

Thermoanalytical investigations for the recycling of PVC

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Abstract

Within a research project for the recycling of soft poly(vinylchloride) (PVC), analytical work has to be done. On the one hand, the raw material for the process needs to be checked for PVC content and for additional polymers and on the other hand, the recycled PVC needs to be characterized. In both cases, thermoanalytical methods especially coupled methods with gas analysis systems, can deliver suitable information for this characterization. The different investigations are presented, and evaluated regarding their informative capability. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Regarding its output (approximately 1.4 Mt in 1995 in Germany), poly(vinylchloride) (PVC) is the second important plastic in western Europe. Its main field of application is in the area of building materials such as pipes, windows and floor coverings [1]. The ecological and political discussion in Germany concerning the chlorine content of PVC was proven by the Enquete commission. As a result, no doubts were raised with intended use and the advancement of recycling activities was recommended.

Due to the dehydrochlorination of PVC during thermal treatment, many of the common recycling procedures (e.g. regranulating of the material [2]) end

in a ‘down cycling’ of the material. A new development within this area, which avoids the disadvantage mentioned, is the recycling by means of selective dissolving of the desired component. Accompanying to the development of the technical process, analytic techniques for the control of the raw material as well as the evaluation of the recycling product must be developed.

Here thermoanalytic investigations can supply very valuable results as preliminary investigations have shown [3].

2. Experimental

The investigations were carried out using a Netzsch Simultaneous Thermal Analyzer STA 429 coupled with a Balzers quadrupole mass spectrometer QMG 420 using a two-stage orifice system as interface. For the calibration of the system and the degradation

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studies on PVC we used a standard PVC from the BASF company. The raw material for the recycling process was delivered from the Fraunhofer Institut für Verfahrenstechnik und Verpackung, who is our partner in the research project and responsible for the recycling process. The investigations were carried out under dynamic atmospheres (nitrogen or synthetic air) using a flow rate of 120 ml/min. The heating rate applied was 10 K/min from ambient temperature to 800°C. The pressure within the mass spectrometer was adjusted to 6×10^{-3} Pa and kept constant during the measurement. The mass spectrometric investigations were carried out in either the scan mode (mass range 10–150 amu) or the MID mode with pre-selected mass per charge values.

3. Results and discussion

For the characterization of the raw material and the determination of the PVC content, it is necessary to know the thermal behavior of PVC itself. For this reason, a standard PVC was investigated under synthetic air as well as in nitrogen atmosphere. A weighted sample of about 25 mg was treated from ambient temperature up to 800°C using a heating rate of 10 K/min. The thermal degradation occurs as

described earlier [4]. Under synthetic air, the degradation lasts in three steps to nearly 100% weight loss (cf. Fig. 1).

The first degradation step results in a weight loss of 64%. Since PVC has a theoretical HCl content of 58.3%, this step cannot be only due to the dehydrochlorination of PVC. The mass spectrum of this degradation step in Fig. 2 taken near the minimum of the DTG-curve at 260°C acknowledges this assumption. Besides HCl water, benzene (*m/e* 78) and naphthalene (*m/e* 128) as well as toluene and other alkylated benzenes (*m/e* 91) were detected. An oxidation of the sample indicated by the release of CO₂ does not occur within this degradation step.

The temperature depending occurrence of these molecules is shown in Fig. 3. The second and third degradation steps are accompanied only by the evolution of CO₂ and water, which indicate the burning of the residual polymer backbone.

In order to avoid a possible destabilization of the polymer by the oxygen, investigations were carried out in nitrogen atmosphere. The results of the thermo-analytical investigations are represented in Fig. 4. The degradation appears in two steps to 90% weight loss. The first step also leads to a weight loss of about 64%. The mass spectroscopic investigations of the released gases show the same findings as under synthetic air.

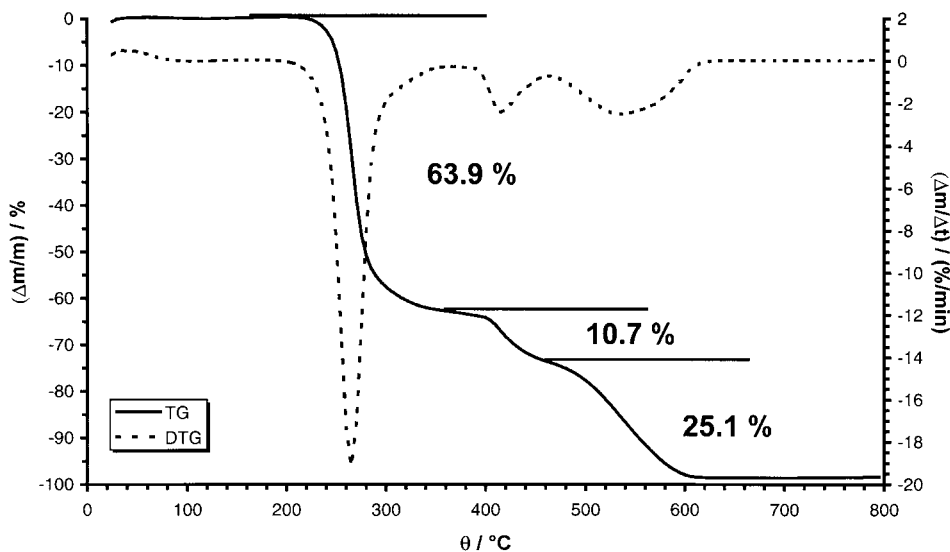


Fig. 1. TG- and DTG-curves of PVC in synthetic air.

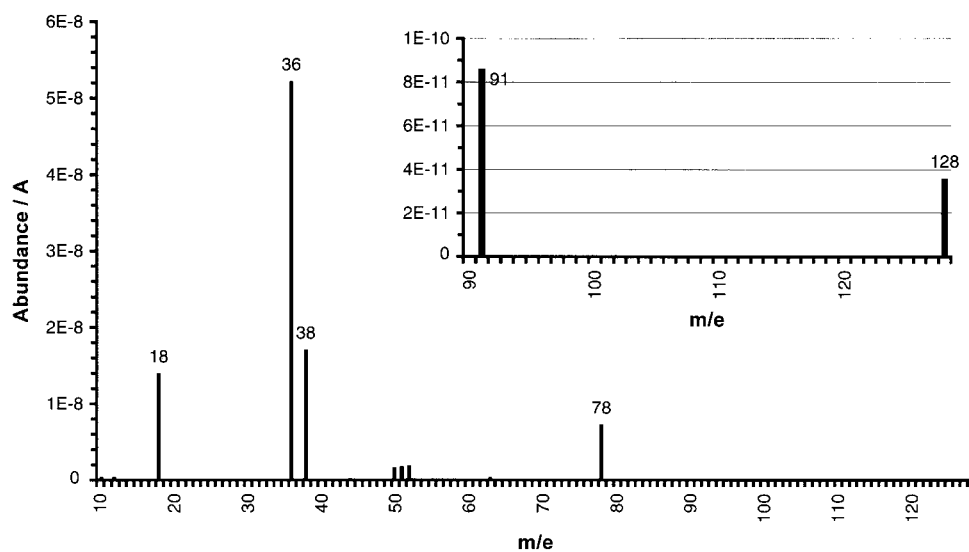


Fig. 2. Mass spectrum from PVC at 260°C (synthetic air).

Besides HCl water, benzene, alkylated benzenes and naphthalene were detected (cf. Fig. 5). A release of CO_2 was also not detected.

Since soft PVC is highly added by softeners, normally phthalates, we have investigated the softener bis(2ethylhexyl)phthalate which is widely used. The

mass spectrum of this substance from the NIST is given in Fig. 6. From this spectrum we selected m/e 149 as the most abundant mass to be monitored simultaneously with some fragments of PVC. As in Fig. 7 the evolution of the softener appears at ca. 300°C (maximum at 340°C). This is at the end of the

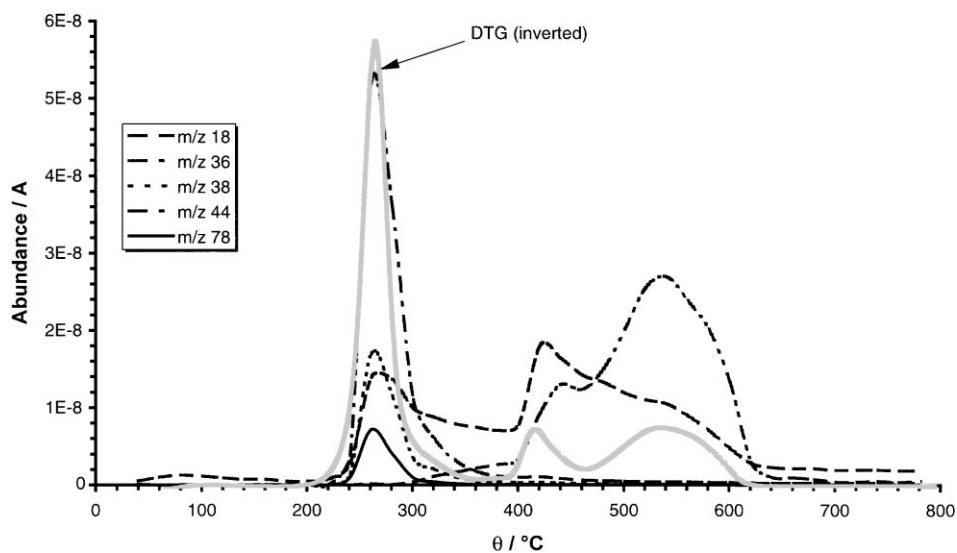


Fig. 3. Temperature dependent occurrence of water (m/e 18), HCl (m/e 36, 38), CO_2 (m/e 44) and benzene (m/e 78) during the thermal degradation of PVC (synthetic air).

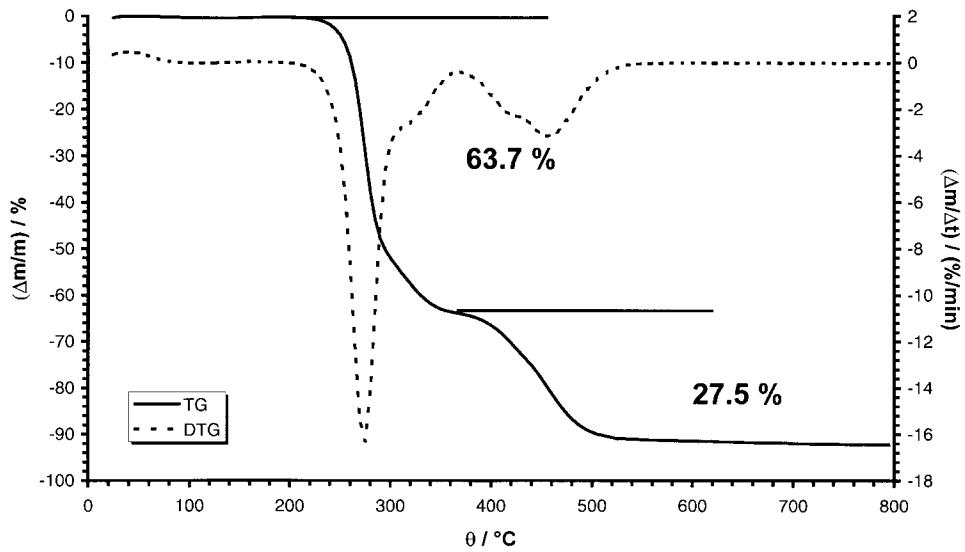


Fig. 4. TG- and DTG-curves of PVC in nitrogen atmosphere.

first degradation step of PVC. Assuming for the recycling process a technical PVC product with a variety of softeners added, a separation of the degradation of PVC and the softeners cannot be done by thermogravimetric analysis.

On this basis, a characterization of the material can be done with respect to inorganic fillers and residues

by the determination of single degradation steps which appear at temperatures above 600°C as well as the residue of the thermal degradation.

A characterization and determination of the organic part, e.g. additives, pollutants and the PVC itself cannot be done by an evaluation of individual degradation steps or the total weight loss, but only by a

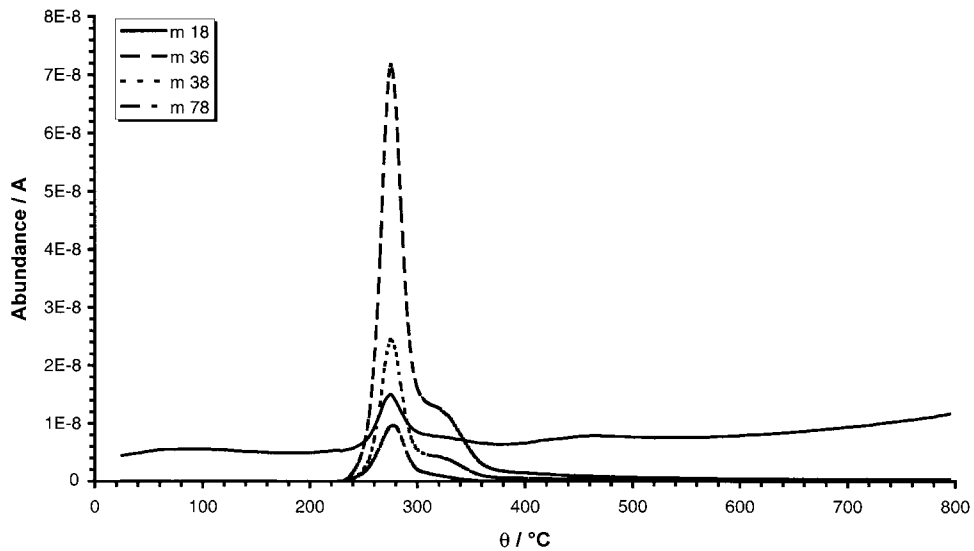


Fig. 5. Temperature dependent occurrence of water (*m/e* 18), HCl (*m/e* 36, 38) and benzene (*m/e* 78) during the thermal degradation of PVC (nitrogen).

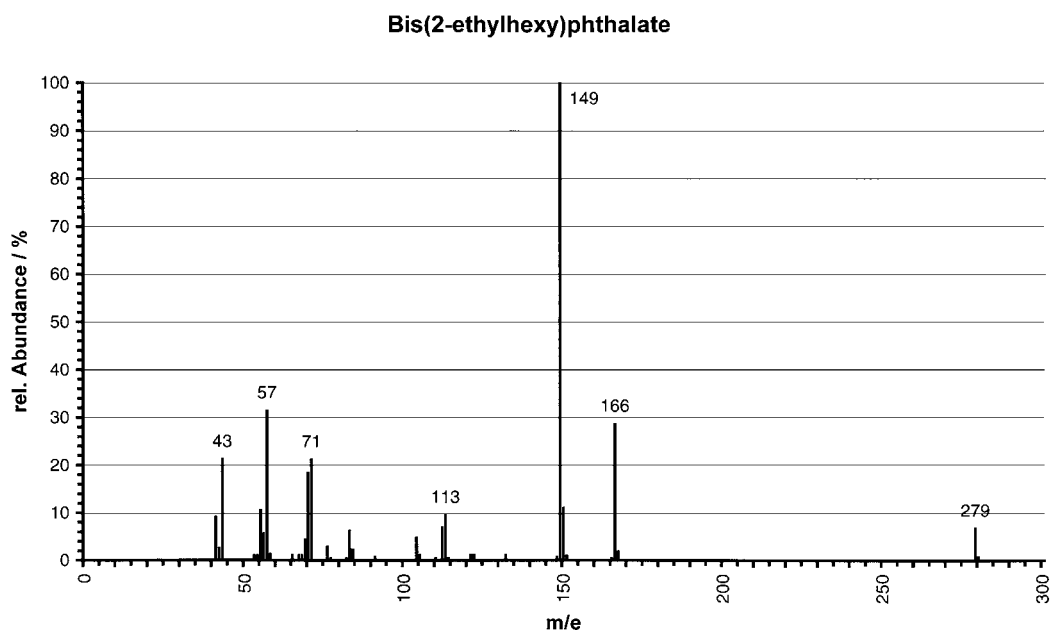


Fig. 6. Mass spectrum of bis(2-ethylhexyl)phthalate from NIST [7].

quantitative determination of individual substances as HCl, phthalates and others. The quantitative determination of individual gaseous components with the mass spectrometer can be achieved with the help of the pulsed thermal analysis (PTA) [5].

Since the handling of gaseous HCl is very difficult and most of the substances of interest (phthalates, etc.) are not in the gaseous state at ambient temperature, a different way for the calibration must be chosen. We calibrated our system to HCl by different weighted

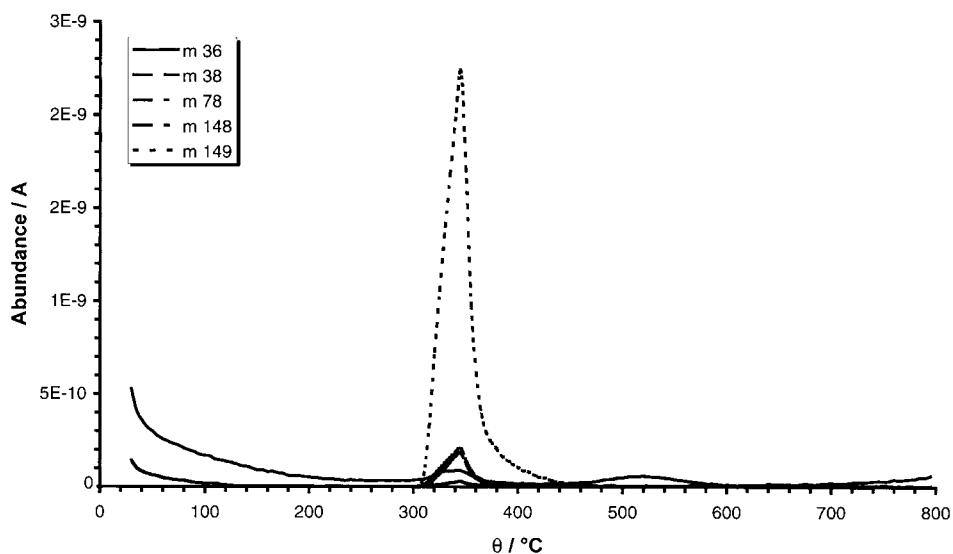


Fig. 7. Temperature dependent occurrence of m/e 36, 38, 78, 148 and 149 from bis(2-ethylhexyl)phthalate.

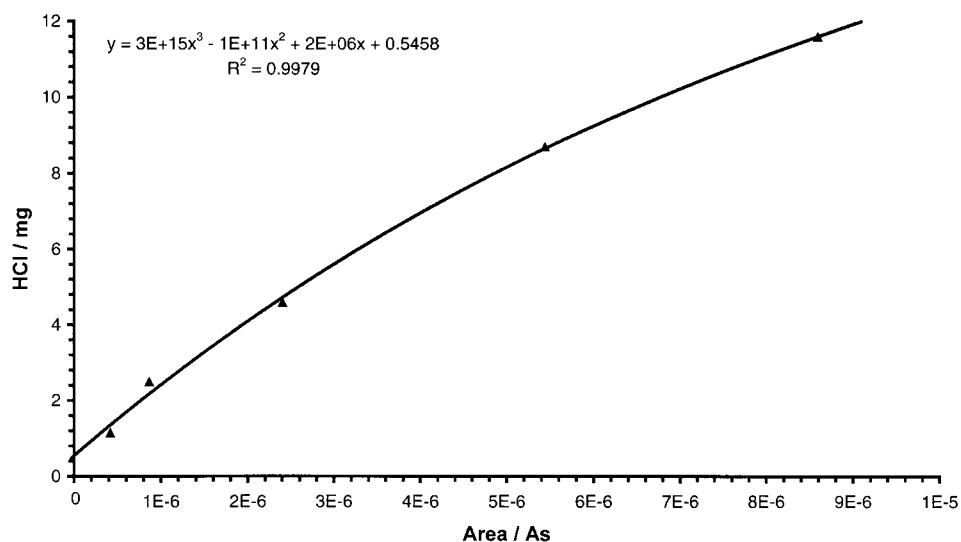


Fig. 8. Mass spectrometric calibration for HCl.

samples of pure PVC. The calibration for HCl was done by evaluation of the areas of the $H^{35}Cl$ isotope peak in dependence of the theoretical HCl content. The best fit for the calibration curve in Fig. 8 was a third degree polynomial.

The calibration for the softeners was done with different weighted samples of a standard PVC, containing 15% of diisooctylphthalate. To our surprise, we found m/e 149 with only a very low abundance while m/e 148 appeared very strong (10 times higher).

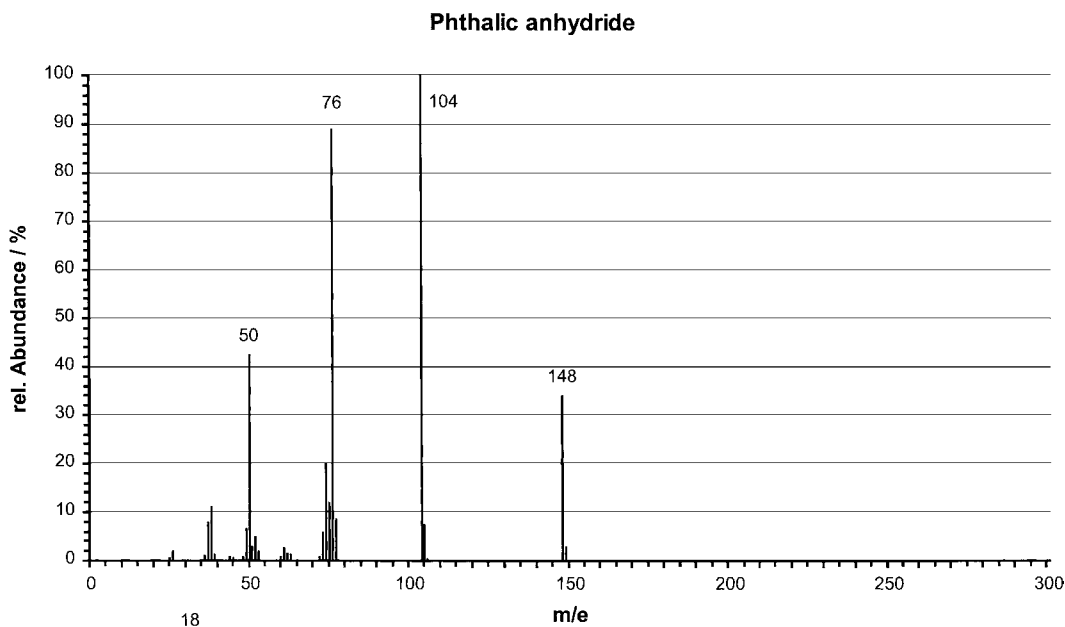


Fig. 9. Mass spectrum of phthalic acid from NIST [7].

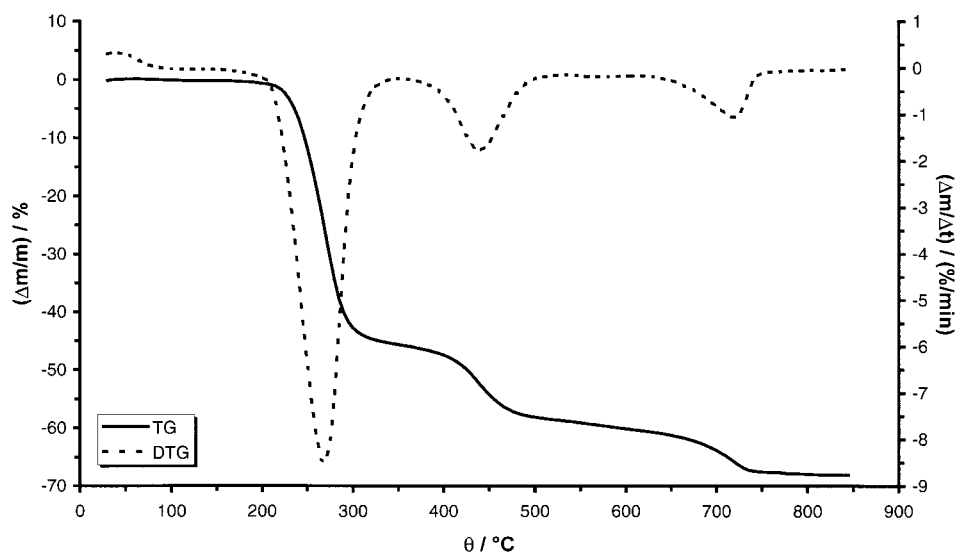


Fig. 10. TG- and DTG-curves of raw PVC recycling material.

The library mass spectrum from the NIST for phthalic acid in Fig. 9 shows this ratio. Due to this finding, it can be assumed that an acid catalyzed cleavage of the ester occurs.

The curves of the thermal analysis of a raw PVC sample for the recycling process is given in Fig. 10. The degradation lasts in four steps to 68% total

weight loss. From the mass spectrometric investigation of the volatiles, we found a CO_2 emission during the first degradation step (cf. Fig. 11). This is due to a reaction of the formed HCl with the calcium carbonate filler. This effect was already described for PVC based automobile undercoating [6].

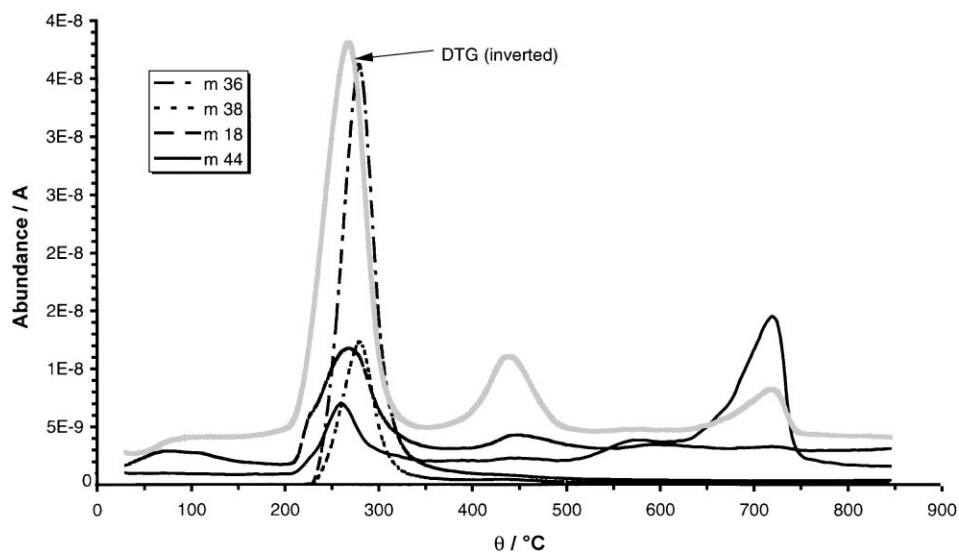


Fig. 11. Inverted DTG-curve and temperature dependent occurrence of HCl (*m/e* 36, 38) and CO_2 (*m/e* 44) from PVC recycling material.

Based on this findings, the raw material can be characterized. By an iterative process, regarding the last degradation step, the area of its corresponding CO₂ peak as well as the area of the CO₂ during the first degradation step, the inorganic filler material (CaCO₃) can be quantified. With the correct amount of CO₂ evolved during the first degradation step, the total HCl evolution representing the PVC content can be determined. Due to the reaction of the phthalic esters catalyzed by HCl, the content of softener can be determined only half-quantitatively by mass spectrometry.

Further work using TG-FTIR as well as TG-MS will help to solve this problem.

4. Conclusion

This report has shown that EGA methods are very suitable methods for the characterization of the raw material for the PVC recycling process. They can give information about the PVC content as well as the inorganic filler materials and softeners which are important values for the recycling process.

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