaluation software. Blank run was performed prior to the analysis using identical test parameters.

3. Results and discussion

A typical curve for carbon black content analysis is shown in Fig. 1. The hump at 550°C is due to the introduction of the second gas and is presumed to have been caused by the difference in the density of the gases. It was noted that the scan in oxygen results in bigger hump than the scan in air. Several computing techniques were applied in the analysis of the carbon black to show the effect of oxygen as compared to air as the oxidising gas.

Method I

The step analysis was performed from 530°C to say 700°C and the weight loss during this stage was taken to be the carbon black level. Table 1 shows the result of the analysis in oxygen (Column 2) and in air (Column 3). It can be observed clearly that the analysis in the oxygen gives a significantly higher values than those carried out in air.

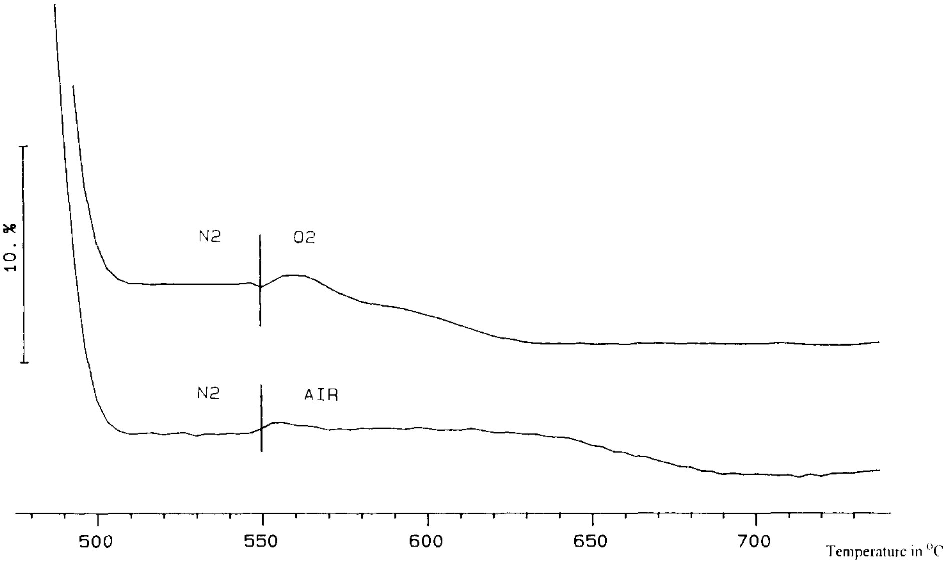

Fig. 1. Typical thermogravimetric curves for carbon black content analysis in oxygen (top) and in air (bottom). Note the bigger hump for the analysis in oxygen.

Table 1
Carbon black content in HDPE analysed under various conditions

Sample	Carbon black content (%)				
	OXY	AIR	N_2 only	BCORR	TGA850
A1	2.94	2.14	2.09	2.08	2.01
A2	3.01	2.12	2.10	2.08	2.00
A3	2.55	2.31	1.97	1.97	2.00
Mean	2.83	2.14	2.05	2.05	2.00
SD	0.25	0.13	0.07	0.06	0.01
B1	2.96	2.00	2.13	2.12	2.04
B2	2.68	2.12	2.24	2.24	2.02
B3	2.79	2.04	1.75	1.74	1.99
Mean	2.81	2.05	2.04	2.03	2.02
SD	0.14	0.06	0.26	0.26	0.03
C1	2.51	2.00	2.10	2.09	2.08
C2	3.29	2.13	2.25	2.22	2.09
C3	2.63	2.02	1.89	1.89	2.07
Mean	2.81	2.05	2.08	2.07	2.08
SD	0.42	0.07	0.18	0.17	0.01

Note: OXY – run in oxygen; AIR – run in air; N_2 – run in air but step evaluation in nitrogen region only; BCORR – run in oxygen, after buoyancy correction; TGA850 – run using Mettler TGA850 c/w horizontal furnace.

Table 2
Carbon black content analysis using calibrated samples

Sample	Carbon black content (%)				
	OXY	AIR	N_2 only	BCORR	INPUT
C1OXY	2.09		1.75	1.72	1.87
C2OXY	2.97		2.36	2.35	2.45
C3OXY	3.51		2.73	2.72	2.86
C1AIR		2.21			2.36
C2AIR		1.82			1.96
C3AIR		2.25			2.36

Note: *Cn*OXY – calibrated samples analysed in oxygen; *Cn*AIR – calibrated samples analysed in air; INPUT – actual percentage carbon black content input into the samples.

Method II

To negate the effect of oxygen for the samples analysed in the oxygen purge gas, the step analysis was performed from 50 to 530°C and the residue at 530°C was taken to be carbon black. This is only acceptable if no other mineral filler or ash is known to be present in the samples. The result is shown in Column 4 of Table 1. It may be seen that if analysis is performed before the introduction of oxygen, then the carbon black content results tend to be closer to the previous values as analysed in air.

Method III

When the step analysis was performed for the samples in oxygen, it was observed that the final mass of the microbalance (*ResiC* in Fig. 1) was not zero but gave substantial negative results. This indicates a buoyancy (lifting up) effect due to the oxygen purge gas. If the carbon black content is recalculated by considering the buoyancy effect, that is, by subtracting the *ResiC* values, then the carbon black content results (Column 5, Table 1) tend to agree with those performed in air (Column 3) or those calculated in the nitrogen region (Column 4). This clearly shows that the buoyancy effect of the oxygen is the cause of the significant increase in the result of the carbon black content analysis.

To validate the results of the analysis, some 'calibrated' samples of carbon black in HDPE were prepared. A known amount of carbon black filler was introduced into HDPE resin granules and the samples were subjected to the same analyses as above, that is, in oxygen and air. The results are shown in Table 2. It was observed that, as expected, the analysis in oxygen gives significantly higher results. For the analysis performed in air or corrected versions of analysis in oxygen, the analysed carbon black content values are marginally lower than the actual input. This is perfectly acceptable since trace losses of the carbon powder is inevitable. Basically the analysed results are in agreement with the actual amount of carbon black put into the samples. Thus the accuracy of the thermogravimetric analyser and the computing technique can be validated and may support the above argument on the buoyancy effect of oxygen.

For additional cross-checking, the Samples A, B and C were also analysed using the latest Mettler TGA850 thermogravimetric module with a horizontal furnace; a better design to minimise the disturbing influence of the purge gas. The results of the analysis as shown in Column 6 of Table 1 (run in air), agree with the previous run (in air) using the TG50 system. These results further show that the inflated values of the carbon black initially acquired using the TG50 system are due to the buoyancy effect of the oxygen purge gas. It is believed that this effect is prominent for analysis performed by the TG50 analyser due to the vertical design of the balance/furnace system.

Overall it may be concluded that for greater accuracy of carbon black determination, using thermogravimetric analyser, air (instead of oxygen) is the better choice for purge gas. It is also noted that air gives better reproducibility of results when compared to oxygen.

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