Comparing Polycarbonate Roof Tiles Using MALDI-TOFMS

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Introduction

Fitness for Purpose

- For a polymer to be fit for its intended use it must be stable to the environmental conditions likely to be imposed upon it throughout the life of its use.

The Problem

- Recently we were asked to investigate a polycarbonate roof tile material that had failed in its practical stability.

A MALDI Solution

- Could MALDI-TOFMS provide an insight into differences between polycarbonate roof tile formulae and so explain the failure?
- The work presented here shows the use of MALDI-TOFMS for the interrogation of a competitor's polymer formulae.

Materials and Methods

- A comparison of the roof tile and that of a competitor's was made by MALDI-TOFMS.
- The method used followed that described on the NIST database of MALDI methods
- Roof tiles produced from two different polycarbonate suppliers (Sample 1 and Sample 2) were cut into small squares, weighed and washed in methanol.
- Each square was steeped in tetrahydrofuran (THF) over 3 days.
- An aliquot of the steeping liquor was diluted 1:2 with THF and 0.5 µl was evaporated onto a MALDI target slide.
- On top of the dried sample spots was applied 0.5 µl of the matrix solution (20 mg/ml 3b-indoleacrylic acid in THF). A blank of THF held in the same extraction tube over 3 days was included in the analysis.
- The samples were externally calibrated using a peptide mixture deposited onto adjacent wells.
- MALDI-TOFMS was performed on an SAI LaserTof, LT-3 mass spectrometer.

Results and Discussion

- The spectra showing the key differences between the samples is shown in Figures 1a and 1b.
- Figures 2, 3 and 4 shows each polymer series observed in Tile Sample 1, assigned as a, b and c.
- Figures 5, 6, and 7 similarly shows the polymers witnessed in Tile Sample 2, assigned as i, ii and iii.

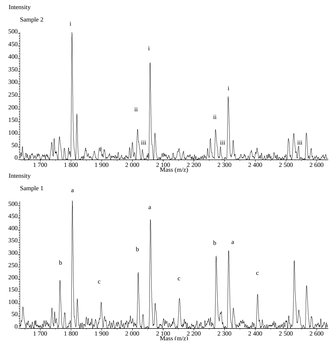

Fig 1a: Mass region showing the presence of series c in Sample 1 compared to Sample 2

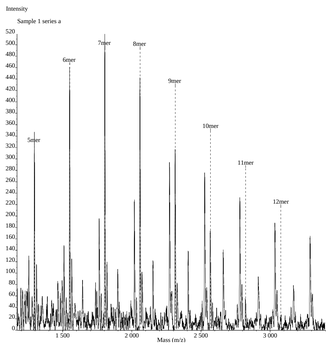

Fig 2: Tile Sample 1 - series b

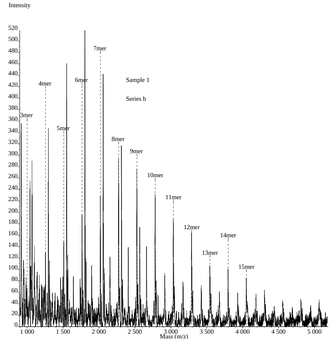

Fig 3: Tile Sample 1 - series b

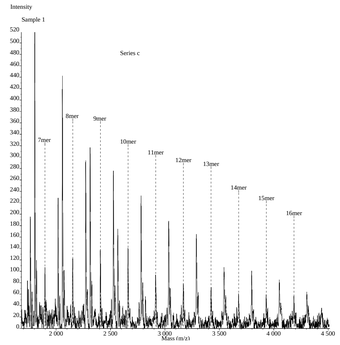

Fig 4: Tile Sample 1 - series c

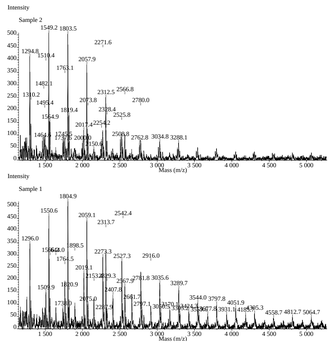

Fig 1b: Comparative spectra across the full mass range

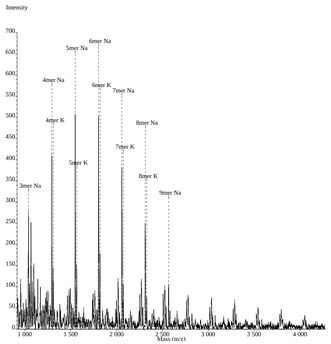

Fig 5: Tile Sample 2 -series i

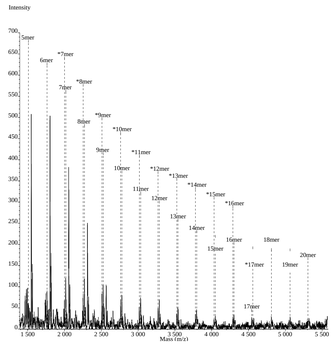

Fig 6: Tile Sample 2 - series ii

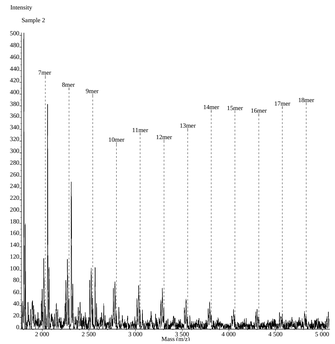

Fig 7: Tile Sample 2 - series iii

Summary

Table1: calculated polymer characteristics

Series	*Most Abundant Molecular Weight (Mp)	*Number Average Molecular Weight (Mn)	*Weight Average Molecular Weight (Mw)	Poly dispersity (Mw/Mn)	*M	*T	Proposed Structure
Sample 1 – a	1804.91	1918.09	2012.54	1.05	254.5	25.4	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= sodium? (no termini or cyclised)
Sample 1 – b	2273.26	2524.49	2776.59	1.10	254.3	236.2	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= Monomer fragment ?
Sample 1 – c	2661.70	2716.66	2921.54	1.08	254.1	120.4	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= $HC(CH_3)_2C_6H_5H$ (120.2 Da)
Sample 2 – i	1803.55	1739.13	1870.96	1.08	254.4	0	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= none, or cyclised
Sample 2 – ii *	2017.38	2798.14	3126.40	1.12	253.9	237.8	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= $CO_3C_6H_4C(CH_3)_2C_6H_5$ (238.3 Da)
Sample 2 – iii	2541.01	3213.15	3479.76	1.08	254.2	223.2	m= $CO_3C_6H_4C(CH_3)_2C_6H_4$ (254.3 Da) t= $HCOC_6H_4C(CH_3)_2C_6H_5$ (223.3 Da)

* Daltons

The Differences

- Tile Sample 1 differed from Tile Sample 2 by the presence of an extra polymer series, c (Figure 1a). This polymer series was software-predicted as:

  $HC(CH_3)_2C_6H_4[CO_3C_6H_4C(CH_3)_2C_6H_4]nH$

- Tile Sample 1 also differed by possession of polymers of higher mass (Figure 2)

Similarities

- In both tile samples the dominant series ("a" and "i") appears to be a cylised $CO_3C_6H_4C(CH_3)_2C_6H_4$.

Conclusions

Use of MALDI-TOFMS

- The analysis and use of polymer prediction software revealed differences of polycarbonate composition between the two tiles.
- MALDI-TOF-MS gave a quick comparison of polycarbonate formulae from two different manufacturers.

References

Org. Mass Spectrom. 28, 923-5: 1995