

Combined Thermal-Desorption and Pyrolysis GC Using a PTV Injector. Part II: Polymer Characterization.

Mark van Lieshout^{*}1, Hans-Gerd Janssen¹, Carel Cramers¹, Martin J.J.Hetem² and Huub J.P. Schalk²

1. Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands.
2. General Electric Plastics B. V., Analytical Technology Dept., P.O. Box 117, 4600 AC Bergen op Zoom, the Netherlands.

Keywords

High temperature gas chromatography
PTV injectors
Thermal desorption
Pyrolysis GC
Polymer analysis

Summary

The hyphenation of thermal sample treatment techniques such as thermal desorption and pyrolysis with gas chromatography gives a versatile and powerful tool in the study of polymers. 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. The absence of a heated transfer line and switching valves, which are often present in conventional set-ups, eliminates the risk of losses of high molecular weight components. Further advantages of the technique proposed are the simplicity and versatility as well as its inexpensive nature.

1 Introduction

In recent years, chromatography is gaining popularity in polymer characterization. Techniques as Size Exclusion Chromatography (SEC) [1] and High Performance Liquid Chromatography (HPLC) [1] 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 analysing 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) [2,3]. In the past GC was only used to analyze impurities and residual monomers in polymers. At present, pyrolysis-GC [1-5] 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. A further development in the field of GC analysis of polymers is the use of a thermal desorption step prior to pyrolysis. In the present paper a simple, inexpensive

GL Sciences B.V.

De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 E-mail: info@glsciences.eu
Internet: www.glsciences.eu

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 pyrolyser. 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 those of the final material

2 Instrumentation

The GC used is a Shimadzu 17A (Shimadzu, Kyoto, Japan) which is able to program to a temperature of 450 °C and can be used for high temperature purposes. The analytical column was an Ultimet HT Simdist 10 m x 0.25 mm X 0.15 µm (Chrompack, Middelburg, the Netherlands). The injector used was an OPTIC 600 PTV injector (Ai Cambridge, Cambridge, UK). The maximum temperature of the injector was 600 °C. 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 directly below the injector. This trap is made of glass [6]. The cooling agent is liquid nitrogen. The temperature sensor used to control the trap temperature is positioned in the centre 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 thermocouple used is a 0.2 mm K couple with a temperature range from –200 °C to 500 °C. 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, CT USA). The polycarbonate-polybutyleneterephthalate 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		Mol.w.	%
PBT	Polybutyleneterephthalate	56500	53
PC	Polycarbonate	28500	26
ABS	Acrylonitril-Butadiene-Styrene	n.a.	20
PETS	Pentaerythritoltetrastearate	n.a.	0.25
Irganox 1076	Octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate	537	0.15
AO 2246	2,2' methylene bis (4-methyl-6-t-butylphenol)	340	0.2

The instrumentation used for the TGA analyses was a series 7 Thermal Analysis System (Perkin Elmer, Norwalk, CT, USA)

3 Results and Discussion

3.1 Temperature levels

Thermal desorption followed by pyrolysis can give important information on the composition of polymeric materials. It is of utmost importance to select the proper desorption- and pyrolysis temperature levels. If incorrect temperatures are selected, or if not sufficient levels are used, significant information can be lost. The initial desorption 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. An important tool for determining the proper desorption and pyrolysis temperatures are TGA-plots of the polymer blend (**Figure 1**). 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 weightloss 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 [7]. This reaction occurs between 270 °C and 310 °C. Above 350 °C the polymers start to degrade significantly as is evident from **Figure 1**.

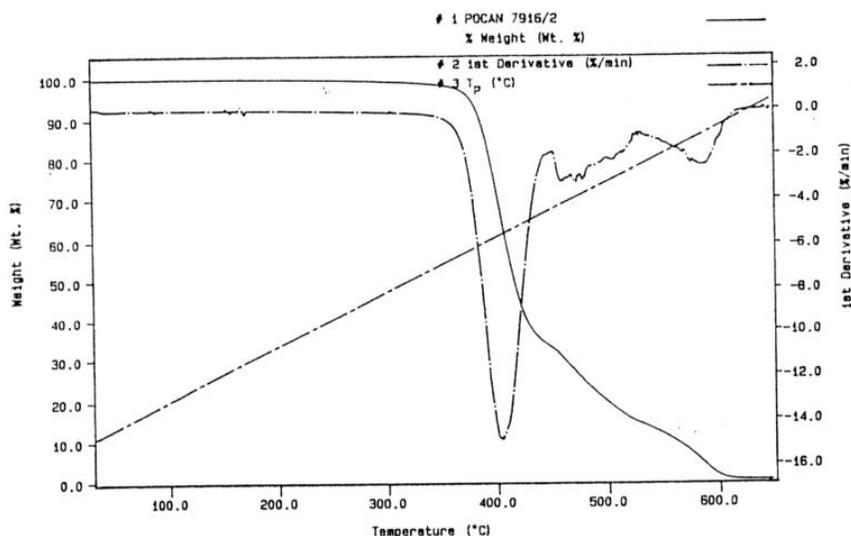


Fig. 1. TGA-plot of the polymer blend.

The explanation of the TGA plot summarized above, forms the basis for the selection of the temperature plateaus in the thermal 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

GL Sciences B.V.

De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
 Tel. +31 (0)40 254 95 31 E-mail: info@glsciences.eu
 Internet: www.glsciences.eu

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. Summarizing, the temperature levels selected for the blend studied in this paper are 200, 320, 500 and 600 °C. This means the total analysis of one sample consists of four separate (subsequent) GC runs.

3.2 Chromatographic conditions

The GC temperature program in all experiments started at 50 °C (6 minutes) and ended at 425 °C. The programming rate was 10 °C/minute. The desorption- and pyrolysis times were 5 minutes. 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/sec. The initial injector temperature in all experiments was 50°C.

3.3 Chromatographic results

Figure 2 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 ($T = 200^{\circ}\text{C}$). 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 minutes. Anti-oxidant AO 2246 is contained in a cluster of other peaks at approximately 23 minutes. 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 thermal desorption approach over the use of conventional thermal 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 mould after moulding easier. Hence these compounds are situated on the outside of the polymer particles, firmly attached to the surface. As a result, 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.

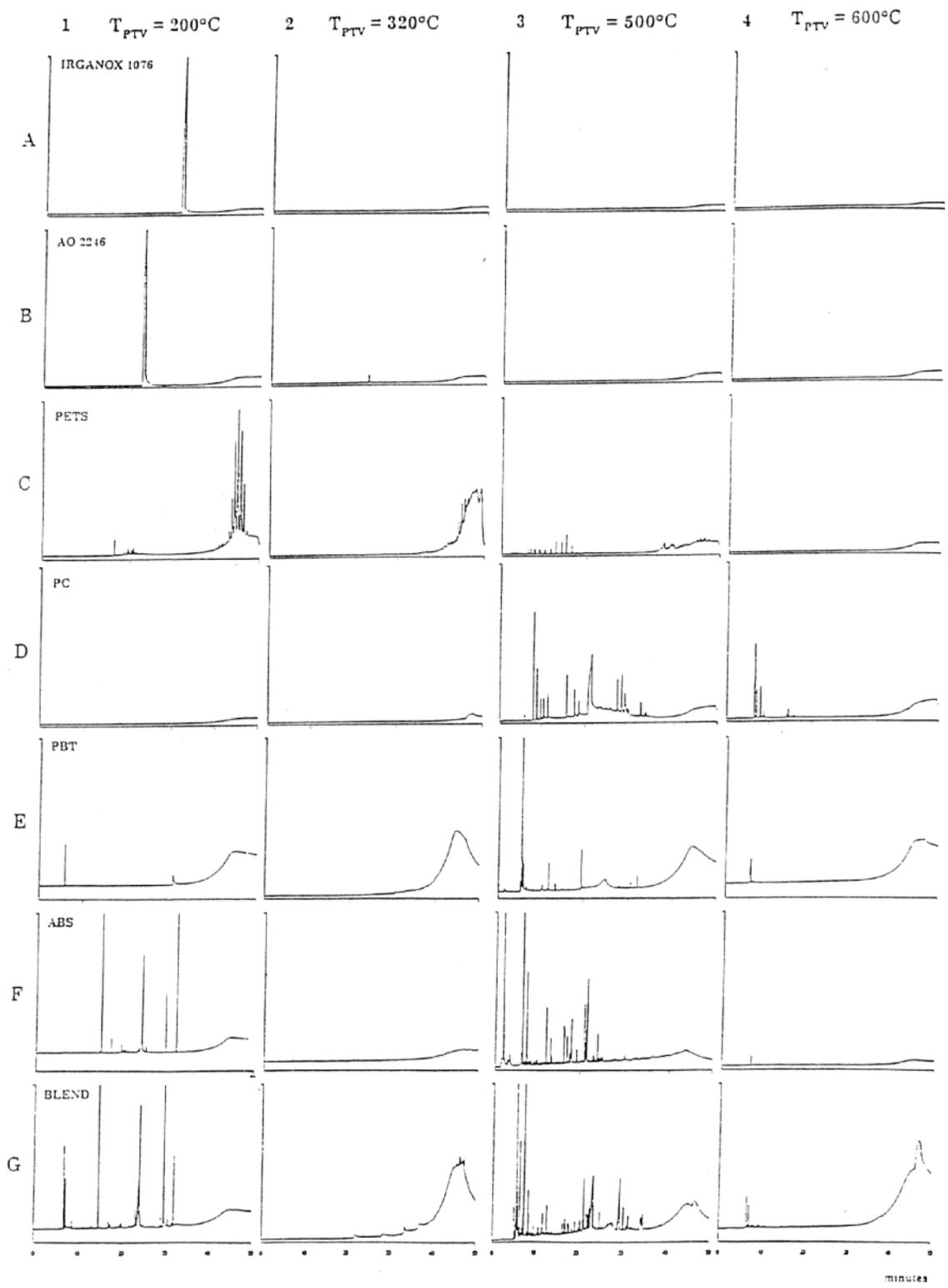


Fig. 2. All chromatograms of the polymer blend and its pure constituents.

GL Sciences B.V.

De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
 Tel. +31 (0)40 254 95 31 E-mail: info@glsciences.eu
 Internet: www.glsciences.eu

The chromatogram from the next step (at 500°C) shows several degradation products of the Stearic (C18) chains 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 visible 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 visible in the analysis of the blend (G3). Especially the large, overloaded peak at approximately 22 minutes 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 polycarbonate 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. Also degradation products of the ABS formed at an injector temperature of 500°C can be identified in chromatogram G3. Investigation of the reproducibility of peak areas showed large variations in absolute peak areas. For relative peak areas relative standard deviations were acceptable (RSD = 10%).

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. 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 might easily be lost.

References

1. H.G. Barth, J. W. Mays, "Modern Methods of Polymer Characterization", Wiley & Sons, New York, (1991), chapter 1.
2. J. Haslam, H.A. Willis, "Identification and analysis of plastics", Van Nostrand Company, London, (1965) .
3. V.G. Berezkin, V.R. Alishoyev, I.B. Nemirovskaya, "Gas chromatography of Polymers", Elsevier Publishing Company, Amsterdam, (1991).
4. S.A. Liebman, T.P. Wampler, E.J. Levy, "Sample Introduction in Capillary Gas chromatography", Vol. 1, P. Sandra (ed.), Huethig Verlag, Heidelberg, (1985), chapter 9.
5. M. Wandel, H. Tengler in "Die Analyse von Weichmachern", H. Ostromov (ed.) Springer verlag, Berlin (1967).
6. T.H.M. Noij, "Trace Analysis by Capillary Gas chromatography, Theory and Methods", Thesis, Eindhoven University of Technology (1988).
7. M. Pellow-Jarman, M. Hetem, *Plast. Rubber Compos. Process. Appl.*, 23 (1995) 41.