Characterization of Polymers by Multi-Step Thermal Desorption/Programmed Pyrolysis Gas Chromatography Using a High Temperature PTV Injector

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Summary

Thermal treatment hyphenated with gas chromatography is a versatile and powerful tool in the study of polymer characterization. An inexpensive system where thermal treatment at different temperatures occurs inside a Programmable Temperature Vaporization injector (PTV) is described. The samples investigated, commercial plastics, are complex mixtures that contain several polymers and additives. These plastics as well as their pure constituents are subjected to multi-step thermal treatment. The individual chromatograms of the various constituents of the polymeric sample are correlated with those of the final material in order to identify additives (thermal desorption) and degradation products (pyrolysis). Results obtained with the new method indicate the interesting potentials of the technique for the characterization of polymer compositions. Reproducibility of absolute and relative peak areas has been considered and found to be acceptable. The absence of a heated transfer line and switching valves, which are always present in conventional set-ups, eliminates the risk of losses of high molecular weight components. Further advantages of the technique proposed are simplicity, versatility, and its inexpensive nature.

1 Introduction

Throughout the years a wide variety of analytical techniques has been developed for characterization of polymers and plastics. Some of these methods are used for determining physical properties whereas others are used for chemical structure identification. Methods for the determination of physical properties are mainly thermo-analytical techniques [1]. Thermal analysis is extremely diverse, embracing a large number of different methods. In this group of techniques material properties are measured as a function of either temperature or time while the samples under investigation are subjected to a controlled temperature program. Thermal Gravimetric Analysis (TGA) is a mass depending technique and involves continuous monitoring of the weight of the sample as a function of temperature. TGA yields information regarding thermal stability, losses of residual volatiles and degradation of the material. Derivative Thermal Gravimetric analysis (DTG) monitors the rate of change of weight against temperature. This information is useful in studying temperatures of initial onset of decomposition and can be relevant in optimizing production and processing conditions.

In recent years, chromatography is gaining popularity in polymer characterization. Techniques as Size Exclusion Chromatography (SEC) [2] and High Performance Liquid Chromatography (HPLC) [2] are nowadays an integral part of any polymer laboratory. SEC, or Gel Permeation Chromatography (GPC), is not only used for the determination of molecular weight distributions, but also for copolymer composition analysis. HPLC is frequently used for analyzing monomers, oligomers and solvent residues, often in combination with SEC. In this case the smaller molecules are separated from the polymers in the SEC mode and are subsequently analyzed by HPLC.

Another chromatographic technique that is becoming increasingly important in polymer analysis is gas chromatography (GC) [3,4]. In the past GC was only used to analyze impurities and residual monomers in polymers. At present, pyrolysis-GC [2-6] is a powerful technique which not only reveals information about the nature or composition of the polymer, but also about the polymer additives in the sample. The most commonly used Pyrolysis-mode is the pulsemode, in which a rapid temperature change is applied for a short period of time (2 to 20 s) [7]. A second type of pyrolysis is the programmed-mode, where heating rates correspond with those of conventional thermal analyzers such as TGA or DSC. A further development in the field of GC analysis of polymers is the use of a thermo-desorption step prior to pyrolysis. Hu [8] reported a three step analysis with a first step of programming the pyrolyzer to 300°C, a second step to 1000°C and a cleaning step at again 1000°C. In his work Hu used a conventional pyrolyzer. More recently, Watanabe *et al*. [9] developed a two-stage pyrolyzer. In a first desorption step at 300°C, various additives such as dioctyl adipate and dioctyl phthalate were released from an acrylonitrile-butadiene rubber. After the desorption step pyrolysis of the remaining polymer fraction occurs, giving detailed information about the polymer structure. The instrument developed by Watanabe consisted of two separated ovens. One for desorption and one for pyrolysis.

In the present paper a simple, inexpensive and versatile multi-step thermal desorption/pyrolysis GC-system is described. A Programmed Temperature Vaporization-injector (PTV) is used both as thermo-desorption unit and as programmed pyrolyzer. The applicability of the technique of multi-step thermal desorption followed by pyrolysis for the characterization of plastics is studied. Plastics as well as their pure

constituents are subjected to multi-step thermal treatments. Attempts are made to correlate the chromatograms of the various constituents of the polymeric sample with that of the final material.

2 Instrumentation

Because high oven temperatures are necessary to elute fragments of high molecular weight formed during de sorption and pyrolysis, the chromatographic system used for separation of the products formed should be able to program to a maximum of at least 450°C. The GC used is a Shimadzu 17A (Shimadzu, Kyoto, Japan) which meets this requirement. The analytical column was an HT Simdist 10m x 0.25 mm x 0.15 µm (Chrompack, Middelburg, the Netherlands). This ultimetal-type column is far more rugged than columns drawn from fused-silica. For the on-column experiments a 0.53 mm i.d. metal retention gap (Chrompack) was installed. The injector used was an OPTIC 600 PTV injector (Ai Cambridge, Cambridge, UK). **Figure 1** shows the OPTIC 600 PTV injector. The maximum temperature of the

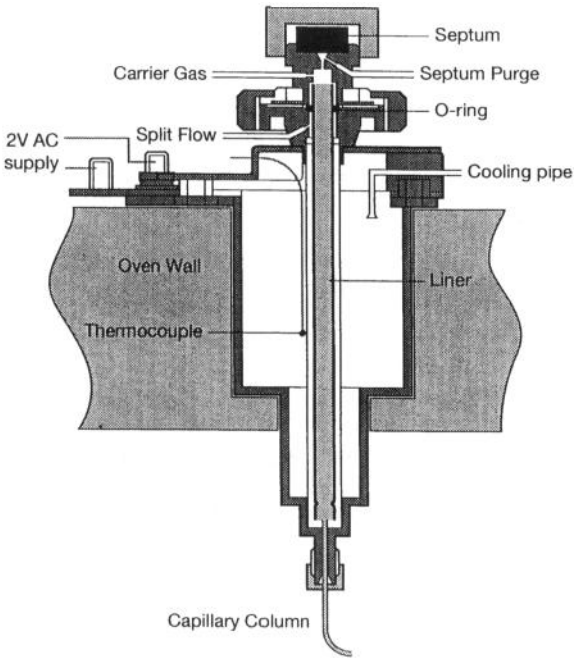

Figure 1. The OPTIC 600 PTV injector

injector was 600°C. This is high enough for pyrolysis of polymer samples and subsequent discrimination free transfer of the products to the GC-column [10-12]. The liner of the injector has an internal diameter of 3.4 mm. The polymer samples were loaded directly into the liner. To hold the sample in place, the liner contains a glass frit in its bottom section. These glass frit liners were made in house. Care was taken to keep the pressure drop over the glass frit as low as possible. Moreover, the frit should be as thin as possible to keep activity to a minimum. The detector used was an FID. Because thermal desorption is a relatively slow process, cryogenic refocusing of the products formed at the entrance of the column is necessary. This was achieved by mounting a home-made cold trap [13] directly below the injector. A detailed representation of this cryotrap is shown in **Figure 2.**

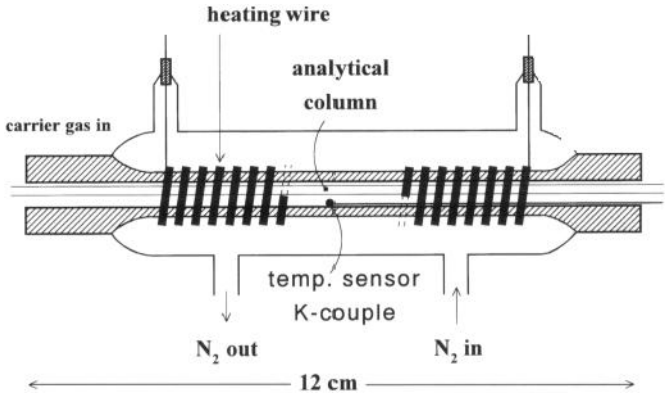

Figure 2. Schematic representation of the cold trap.

The trap is made of glass. The heating wire and the electrical leads are connected with glass-metal connections. The cooling agent is liquid nitrogen. The temperature sensor used to control the trap temperature is positioned in the center of the trap, close to the column. The glass wall of the trap keeps heat transfer from cryotrap to oven or from trap to injector to a minimum. The thermo-couple used is a 0.2 mm K-couple with a temperature range from -200 °C to 500 °*C*. The GC temperature program in all experiments starts at 50 °C (6 min) and ends at 425 °*C*. The programming rate was 10 °/minute. The FID was maintained at a temperature of 435 °*C*. The inlet pressure was 65 kPa, which resulted in a column flow of 2.4 ml/min. A split ratio of 1:54 was used. The linear gas-velocity inside the column was 58 cm/s. The Advanced Flow Control option of the GC was used to keep the column flow constant during the temperature programmed analysis.

For data acquisition a Perkin Elmer Nelson 1022 system is used (Perkin Elmer, Norwalk, USA). The system is controlled by a home-made Multilab data acquisition system, which links all separate parts of the instrument together. The polycarbonate-polybutylene-terephthalate (POCAN) polymer sample as well as the pure constituents were obtained from General Electric Plastics (GEP, Bergen op Zoom, the Netherlands). The composition of the sample is listed in **Table 1.**

Table 1. Composition of the polymer blend.

Component		MW	%
PBT	Polybutyleneterephthalate	56500	53
PC	Polycarbonate	28500	26
ABS	Acrylonitrile-Butadiene-Styrene	n.a.	20
PETS	Pentaerythritoltetrastearate	n.a.	0.25
Irganox 1076	Octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate	537	0.16
AO 2246	2,2′-Methylene-bis(4-methyl-6-*t*-butylphenol)	340	

The instrumentation used for the TGA analyses was a series 7 Thermal Analysis System (Perkin Elmer). The SFE-instrument used was a Carlo Erba SFC 3000 series (Carlo Erba, Milan, Italy). For identification of the SFE-extract, a GC equipped with an on-column injection port and coupled to a QMD 1000 mass spectrometer (Carlo Erba) was used.

3 Results and Discussion

3.1 *Temperature Levels*

Thermal desorption at one or more temperatures followed by pyrolysis gives important information on the composition of polymeric materials. For maximum performance careful selection of the temperature-levels for desorption and pyrolysis is of utmost importance. If incorrect temperatures are selected, or if not sufficient levels are used, significant information can be lost. The lowest temperature should be selected in a way that residual monomers can be determined. Analysis at intermediate injector temperatures gives information on, *e.g.* which additives are used, and what is the release agent applied. At higher temperature levels, information on the structure of the polymers in the blend can be obtained.

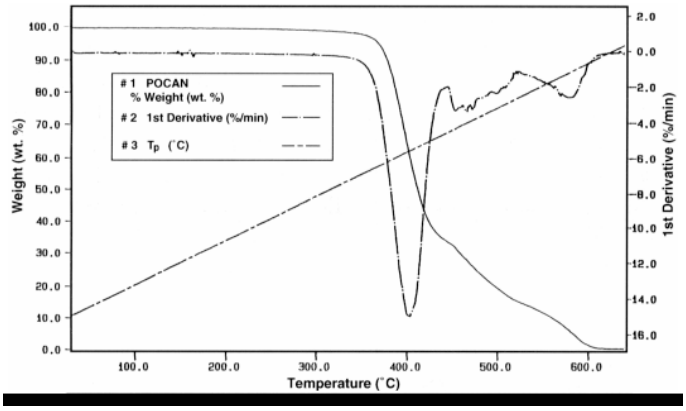

Figure 3. TGA-plot of the polycarbonate-polybutadieneterephthalate blend. The first upper curve is the loss of weight (%). the second is the first derivative of the loss of weight and the third is the linear temperature program.

An important tool for determining the proper desorption and pyrolysis temperatures are TGA-plots of the polymer blend **(Figure 3).** From the first part of the TGA curve the precise temperature(s) for the release of volatile components, *e.g.* residual monomers and processing solvents, can be determined. At elevated, but still moderate temperatures, additives used as *e.g.* flame retardants, release agents, stabilizers and anti-oxidants will start to migrate out of the polymer matrix. In polymer blends, it is also likely that reactions will occur between the individual polymers or between polymers and additives. Volatile reaction products will be released from the polymer matrix and in the TGA-thermogram a weight loss will be observed. At higher temperatures, the individual degradation processes of the polymers in a blend can be observed in complex weight-loss profiles. In case of PBT/PC blends it is known that trans-esterification reactions can occur between the PBT and the PC polymer resulting in PBT-PC block copolymers and, as the reaction propagates, also in random copolymers [14]. This reaction occurs between 270°C and 310°C.

Above 350 °C the polymers start to degrade significantly as is evident from Figure 3. The explanation of the TGA plot summarized above, forms the basis for the selection of the temperature plateaus in the thermo-desorption and pyrolysis experiments of the PBT/PC blend. The plateau at 200 °C was selected for characterization of residual monomers and process solvents, together with very volatile additives. The temperature of 320 °C was selected to monitor reaction products formed in trans-esterification reactions between PBT and PC, *e.g.* butanediol and tetrahydrofuran, together with the release of additives and stabilizer residues. Treatment at 500°C was applied for the characterization of the polymer degradation products: small oligomeric species originating from all polymers present in the blend and therefore very characteristic for the blend composition. Finally, a last thermal treatment was performed at 600 °C for characterization of the pyrolysis products of the remaining polymeric material. It is of course possible to further fine-tune the number of temperature levels for a more detailed study of the thermal behavior and stability of a specific polymer, a polymer blend or its pure components. This, however, is outside the scope of the present paper. Summarizing, the temperaturelevels selected for the blend studied in this paper are 200, 320, 500, and 600 °C. This means the total analysis consists of four separate GC runs.

3.2 *Procedures*

For analysis the proper amount of sample was weighed into the liner. For the polymer blend a sample of 5 mg was used. For pure substances the amount was 1 mg or less. Pure substances such as Irganox 1076 elute as a single peak. In this case only 0.5 mg of the pure substance was weighed into the liner. After inserting the liner into the injector, the liner is flushed with carrier gas for a few minutes to remove air prior to starting the analysis. The presence of air might lead to the formation of undesired reaction and degradation products and might also give rise to rapid degradation or deterioration of the GC column. The temperature programs of injector, gas chromatograph and cold trap are shown in **Figure 4.** At the start of the analysis the injector is cold (50 °C) and the cold trap is cooled to its initial temperature of -100 °C with liquid nitrogen. Once this temperature is reached, the injector is heated at a rate of 8 °/s to the first desorption plateau

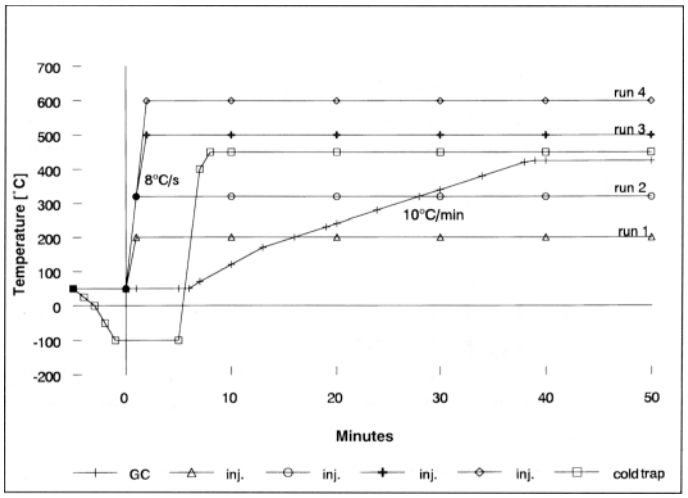

Figure 4. Temperature programs of injector, cryotrap, and GC oven.

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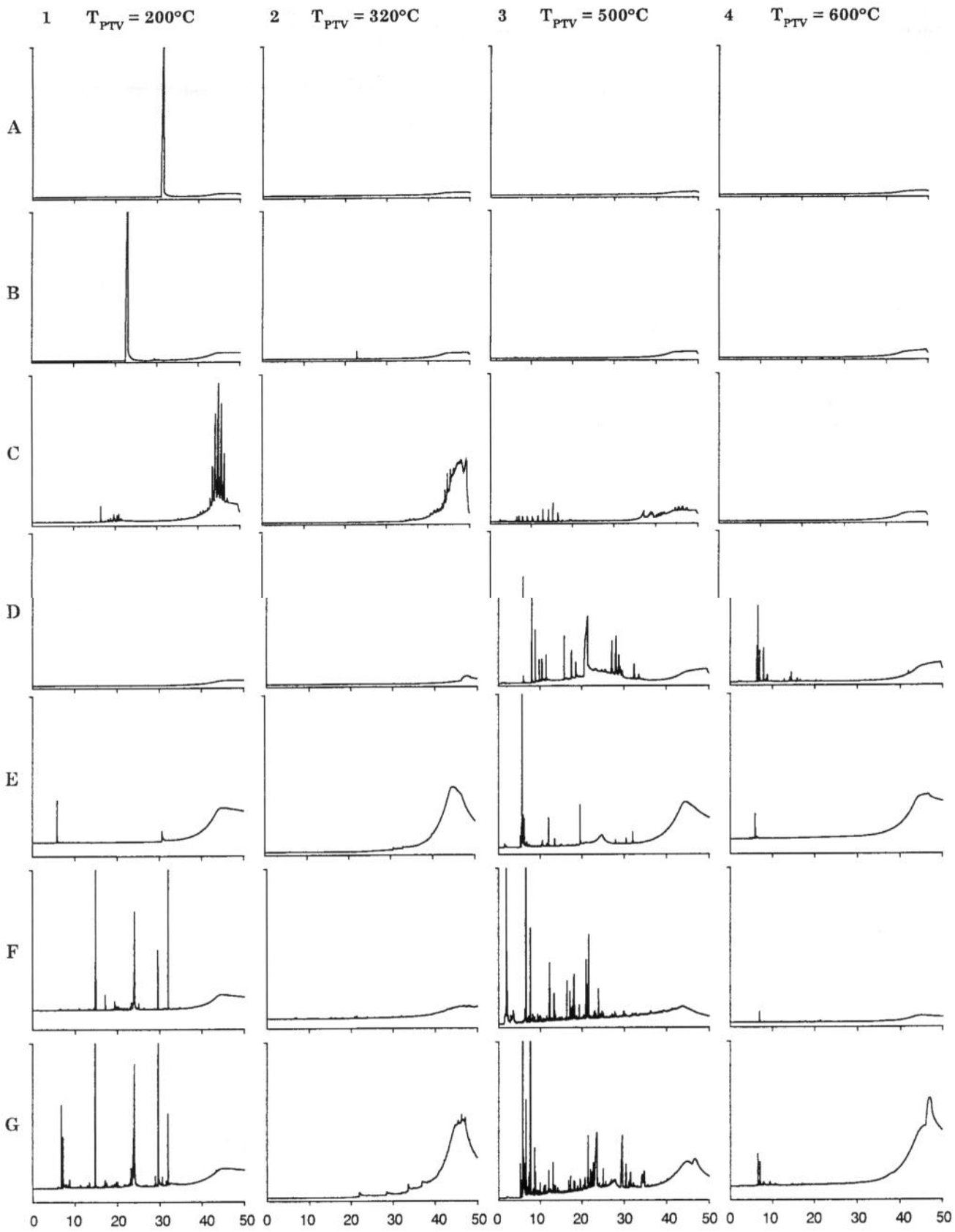

Figure 5. Chromatograms of the polymer blend and the pure constituents at the four PTV-temperature levels investigated. **A,** Irganox 1076; **B,** AO 2246; **C,** PETS; **D,** PC; **E,** PBT; **F,** ABS; **G,** polymer blend.

temperature, in this case 200 °C. Simultaneously the GC system and data acquisition are started. The injector was kept at the desorption temperature during the entire GC run. It was experimentally observed that desorption was complete within 5 min. After desorption the cooling of the cold trap is stopped and the trap is heated to 450 °C. The heating step takes approximately 1 min. After the first run, the GC, the cold trap and the injector are cooled to their initial temperatures and the second, third and fourth step are performed subsequently, all with the same sample.

3.3 *Chromatographic Results*

Figure 5 shows the chromatograms obtained from the polymer blend and the six constituents of the blend. The analysis of each component consists of four chromatograms, each recorded at a different injector-temperature level. This results in 28 chromatograms. From top to bottom the chromatograms are labeled **A** to **G** and from left to right **1** to **4.** The upper two series of chromatograms (series **A** and **B)** represent the analysis of the polymer additives. For these compounds transfer to the column is complete already at the first desorption temperature *(T* = 200 °C). Chromatogram **B2** shows only a small residual peak of the additive AO 2246. The vast majority of this compound is already transferred to the column in the first step. The concentration of both anti-oxidants in the final material is only approximately 0.2 % (see **Table 1).** Therefore, in the chromatogram of the blend **G1,** Irganox 1076 and AO 2246 give only small, but still recognizable peaks. The Irganox 1076 peak elutes at a retention time of 31 min. Anti -oxidant AO 2246 is contained in a cluster of other peaks at approximately 23 min. The chromatograms in series **C** show chromatograms of PETS, a mixture of high molecular weight compounds used as release agent. The elution temperature of the PETS in the GC run is 425 °C. This illustrates the high molecular weight nature of the PETS components. Here a distinct advantage of the PTV thermo-desorption approach over the use of conventional thermo-desorption units becomes apparent. As the current system does not contain a heated transfer line even very high molecular weight components can be transferred to the GC column without the risk of losses in the transfer line or in coupling pieces etc. The purpose of PETS is to make release of the final product from the mold after molding easier. Hence these compounds are situated on the outside of the polymer particles, firmly attached to the surface. As a results, in the blend (series **G)** transfer of the components to the column requires a PTV temperature of 320 °C whereas the pure substance is already transferred at 200 °C. The chromatogram from the next step (at 500 °C) shows several degradation products of the stearic (C_{18}) chain of the PETS. Because the concentration of PETS in the finished material is only 0.25% only small peaks are observed in chromatogram **G2.** The even smaller degradation peaks visual in **C3** are obscured by a large number of other peaks in chromatogram **G3.** At an injector temperature of 500 °C polycarbonate starts decomposing **(D3).** The degradation products formed are also clearly visual in the analysis of the blend **(G3).** Especially the large, overloaded peak at approximately 22 min is very characteristic for the presence of polycarbonate in the polymer sample.

PBT is the main constituent of the polymer blend. It is present in the sample at a relative concentration of 53%. This means that high intensity degradation peaks from the PBT will be present in the chromatogram of the blend. Indeed most of the peaks in the chromatogram of the pure substance **E3,** can also be found in the chromatogram of the blend, **G3.**

The F series of chromatograms shows the four thermal steps for the analysis of ABS, a component used as an impact modifier. Most of the additives found in the thermal desorption of the blend **(G1)** originate from the ABS. The main constituents were identified using GC-MS (see Section 3.4). Also degradation products of the ABS formed at an injector temperature of 500 °C can be identified in chromatogram **G3.**

3.4 *Identification of Polymer Additives*

In all experiments described above, a flame ionization detector was used as the detector. Identification can hence only be carried out on the basis of retention times. Coupling with mass spectrometry would be an attractive alternative. Unfortunately, the combination of high-temperature GC with MS is still difficult at best. To analyze as much as possible of the unknowns a super-critical fluid extraction of the polymer blend was carried out. 1.5 gram of sample was extracted for 10 min at 300 bar and 100 °C using pure CO_2. The extract was dissolved in dichloromethane and analyzed using GC-MS. The resulting chromatogram is shown in **Figure 6.** This chromatogram corresponds more or less to that found in the first temperature step of the multi-step desorption method (see **Figure 5,** chromatogram **G1).** The components identified are listed in **Table 2.**

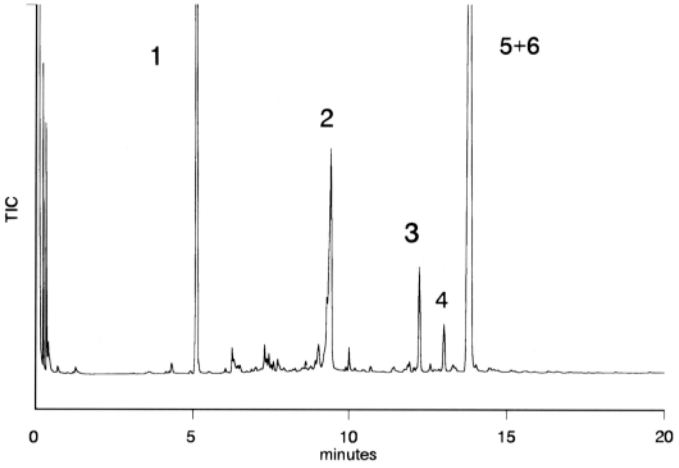

Figure 6. Total ion current chromatogram of the SFE-extract of POCAN .

High Temperature-GC with on-column injection and FID detection of the extract showed that also the PETS were extracted from the sample, but these high boiling components could not be analyzed with conventional GC-MS. The HT-GC-FID experiments were also performed on the Shimadzu GC 17A. For these experiments, in which on-column injection was used, the PTV- injector was equipped with an on-column liner and a retention gap was installed. This illustrates the versatile nature of the PTV injector. Various injection techniques can be performed using the same instrument. In conclusion, the analysis described above shows that the first step in the newly developed multi-step thermal desorption/pyrolysis-method is a good alternative for time consuming extractions as required in the conventional methods for the analysis of various polymer additives in polymer blends.

Table 2. Identification of polymer additives.

Peak no.	Name	
1	Ionol CP	Dibutylhydroxytoluene
2	Dressinate	Decahydromethyl-1-methylethyl-1-phenanthrenecarboxylic acid
3	Unknown	
4	Cyclic PBT trimer	
5	Irganox 1076	Octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate
6	Irganox PS800 (DLTDP)	Dilauryl thiodipropionate

3.5 *Reproducibility*

To investigate the reproducibility of the proposed method, the polymer blend was analyzed several times. All four steps (four different temperatures) were carried out subsequently. First the reproducibility of retention times was studied. Five peaks were selected from the chromatogram obtained in step three (500 °C), varying from early eluting peaks to high molecular weight compounds. The data of these five peaks is also used for establishing the reproducibility of absolute and relative peak areas. Since plateau three contains the largest number of degradation peaks, this step probably gives the largest relative standard deviation in absolute as well as relative peak areas.

In **Table 3** retention time data is listed. As can be seen from this table the relative standard deviation (RSD) is acceptable. It is also clear from the table, however, that early eluting peaks show some what larger variations compared to later eluting peaks. The longer the retention time, the better the RSD value. This is most likely due to the more efficient refocusing in the cold trap obtained for the later eluting components. At an injector temperature of 500 °C a large amount of volatiles is formed. Hence the possibility of breakthrough is more obvious.

Table 3. Reproducibility of retention times (min).

Peak no.	Run 1	Run 2	Run 3	Run 4	Mean	σ	RSD %
1	7.527	7.483	7.045	6.897	7.238	0.273	3.8
2	10.447	10.442	10.303	10.192	10.346	0.106	1
3	15.188	15.037	14.995	14.843	15.016	0.123	0.8
4	19.403	19.323	19.238	19.098	19.266	0.113	0.6
5	23.672	23.618	23.453	23.352	23.524	0.128	0.5

Table 4. Reproducibility of absolute peak areas (area counts).

Peak no.	Run 1	Run 2	Run 3	Run 4	Mean	σ	RSD %
	15466678	16700928	12599820	12591722	1.43E+07	1.80E+06	12.5
	8351131	11653466	4673462	5859595	7.60E+06	2.70E+06	35
	7703028	7420008	7006812	6269278	7.10E+06	5.00E+05	7.6
	35192624	46366636	28421978	25679908	3.39E+07	8.00E+06	23.5
	4617389	3619094	3972387	3251386	3.90E+06	5.00E+05	13

Table 5. Reproducibility of relative peak areas.

Peak no.	Run 1	Run 2	Run 3	Run 4	Mean	σ	RSD %
1	21.7	19.5	22.2	23.5	21.7	1.443	6.6
2	11.7	13.6	8.2	10.9	11.1	1.94	7.5
3	10.8	8.7	12.4	11.7	10.9	1.391	2.8
4	49.3	54.1	50.1	47.9	50.4	2.304	4.6
5	6.5	4.2	7	6.1		1.06	17.8

Table 4 and **5** show the reproducibility data for peak areas. As expected, large differences are found in absolute areas and to a lesser extent also in relative areas. The high RSD values of the absolute areas (7 to 35%) arise from the differences in the amount of sample weighed into the liner. Accurate weighing in the low milligram range proved to be very difficult. The spread in RSD in relative peak areas ranges from 5 to 18%, which is acceptable in view of the inhomogeneity of the sample in combination with the small sample amounts investigated.

4 Conclusion

The newly developed multi-step thermal desorption/programmed pyrolysis method has interesting potentials for the characterization of polymer compositions. The lower temperature stages reveal information about residual solvents and monomers as well as of additives present in the polymer. Higher temperatures give information about the main polymers in the blend. Many components from the blend can be identified by comparing retention times from blend peaks and pure component peaks. Investigation of the reproducibility of peak areas showed large variations in absolute peak areas. For relative peak areas relative standard deviations were acceptable. Therefore, at this point the method is useful mainly for qualitative analysis. For use in quantitative analysis the reproducibility has to be improved. The main advantages of the technique proposed are the simplicity and versatility of the system. Moreover the system is inexpensive in comparison with dedicated thermal desorption and pyrolysis instruments. As the instrument does not contain a heated transfer line or additional switching valves it is also applicable for the analysis of high molecular weight analytes such as anti-oxidants, UV stabilizers and high molecular weight pyrolysis products, that otherwise easily be lost.

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