

Investigation of the Detection Limit for the Determination, by Pyrolysis-Capillary GC, of the Thickness of Ultra Thin PMMA Layers Coated on to PET Film

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Key words:

Pyrolysis-capillary GC

Quantitative analysis

Detection limit

Ultra-thin layer poly(methyl methacrylate)

Poly(ethylene terephthalate)

Summary

The determination of nanometer thick layers of poly(methyl methacrylate) coated on to the surface of poly(ethylene terephthalate) film has been investigated by high resolution pyrolysis gas chromatography without sample pretreatment or modification of the instrumentation used. A good linear relationship was observed between the quantity of the characteristic pyrolysate and the thickness of the poly(methyl methacrylate) layer; the detection limit was sufficient to enable the quantitation of poly(methyl methacrylate)-to-poly(ethylene terephthalate) film thickness ratios of 1:20000 in composite materials.

1 Introduction

The characterization of polymer surfaces has, in general, been performed by spectroscopic means such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR); these techniques are useful for analyzing surface layers as thin as 1-10 nm [1, 2].

Pyrolysis - gas chromatography (Py-GC) has many advantages which make it suitable for application to polymer analysis. Minimum sample preparation is required and the technique can be applied even to complex mixtures of formulated and treated products such as composite polymers. The small amount of sample required, the high resolution separation, and the qualitative and quantitative information available from this technique have made Py-GC an essential tool in polymer analysis [3]; even so, the technique has been applied relatively rarely to studies involving micro quantitative analysis. Hida et al. recently reported that the presence of metal powder and inorganic salt additives is effective in improving the sensitivity and reproducibility of pyrolysis [4]. The trace determination of poly(vinyl pyrrolidone) in complex mixtures [5] and in the end groups of macromonomers [6, 7] has been performed by Py-GC with the highly sensitive and selective detectors. TSD, FPD, and NPD.

In the present work, we have applied high resolution Py-GC to the determination of ultra thin (nanometer thick) poly(methyl methacrylate) layers coated on to the surface of poly(ethylene terephthalate) (PET) films, an analysis previously performed only by XPS, SIMS, and special FTIR-ATR. We have investigated the

detection limit which may be achieved without sample pretreatment or modification of the instrumentation.

2 Experimental

2.1. Sample Preparation

Dilute solutions of different concentrations of PMMA in chloroform were deposited on PET film (thickness 120 μ m) by means of a microsyringe; the solvent was then slowly evaporated, at a relatively low temperature, in an environment nearly saturated with chloroform. The thickness of the PMMA layer was estimated from the weight increment and the bulk density of 1.19 g/cm³ for PMMA; samples with layers 10, 24, and 36 nm thick were selected as calibration standards.

2.2. Apparatus

Pyrolysis GC was performed with a Model JHP-3 Curie-point pyrolyzer (Japan Analytical Industry Co.) combined with an on-line Model HP 5890A gas chromatograph (Hewlett-Packard) and a Model D-2520 integrator (Hitachi). The chromatograph was equipped with flame ionization detection and a 30 m x 0.25 mm i.d. fused silica capillary, column coated with a 0.25 μ m film of DB-1701 (immobilized poly(phenyl cyanopropyl) polydimethylsiloxane; J & W). Identification of the pyrolysates was performed with a quadrupole mass spectrometer (Model QP 2000A, Shimadzu) equipped with an EI ionization source and interfaced directly with the Py-GC.

2.3 Conditions for Py-GC

A piece of the sample film (0.4-0.5 mg) was wrapped in Pyrofoil-500°C (8 x 23 x 0.05 mm) in a manner ensuring good contact between both. The sample and foil were loaded into a quartz pyrolysis chamber (40 x 4 mm i.d.) maintained at 200°C, and heated inductively for 5 s. The column temperature was maintained at 30°C for 10 min following pyrolysis and then programmed to 300°C at 8°C/min. Helium was used as carrier gas; the total flow of 50 ml/min was split at a ratio of 50:1. The EI source of the mass spectrometer was operated at 70 eV and 250°C.

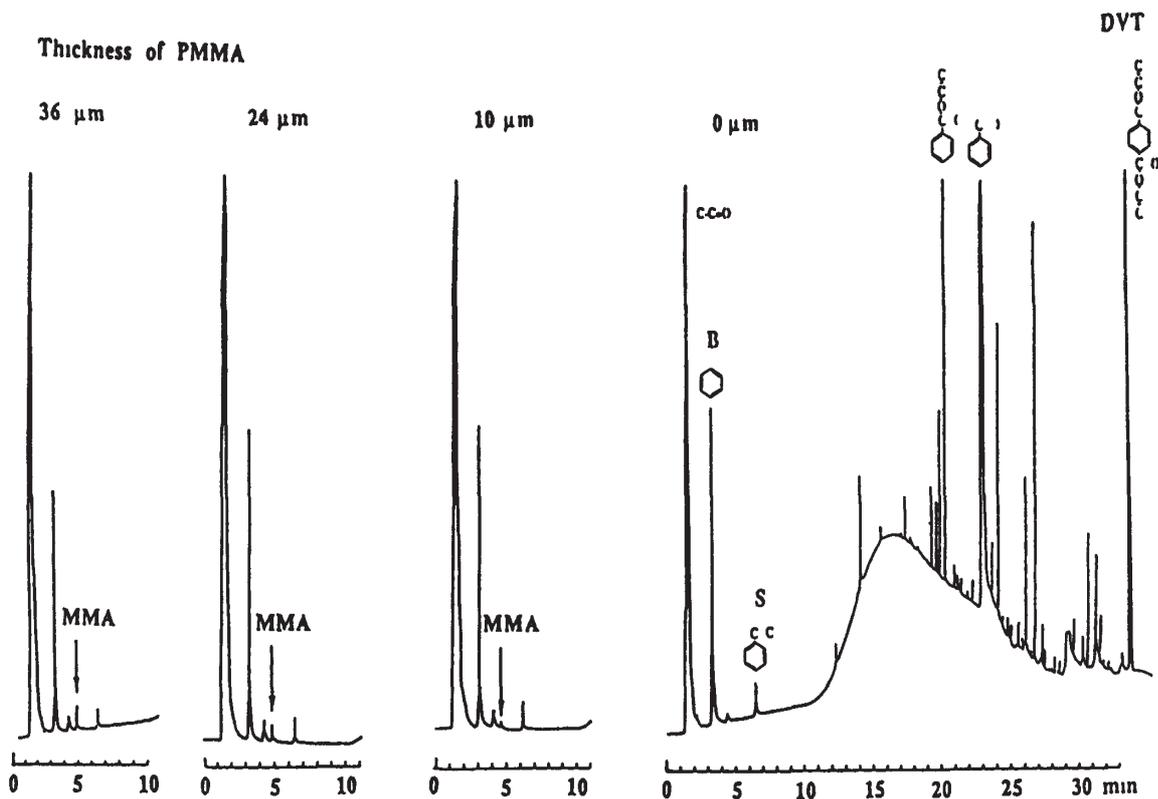


Figure 1

Pyrograms of PET coated with ultra thin layers of PMMA pyrolysis temperature 500 C.

Table 1

Calibration data for standard films of PMMA on PET

	PMMA thickness (nm)			
	0	10	24	36
Peak area [a u]				
MMA	0	2 118	5 463	5 610
B	-	94 294	108 073	85 989
S	-	8 624	9 019	6 663
DVT	-	105 707	104 281	74 924
Peak area ratio				
MMA/B $\times 10$	0	2 25	5 05	6 52
MMA/S $\times 10$	0	2 46	6 06	8 42
MMA/DVT $\times 10$	0	2 00	5 24	7 49

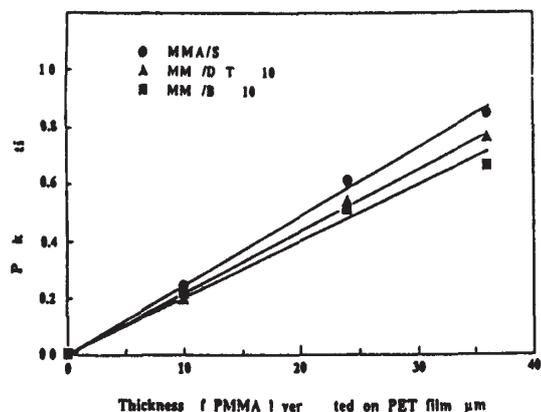


Figure 2

Calibration curves for ultra thin PMMA layers coated on to PET films

3 Results and Discussion

3.1 Pyrogram

It is well known that the major component formed upon pyrolysis of PMMA is the monomer methyl methacrylate (MMA): the amount of the compound in the total pyrolysate sometimes approaches 100 % [6].

The features of the thermal degradation of PET have also been extensively studied. The origins of the main pyrolysates, such as oligomers, monomer (divinyl terephthalate, DVT), benzoic acid, vinyl benzoate, benzene (B) and styrene (S), etc., appear to be reasonably understood: their formation is based mainly on chain

scission, ester exchange, p-CH transfer, in addition to secondary pyrolysis [8, 9].

Relative to the amount of PET, the quantities of PMMA in the samples studied in this work were extremely small (PMMA : PET film thickness ratio of 1 : 3.000 to 1 : 10.000 for standard films). All experimental parameters, especially sample size, pyrolysis temperature, and GC separation conditions, would, therefore, have a significant influence on the quantitative measurement of the PMMA fraction against the PET background. When the samples were pyrolyzed at the lowest temperatures investigated (315 and 423° C) they were not completely degraded, even after extended pyrolysis times. Pyrolysis at the highest temperatures tested (e.g. 590°C), on the other hand, resulted in the formation of large

Table 2**Results from the determination of PMMA film thickness on samples with unknown characteristics.**

Sample code	Peak area [a.u.]			Area ratio		PMMA thickness [nm]	
	MMA	B	S	MMA/B	MMA/S	Experimental	Average
X	4,875	230,212	19,656	2.12×10^{-2}	2.48×10^{-1}	10.8 10.4	10.6
Y	1,538	132,930	10,533	1.16×10^{-2}	1.46×10^{-1}	6.2 6.0	6.1

amounts of the lower boiling point pyrolysates, the peaks from which overlapped the very weak peak from MMA. As a result of these observations, a pyrolysis temperature of 500°C was chosen for the analysis.

Rather large sample sizes were necessary for the determination of the trace amounts of PMMA in the layers; because heat is transferred more slowly in large samples, however, this has been found to influence reproducibility, [8]. The data obtained in this study showed that the smaller the sample size, the more homogeneous was the sample temperature and the wider the linear dynamic range of the calibration graph: a reasonable sample size range was found to be 0.4-0.5 mg (incorporating 0.05-0.15 µg PMMA). The GC conditions presented in Section 2.3 were found suitable for separating the MMA peak from other peaks within a relatively short analysis time; the pyrograms obtained from standard calibration samples under these conditions, following Pyrolysis at 500°C, are illustrated in Figure 1 in which the small but remarkably distinct MMA peak is clearly apparent.

3.2 Calibration

Those structurally characteristic pyrolysates from PET, such as benzene (B), styrene (S), and divinyl terephthalate (DVT), etc., which are completely separated in the pyrograms may be used as internal standards for the quantitative analysis. The peak areas observed for MMA, B, S and DVT, and the peak area ratios MMA/B, MMA/S, and MMA/PET obtained from samples of PET coated with various thicknesses of PMMA are listed in Table 1. The plots of the peak area ratios MMA/B, MMA/S and MMA/DET against the thickness of the PMMA film are shown in Figure 2, excellent linear relationships may be observed. Figure 2 also shows the dependence of the peak area ratio on the identity of the internal standard chosen: we advocate the use of peaks, such as those of benzene and styrene, with intensities and retention times comparable with those of the MMA peak, as being the most suitable for use as internal standards in this work. The relative standard deviation resulting from 5 replicate measurements was within 4%.

3.3 Determination of Unknown Samples

Figure 2 can be simply used for quantitative determination of ultra thin layers of PMMA coated on to PET films within a PMMA/PET film thickness ratio of 10^{-4} . Two unknown samples, coded X and Y, were analyzed on the basis of these calibration curves, the data are summarized in Table 2. The correlation of the values obtained from the different calibration curves indicates the suitability of the method for the quantitative trace analysis of ultra thin layers of PMMA coated on to PET film. In addition, the thickness measured for the PMMA film of sample Y implies that the detection limit is low enough for application of the method to the detection of PMMA films when the PMMA/PET film thickness ratio of the composite material is as low as 1/20,000.

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Ms received: August 25, 1991

Accepted: September 26, 1991