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Applications of thermal analysis in the rubber industry [1]

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Abstract

Thermal analysis is used increasingly in measurements of elastomers for quality control of rubber mixtures and finished parts.

This paper describes examples of applications taken from the rubber industry using thermogravimetry (TG) and heat-flux differential scanning calorimetry (DSC).

INTRODUCTION

Thermal analysis is becoming an increasingly important technique, particularly in the rubber industry. Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements are generally quicker and more reliable than other traditional methods, especially in the area of compositional analysis.

These techniques (DSC, TG) are simple and ideal for routine analysis and therefore find many applications within the rubber industry for material characterization, research and development, as well as for quality control/assurance.

In this paper, the following examples from the rubber industry [1] were investigated at the Applications Laboratory of NETZSCH-Gerätebau, GmbH, using a TG 209 thermo-microbalance and a DSC 200 heat-flux differential scanning calorimeter [2].

(i) Quantitative analysis of a cured natural rubber/ethylene propylene diene monomer (NR/EPDM) blend.

(ii) Rapid quality control of a cured natural rubber (NR) compound.

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(iii) Comparison of two carbon black types, N 234 and N 660.

(iv) Characterization of a cured natural rubber/styrene butadiene rubber (NR/SBR)blend.

(v) Influence of different plasticizers on a cured acrylonitrile butadiene rubber (NBR) compound.

(vi) Influence of different antioxidants on a cured natural rubber/butadiene rubber (NR/BR) blend.

EXPERIMENTAL

Examples (i)–(iii) were investigated using the Netzsch TG 209 thermomicrobalance. The TG 209 has a bottom-mounted vacuum-tight microbalance with a resolution of 1 μg. The micro-furnace and sample holder are housed above the weighing chamber. The microfurance is water-cooled and constructed of stainless steel operating at heating rates from 0.1 to 80 K min^{-1} over the temperature range 20–1000°C. Manual or automatic gas-switching in the sample chamber creates accurate atmosphere control.

Examples (iv)–(vi) were investigated with the DSC 200 heat-flux differential scanning calorimeter. The DSC 200 is of the heat-flux type with a corrosion-resistant cell and high baseline stability. Easy sub-ambient operation optimizes glass transition determination on rubbers, and the low time constant of the DSC 200 provides an excellent separation of overlapping effects, e.g. in a rubber blend.

MATERIALS

The following materials were investigated with the sample weights shown.

(i) Cured NR compound (6.72 mg).

(ii) Cured NR/EPDM blend (4.53 mg).

(iii) Carbon black types N234 (2.40 mg) and N660 (2.82 mg).

(iv) Cured NR/SBR blend (21.12 mg).

(v) Cured NBR compound with different types of plasticizer at the same level (28 parts per hundred parts rubber): 1, etherthioether (25.67 mg); 2, di-2-ethylhexylphthalate (DOP) (24.39 mg); 3, alkylsolfoneacidester (ASE) of phenol (25.15 mg).

(vi) Cured NR/BR blend (80:20) with different types and amounts of antioxidant: 1, without antioxidant (10.05 mg); 2, with 12 phr 2,2,4-trimethyl-1,2-di-hydroquinoline (TMQ) (11.39 mg); 3, with 1.2 phr TMQ and 2 phr *N*-phenyl-*N*′-(1.3-dimethylbutyl)-*p*-phenylene diamine (6PPD) (10.42 mg).

PROCEDURE

(i) The NR/EPDM compound was investigated in a platinum crucible in nitrogen atmosphere (10 ml min^{-1}) at a heating rate of 10 K min^{-1}. At 600°C, the gas was changed to air (10 ml min^{-1}).

(ii) The NR compound was investigated in a platinum crucible in nitrogen atmosphere (10 ml min^{-1}) at a heating rate of 80 K min^{-1}. At 600°C, the nitrogen was replaced with oxygen (10 ml min^{-1}) up to the final temperature of 950°C.

(iii) The two carbon black types were measured in platinum crucibles in nitrogen atmosphere (10 ml min^{-1}) at heating rates of 30 K min^{-1}. At 600°C, the gas was changed to air (10 ml min^{-1}).

(iv) The NR/SBR blend was investigated in a closed 5 mm aluminium pan in a helium atmosphere (50 ml min^{-1}). The heating and cooling rates were 20 K min^{-1}.

(v) Three crosslinked NBR samples with different plasticizers were investigated in a closed 5 mm aluminium crucible at heating and cooling rates of 20 K min^{-1}.

(vi) Three crosslinked NR/BR samples were investigated in closed 5 mm aluminium crucibles with 3 holes in each lid in helium atmosphere. The heating and cooling rates in each case were 20 K min^{-1}. At 150°C, in the second heating, the gas was changed to oxygen (50 ml min^{-1}) to investigate the oxidation behaviour.

RESULTS AND DISCUSSION

(i) Figure 1 illustrates the 4-step decomposition of NR/EPDM in

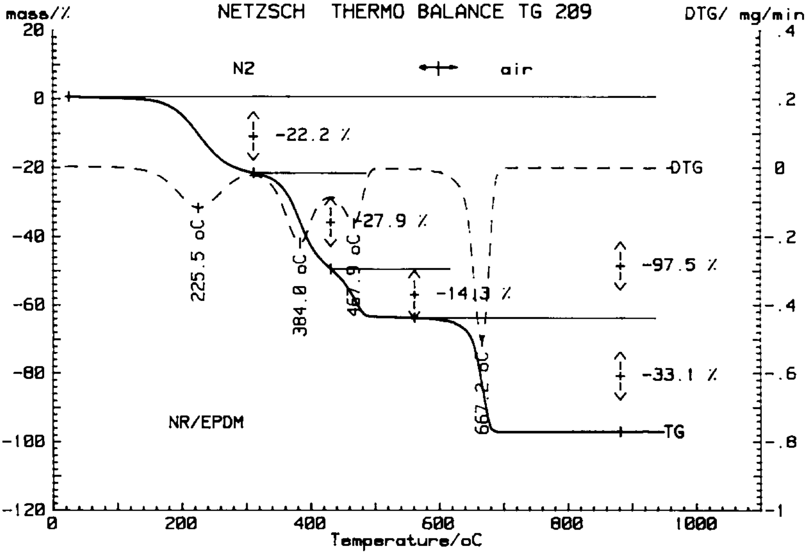

Fig. 1. TG and DTG of an NR/EPDM blend.

nitrogen and then air, in the TG and DTG curves. The 3-stage decomposition in nitrogen begins with a 22.2% mass loss with a DTG peak at 225.5°C corresponding to the emission of volatile plasticizers and residues of the vulcanization system and incorporated antioxidants. The second mass loss of 27.9% with a DTG peak of 384.0°C, corresponds to the decomposition of natural rubber; the third mass loss of 14.3% with DTG peak at 467.9°C is characteristic of EPDM.

Natural rubber and EPDM are clearly separated quantitatively by TG: NR decomposes earlier due to its higher unsaturation. The fourth mass loss of 33.1% (DTG peak 667.2°C) corresponds to the combustion of carbon black in air following the gas change to air at 600°C. The residue of 2.5% consists of an ash content of mainly zinc oxide (activator).

(ii) Figure 2 shows the TG and DTG curves for the decomposition of the NR sample in nitrogen at 80 K $\min^{-1}$. The first mass loss corresponds to the evolution of plasticizers and residues of the vulcanization system and any antioxidants. The next mass loss is due to the decomposition of natural rubber with an onset of 394.3°C. The DTG peak at 420.9°C is characteristic of NR at this high heating rate of 80 K $\min^{-1}$. The third step starts at over 600°C and corresponds to the gas change to oxygen at 600°C. The oxidizing atmosphere leads to the decomposition of the carbon black incorporated as a filler. The DTG peak is at around 779°C and the residue comprises mainly zinc oxide (activator system).

This test is an ideal first check for incoming raw material. In order to obtain more precise mass loss values, a lower heating rate or a larger sample area would lead to higher accuracy, thus avoiding any overlapping decomposition effects.

(iii) Figure 3(a) shows the decomposition behaviour of this highly active carbon black, type N 234. Up to 600°C in nitrogen, there is a mass loss of 2.1% which is due to moisture and organic substances. The combustion starts at 705°C (extrapolated onset) with a DTG peak at 761°C.

Figure 3(b) shows the decomposition of N 660. This carbon black has a medium activity and shows no mass loss in nitrogen up to 600°C. When the gas is changed to air, the total combustion starts at the higher extrapolated onset temperature of 720°C. The DTG peak is higher (791°C) and the combustion is completed at a higher temperature than with N 234.

The TG 209 is a suitable apparatus for investigating the activity of different types of carbon black. It should be mentioned that this is not possible in rubber mixtures.

(iv) Figure 4 clearly shows two distinct glass transition temperatures corresponding to the two separate components, NR and SBR, in this rubber blend. A glass transition T_g of −61.8°C (midpoint) can be seen, corresponding to the natural rubber component, and a further T_g can be evaluated at −50.7°C (midpoint) corresponding to the SBR content.

These two clear glass transitions characterize the material into two

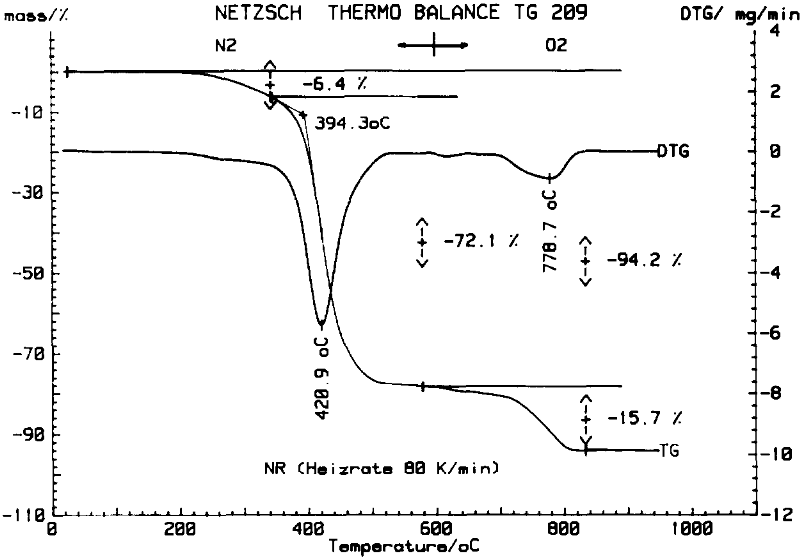

Fig. 2. TG and DTG of an NR compound.

components NR and SBR by their characteristic T_g values. The Δc_p value also gives an indication of the proportions of the two components. The absolute T_g temperatues give an indication of the brittleness temperature corresponding to the low-temperature flexibility.

(v) Figure 5 shows the second heating of 3 cured NBR samples, each of which contain a different plasticizer, but at the same concentration. Curve 1 (NBR with etherthioether) shows a glass transition temperature at −47.2°C (midpoint); curve 2 has a T_g at −40.9°C (NBR with DOP); and curve 3 has a T_g at −39.7°C (NBR with ASE). The addition of different plasticizers clearly lowers the glass transition of NBR as illustrated by the DSC curves. The increased chain spacing between polymer chains minimizes the interchain forces and reduces the glass transition temperature. This information gives quantitative data regarding the low-temperature brittleness of the rubber which may be lowered by the addition of different plasticizers. It is clear from the DSC plot that etherthioether is the most effective plasticizer.

(vi) Figure 6 shows the DSC curves for the different antioxidant systems used in the 3 NB/BR compounds. Curve 1 corresponds to NR/BR containing no antioxidant; a broad first exothermal peak starts at 190°C, with an enthalpy value of 296 J g^{-1}. Curve 2 corresponds to NR/BR compound with antioxidant TMQ added at 1.2 phr; an exothermal peak starts at around 200°C, with an enthalpy of 262 J g^{-1}. Curve 3 is for NR/BR with the same level of TMQ as in sample 2 with an additional 2.0 phr of 6PPD; a first exothermal peak starts at around 210°C, with an enthalpy of 247 J g^{-1}.

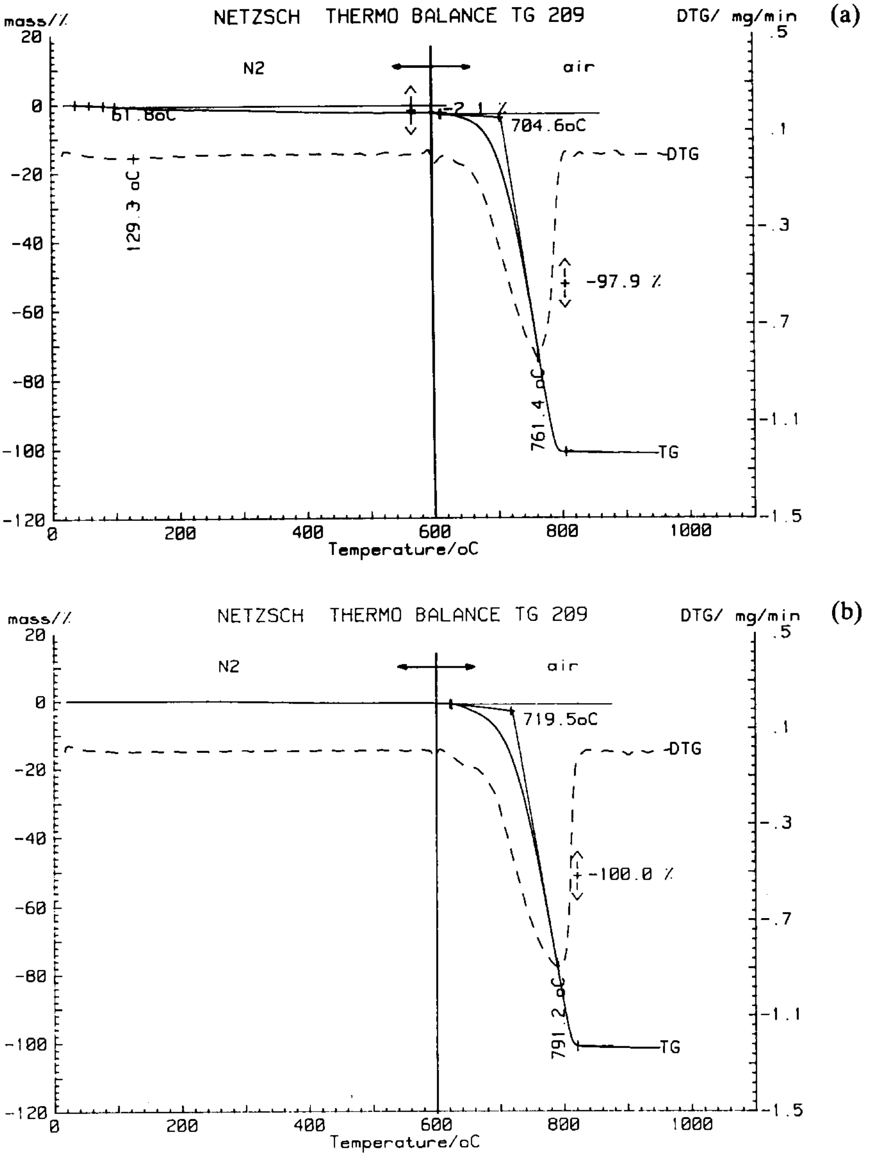

Fig. 3. TG and DTG of (a) carbon black N 234, and (b) carbon black N 660.

The first exothermal peak in each curve corresponds to the oxidation of the NR/BR; curve 1 with no antioxidant shows the highest enthalpy and the fastest oxidation rate with the lowest onset temperature (start of oxidation) of about 190°C.

Curve 2 (NBR with TMQ) has a higher onset temperature, lower enthalpy and lower oxidation rate than curve 1. Curve 3 has a combination

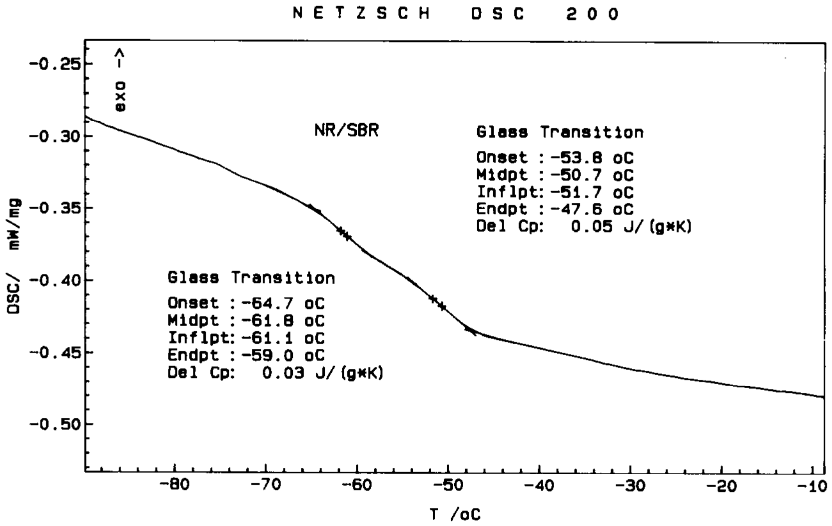

Fig. 4. DSC of an NR/SBR blend.

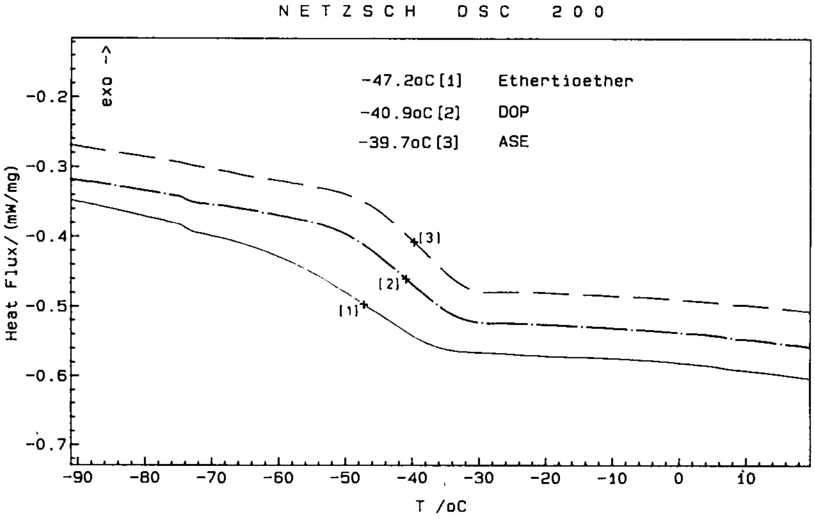

Fig. 5. DSC of NBR compound with different plasticizers.

antioxidant system of TMQ and 6PPD and gives the highest onset temperature (start of oxidation) of about 210°C. The oxidation rate and reaction magnitude are clearly lower than for the other two formulations; this is due to a synergistic effect of the two antioxidants.

Using the DSC 200, the effectiveness of the antioxidation system and the synergistic effects can be evaluated.

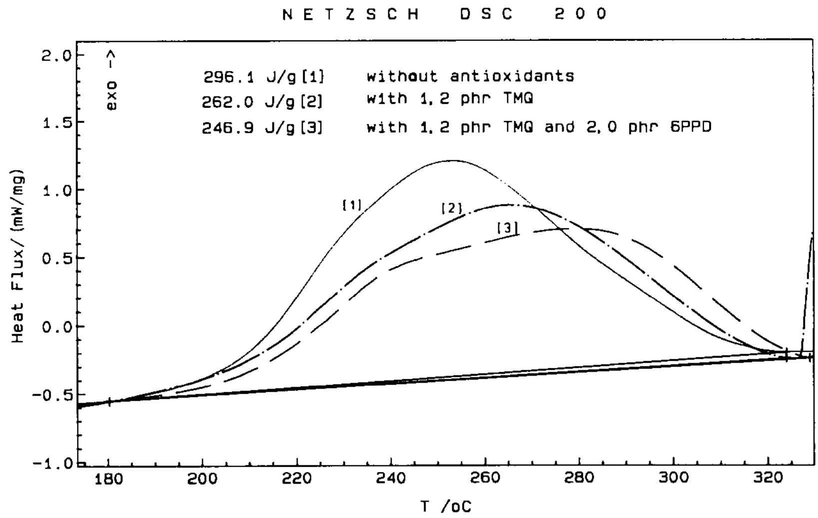

Fig. 6. DSC of an NR/BR blend with different antioxidants (oxidation behaviour).

CONCLUSIONS

From the evidence given in this paper, it is clear that practical material problems within the rubber industry may be solved by thermoanalytical techniques such as DSC and TG.

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