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EXPERIMENTS WITH A NEW SYMMETRICAL THERMO MICROBALANCE TO 1500°C

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ABSTRACT

Buoyancy effects are the main drawback to the precise evaluation of thermogravimetric experiments. A recently introduced thermo microbalance, designed symmetrically with respect to the arrangement of the balance, furnaces and gas flow system, eliminates buoyancy effects at the TG signal. Very small mass changes (resolution 0.1 µg), can be determined over a wide range of temperatures, using sample weights in the range from micrograms up to 1 g. The long term stability is very high with typical TG drift of 0.1 µg/h during isothermal work at high temperatures and below 3 µg on heating to the maximum temperature.

INTRODUCTION

Thermogravimetry is a very useful means for precise compositional analysis in research and quality control applications. However, with most of the available thermogravimetric instruments, the results are superimposed with buoyancy effects. Due to the reduction in density of the atmosphere inside the furnace during heating, an apparent weight increase is displayed, also depending on the volume of sample and sample holder system inside the hot zone of the furnace.

This buoyancy effect can only be determined empirically as the temperature gradient in a furnace and the effective volume of the sample carrier are not constant during a thermogravimetric experiment. Only in a totally symmetric design of the balance, heating system and gas flow path can an elimination of the buoyancy effect be expected.

In the thermo microbalance, NETZSCH model TG 439, total symmetry is used as a design principle (1). Below an electronic microbalance two identical hang-downs are arranged inside two water cooled furnaces with maximum temperature of 1000°C or 1500°C. Evacuation and introduction of inert and purge gas are also done symmetrically on both the sample and the reference side. The volume of gas flow is controlled and maintained exactly by a stepwise electronic push botton control. The change between two gases can be programmed and automatically carried out by the microprocessor temperature programmer via computer control.

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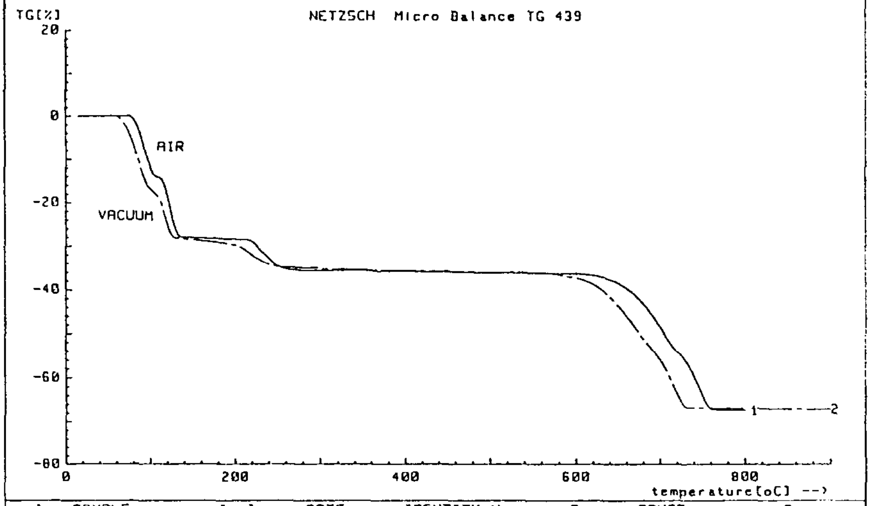
RESULTS AND DISCUSSION

The most effective demonstration of the absence of a buoyancy effect is the comparison between experiments in vacuum and in any gas atmosphere. The well-kown dehydration and decomposition of $CuSO_4 \cdot 5H_2O$ show the same TG plateaus in air atmosphere (1013 mbar) and in vacuum (10 mbar). The shift of the reaction temperatures to lower values in vacuum is a known effect for $CuSO_4 \cdot 5H_2O$.



#	SAMPLE	[mg]	DATE	IDENTITY No.	Seg.	RANGE:	Corr.
1	CuSO4*5H2O	.7	29.10.1986	003/TG/P-DYN	1:	20/25.00/ 850	--
2	CuSO4*5H2O	.9	3 Nov 1986	001/TG/VACC	1:	20/25.00/ 950	--

Fig. 1 Dehydration and decomposition of $CuSO_4 \cdot 5H_2O$ in air and in vacuum

The symmetric distribution of the purge gas and also the inert gas to protect the balance is shown by experiments with gas change. The most typical applications requiring gas change during a test are compositional analysis of rubbers and proximate analysis of coals. Fig. 2 shows a result for natural rubber with filler content. The TG curve resolves very clear by the amount of plasticizer, polymer, soot and ash. The automatic gas change at 600°C from nitrogen to oxygen occurs without any disturbance appearing on the TG curve. The oxidation of the residual carbon and the soot filler starts immediately after the gas change. The use of trace amounts of materials offers the application of the thermo microbalance in the field of forensic science and crime detection.

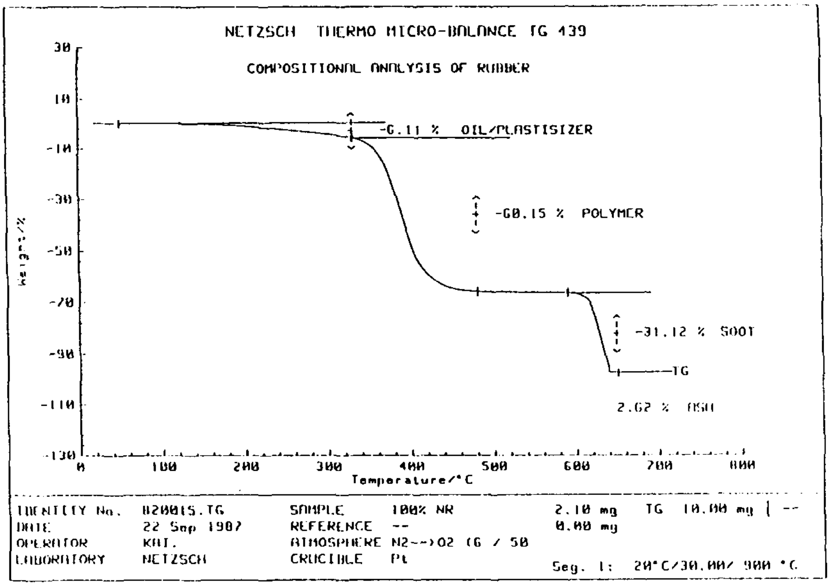


Fig. 2 Compositional analysis of natural rubber with filler

The proximate analysis of coal by themogravimetry is a fast and reliable means to determine the content of moisture, volatiles, fixed carbon and ash in one run (Fig. 3). The stability of the TG-curve over a broad temperature range of nearly 1000°C leads to an increased resolution of single components in often very heterogeneous coals.

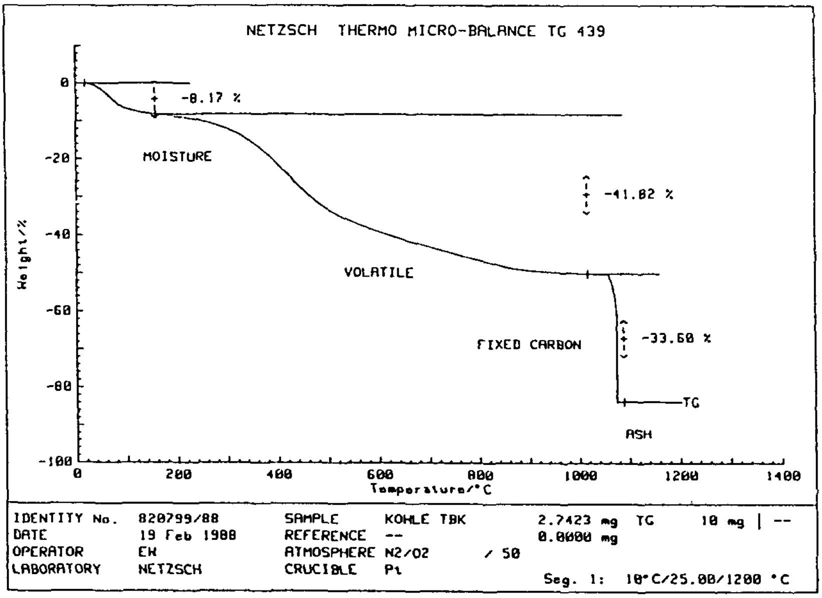


Fig. 3 Proximate analysis of coal with automatic gas change at 1040°C

The analysis yields 8.17% moisture, 41.82% volatiles, 33.6% fixed carbon and 16.41% ash.

The decomposition mass loss of a phenol-formaldehyde resin with 60.5% glass and talc filler was studied in the temperature range 200 to 1000°C. Four different degrees of cure were prepared at the curing temperatures of 250, 225, 200 and 175°C corresponding to degree of cure values of 100, 96.4, 90.7, and 73.8% (Henderson a.o. /2/). It is clear from the comparison of the 4 TG-curves that the degree of cure strongly influences the decomposition kinetics of the resin.

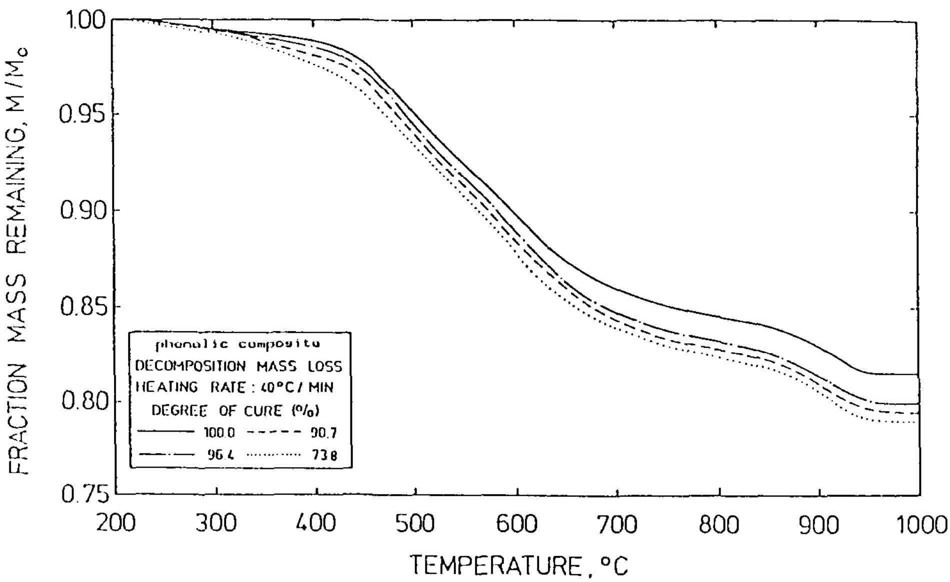


Fig. 4 Decomposition mass loss of phenol-formaldehyde resin for different degrees of cure.

Increasing the degree of cure from 73.8% to 100%, the decomposition mass loss decreases by 2.6%, indicating the higher material performance by higher degrees of cross linking. Decreasing the degree of cure shifts the decomposition mass loss curves to lower temperatures. The thermo microbalance used in this study consistently detected differences in the final mass loss as small as 0.03% at 1000°C during the decomposition cycle.

This excellent resolution, which is a direct result of the symmetrical construction, makes it ideal for studies of the influence of degree and also rate of cure on the thermal stability of this type of resin.

CONCLUSION

The elimination of the buoyancy effect of the TG signal by the described symmetrical construction of the thermo microbalance TG 439 simplifies thermogravimetry. No corrections are necessary for precise evaluations during compositional analysis and the influence of atmosphere (kind of gas, flow rate, gas change) is eliminated from changing the balance signal. Besides the high resolution for very small mass changes, reliable information for reaction kinetics are achieved with this instrument.

REFERENCES

/1/ E. Kaisersberger a.o., ASTM STP 997 (1988), page 160-169

/2/ J. B. Henderson and W.-D. Emmerich, 16th NATAS Conference 1987 page 209-214