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Study of recyclable polymer automobile undercoatings containing PVC using TG/FTIR

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Abstract

A new type of TG/FTIR coupling system is introduced. With results from a measurement made on $CuSO_4{\cdot}5H_2O$ it is shown that, even with low purge gas rates, retention times between 15 and 18 s are achieved. Measurements on two undercoating materials containing PVC and a raw PVC sample demonstrate several of the characterization options offered by a thermobalance coupled with an FTIR gas measuring system. It is shown that this method can be an important aid in the development of environmentally friendly products.

Keywords: TG/FTIR; PVC; Environment; HCl emission; Recycling

1. Introduction

The reutilization and disposal of consumer and capital goods is an important contribution to environmental protection and is strongly supported through legal measures in most industrialized countries. The automobile industry in Germany has started a pilot project for the reutilization of old cars [1,2]. Through planned bills regarding the recycling/reutilization of used cars, the industry is directly confronted with the problem of waste management. Up to now, the conventional reprocessing of automobile scrap has essentially consisted of shredding the parts and metallurgically recycling the metal scrap by melting it in a blast furnace. With the incineration of the plastic, rubber and coated parts which also remain, poisonous and environmentally damaging gaseous compounds

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can develop. Appropriate filters are used or other processing measures taken in an attempt to prevent their emission. Therefore, it must first be known which compounds can occur, in order to develop suitable retention systems.

Thermal analysis, in particular, is a fast, universal and efficient method for the study of thermal processes under differing environmental conditions (reducing, inert, oxidizing atmospheres, high and low heating rates) [3,4]. If the gaseous reaction products are determined qualitatively or, better still, quantitatively as well, the simulation of incineration processes provides considerably more information [5–10].

By coupling a thermobalance with an FTIR spectrometer, the gaseous decomposition products can be identified and assigned to the respective temperatures and TG steps. In this paper, the advantages of the TG/FTIR coupling for the development of environmentally friendly products is demonstrated with two different undercoating materials containing PVC.

2. Apparatus

The tests were carried out using a Netzsch Thermo-Microbalance TG 209, coupled with a Bruker FTIR Spectrometer IFS28 [11]. The basic design is shown in Fig. 1.

The adapter on the balance, the flexible gas transfer line and the gas measuring cell of the FTIR can be heated up to 250°C. This prevents unwanted condensation and guarantees the most quantitative transfer possible of the gaseous decomposition products. The small active volumes of the TG microfurnace (2.4 ml), the transfer line (4.5 ml) and the gas measuring cell (8.7 ml) allow the use of low flow rates for the purge gas (10–20 ml min^{-1}), whereby the dilution effect of the evolved gases is minimized. Thus, high detec-

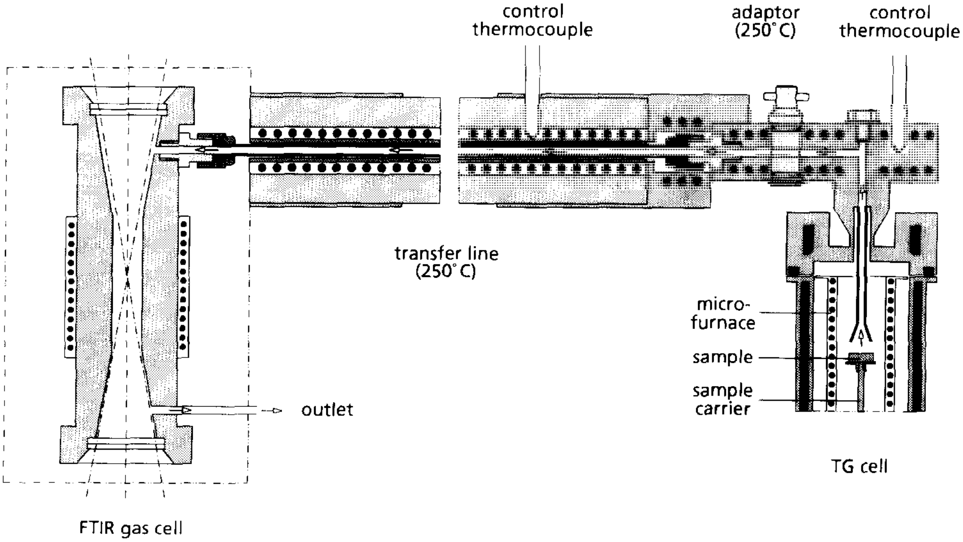

Fig. 1. TG/FTIR coupling system.

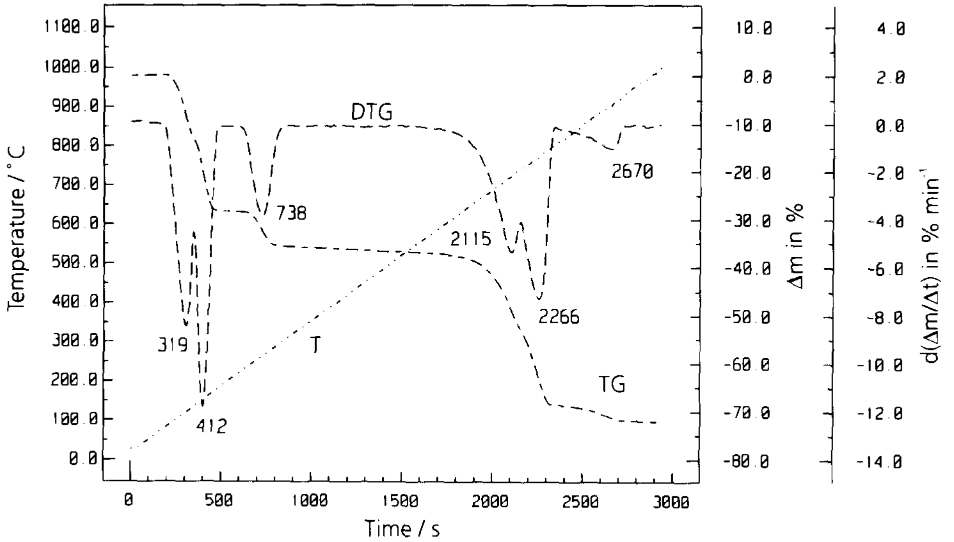

Fig. 2. TG and DTG curves for $CuSO_4{\cdot}5H_2O$.

tion sensitivity and, at the same time, good separation of the gases evolved during individual and overlapping TG steps are possible.

Figs. 2 and 3 depict the TG, DTG and Gram-Schmidt curve for a measurement on $CuSO_4{\cdot}5H_2O$. The measurement was carried out at a heating rate of 10 K min^{-1} in a dynamic N_2 atmosphere (15 ml min^{-1}) and 16.7 mg sample weight. By comparison of the DTG peaks with the maxima of the Gram-Schmidt curve, for example, retention times of

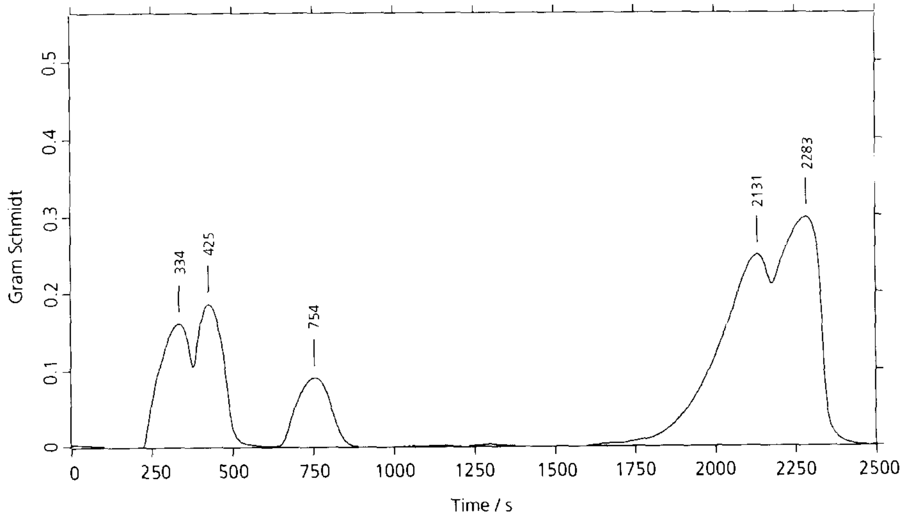

Fig. 3. Gram-Schmidt curve for $CuSO_4{\cdot}5H_2O$.

approximately 15–18 s can be established. The FTIR spectra were recorded in the wave number range 5000–700 cm^{-1}, with a spectral resolution of 4 cm^{-1} and 10 spectra co-added.

3. Experimental

The target of the investigations was the characterization of two different undercoating materials containing PVC, for the emission of HCl gas which develops with the incineration of the PVC component. Pure PVC was also measured as a reference sample. The samples were dried at 50°C for 30 min prior to the actual heating in order to eliminate surface moisture. They were then heated to 900°C at a heating rate of 30 K min^{-1}. Synthetic air at a flow rate of 15 ml min^{-1} was used as the reaction gas. Care was taken that the sample weights were comparable (10.4 ± 0.3 mg).

4. Results

Fig. 4 shows a comparison of the TG curves for the three measurements. Clear differences can be seen between the two undercoating materials. Rapid decomposition of the PVC begins abruptly at approximately 300°C (extrapolated onset), whereby the HCl gas is released. This decomposition starts at a lower temperature with the undercoating materials.

Fig. 5 is a three-dimensional representation of FTIR spectra in the wave number range 3050–2500 cm^{-1} during this TG step. The rotation lines of the HCl are clearly resolved in the wave number range 2850–2500 cm^{-1}. If a suitable rotation line is integrated and the intensity plotted as a function of time (or temperature), direct conclusions can be drawn

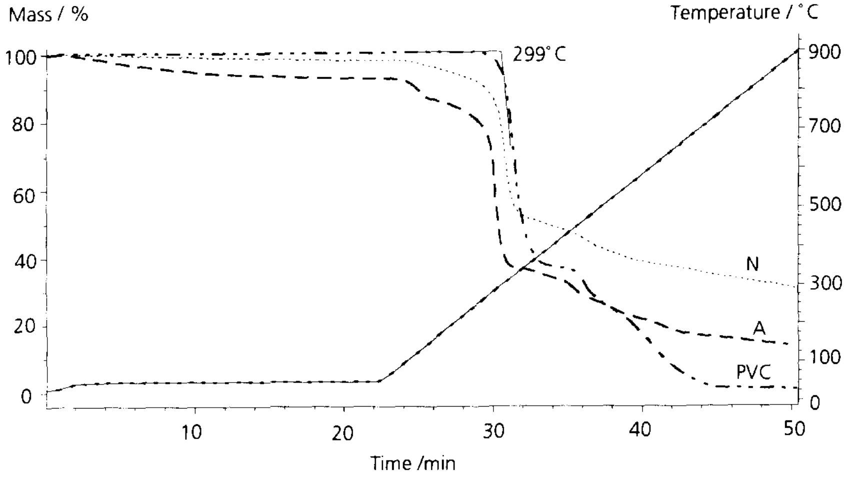

Fig. 4. TG curves for PVC and undercoatings A and N.

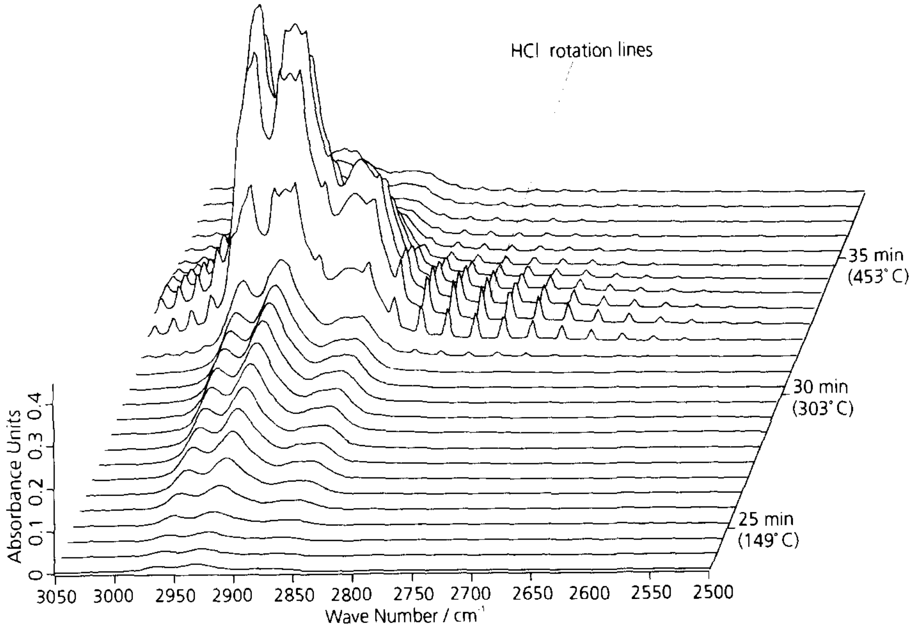

Fig. 5. HCl rotation lines during the PVC decomposition.

about the HCl emission (see Fig. 6). It can be clearly seen that undercoating N emits considerably less HCl than undercoating A. With the assumption that the Lambert-Beers Law is valid for these measurements, a semi-quantitative characterization can be carried out by integrating the peak areas under the traces. The results are given in Table 1.

It can be concluded from Table 1 that through the specific development of formula-

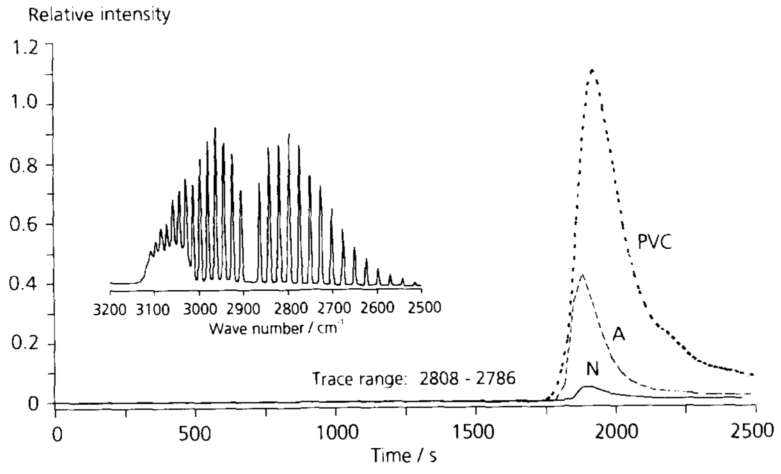

Fig. 6. HCl traces from undercoatings A, N and PVC.

Table 1
Integration of the HCl Traces

Sample	Area/s cm^{-1}	Area/sample weight/s cm^{-1} g^{-1}	Factor
Undercoating A	66.9	6.32	9
Undercoating N	7.0	0.68	1
PVC	265.7	25.90	38

tions, it would be possible to reduce the HCl emission from the new undercoating material by a factor of 9.

5. Conclusion

The coupling of thermoanalytical instruments with gas analysis methods such as FTIR spectrometers offers additional characterization options. The example of the evolution of HCl in undercoating materials containing PVC has shown the efficiency of this method, and a determination of the relative HCl emission of the different samples has been carried out with the aid of the FTIR signal.

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