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ANALYSIS OF RESIDUAL PHOSPHORUS IN POLY(*p*-PHENYLENE BENZOXAZOLE), PBO, FILM BY X-RAY FLUORESCENCE (XRF) SPECTROMETRY

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Summary—Poly(*p*-phenylene benzoxazole), PBO, is a rigid rod polymer which is polymerized in polyphosphoric acid. Oriented POB film shows good mechanical strength, excellent thermal stability and solvent resistance, and low dielectric constant. The measurement of residual phosphorus in the film is necessary since residual phosphorus may impact the physical and electrical properties of the film. A rapid and non-destructive XRF method has been developed for the analysis of residual phosphorus content in PBO thin films (0.1–2 mil). The XRF method demonstrated good linearity over the range of 150–4100 ppm, with a detection limit of *ca* 40 ppm. The residual phosphorus in several PBO thin film samples was also measured using NMR spectroscopy, and excellent agreement with the XRF analysis was obtained.

Poly(*p*-phenylene benzoxazole) (PBO) film is a rigid rod polymer film showing high tensile modulus and strength, excellent thermal stability and solvent resistance, low moisture pick-up, and low dielectric constant.[1] The process of preparing PBO film comprises polymerization in polyphosphoric acid (PPA), extrusion of PPA/ PBO solution (dope) into sheet form, stretching of the PBO dope sheet to make a thin PBO dope film, removal of the acid solvent from the PBO dope film by coagulation with a polymer non-solvent, and then drying to remove the coagulant. The effectiveness of the solvent removal (coagulation) step can be evaluated by measurement of the residual solvent (phosphorus) in the dried PBO film. It is important to measure the amount of residual phosphorus in the finished product to be able to determine if this has any effect on the mechanical or electrical properties of the finished PBO film.

There are several methods available for measurement of residual phosphorus in films and fibers. A method using inductively coupled plasma emission spectrometry (ICP) which involves microwave oven digestion of the sample in a strong acid has been previously developed at Dow. However, there are several steps in the sample preparation for use of the ICP technique that make it less than desirable. For example, a long digestion period for breakdown of the PBO film, tedious dilutions and sample transfers, waste disposal problems, and loss of sample, are often encountered.

A new X-ray fluorescence (XRF) method for analyzing residual phosphorus in PBO thin films (0.1 to 2 mil) has been developed. This method is rapid, non-destructive, and requires as little as 5 mg of sample. The short analysis time (approximately 3 min) and minimal sample preparation make it suitable for routine analysis. Details of this XRF method and the detection limit, linearity, precision, and accuracy associated with it are discussed in this report. In addition, the use of NMR spectroscopy to corroborate the XRF measurements will be discussed.

EXPERIMENTAL

XRF instrumentation

A Kevex 770 XRF system with Toolbox analysis software (Fisons Instruments, San Carlos, CA, U.S.A.) was used for the X-ray fluorescence measurements. Rh tube was used

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for excitation and operated at 8 kV, 0.05 mA with no filter. The counting time was 100 sec. Toolbox software was used for spectral deconvolution including escape peak subtraction, background subtraction, peak integration, and quantitative analysis. An empirical background modeling technique was used to develop a background for phosphorus analysis. Details of the background modeling, escape peak substraction, and a peak integration can be found in Ref. 2.

Data processing for quantitative analysis

An energy-dispersive X-ray analysis using commercial software (EXACT) was used to determine the residual phosphorus level in PBO thin film.[2] This quantitative method requires a standard or a series of standards to establish a calibration coefficient for each element of interest. In addition, it uses fundamental parameter calculations to correct for sample matrix effects.[3,4]

In the XRF analysis of thin film, the fluorescence intensity of the sample increases as film thickness increases until the film is 'infinitely' thick to X-rays, at which point the X-ray fluorescence intensity becomes independent of sample thickness. Since the PBO film sample is not infinitely thick by X-ray standards, the actual PBO film thickness will affect the phosphorus analysis and a film thickness correction routine must be used. For this purpose, the FILM calculation routine supplied by Kevex Corporation[2,5] was also used.

Phosphorus standard preparation

In this study, a known amount of phosphorus was added to a series of phosphorus added polycarbonate thin films and used as standards for quantitative analysis. The standard polycarbonate polymer thin films were prepared by solution casting. The solution was prepared by dissolving bisphenol-A polycarbonate (GE Plastics, Pittsfield, MA, U.S.A.) and triphenyl phosphate (Chemplex Industries, Inc., Tuckahoe, NY, U.S.A.) in methylene chloride. A hand-held blade was used to control the thickness of polycarbonate film (*ca* 0.5 mil). Methylene chloride was evaporated at room temperature for 2 hr and the polymer films were then dried in a 40°C vacuum oven overnight.

Preparation for XRF analysis

For XRF phosphorus analysis, the PBO film was cut into 1.25″ diameter disks using a standard hole-punch and press. The XRF sample holder insert with a 1.25″ counter-bored opening was used to hold the film disk. An O-ring was placed on top of the film sample to keep it from moving under vacuum.

Mass thickness measurement

In order to compensate for PBO film thickness variations on XRF phosphorus measurements, the mass thicknesses of the samples and standards were used in the quantitative computation. The mass thickness was calculated from the weight and area of the respective films.

Sample preparation for NMR study

The solvent was prepared by nearly saturating methanesulfonic acid (MSA) with methanesulfonic acid anhydride (MSAA) to make an MSA/MSAA mixture (*ca* 84%). The MSA (Fluka Chemical Corp., Ronkonkoma, NY, U.S.A.) and MSAA (Lancaster Synthesis Corp., Windhan, NH, U.S.A.) were purified by vacuum distillation before use. The NMR samples were prepared by dissolving the PBO film (7–10 mg) in MSA/MSAA solvent (1.5–2.0 g). A solution of triphenylphosphine in MSA/MSAA was added as an internal standard. To insure complete dissolution, the samples were stirred and/or rolled overnight. The NMR spectra were collected with a GE-300 Spectrometer and collected either overnight or over three days to enhance the signal-to-noise ratio. Typical signal-to-noise values for the triphenylphosphine standard were 80 for overnight runs and 170 for three day runs.

RESULTS AND DISCUSSION

XRF method development

Two peak intensity evaluation methods (peak integration and peak-fitting deconvolution) are commonly used in XRF analysis to extract the fluorescence intensity in the region of interest.

Table 1. Comparison of XRF peak intensity evaluation

	Phosphorus XRF intensity (*cts/sec*)	
	Integration method	Deconvolution method
	49.99	36.38
	50.87	22.43
	50.50	45.92
	56.05	61.06
	51.24	49.47
	52.82	47.46
Average	51.91	43.58
SD	2.25	13.16

The results of the precision comparison of these two methods for a PBO film sample are summarized in Table 1 and show that the results from the peak integration routine are more precise for this measurement. Therefore, for the PBO thin film phosphorus measurement, the peak integration technique was used to extract the net intensity of phosphorus peak (1.90–2.11 keV) for quantitative analysis.

Linearity

The linearity of this method was examined over the range of 150–4100 ppm and the correlation coefficient over this range was 0.997. The excellent linearity over the range of interest suggests that a one point calibration could be used in the Kevex Toolbox EXACT/FILM routine without compromising accuracy. This is very important since the EXACT/FILM routine supplied by Kevex does utilize a single point calibration for the quantitative calculation.

Accuracy

The results of the accuracy study on the fabricated samples are summarized in Table 2.

Table 2. Accuracy study of XRF phosphorus measurement

Sample number	P added (%)	P measured (%)	Recovery (%)
1	0.4105	0.4000	97.4
2	0.4105	0.4000	97.4
3	0.4105	0.4000	97.4
4	0.4105	0.4300	104.8
5	0.4105	0.4200	102.3
6	0.2234	0.2100	94.0
7	0.2234	0.2100	94.0
8	0.2234	0.2100	94.0
9	0.2234	0.2300	103.0
10	0.2234	0.2300	103.0
11	0.1179	0.1200	101.8
12	0.1179	0.1200	101.8
13	0.1179	0.1200	101.8
14	0.1179	0.1300	110.3
15	0.1179	0.1300	110.3
16	0.0585	0.0590	100.8
17	0.0585	0.0590	100.8
18	0.0585	0.0540	92.3
19	0.0585	0.0540	92.3
20	0.0585	0.0530	90.6
21	0.0323	0.0349	108.0
22	0.0323	0.0328	101.6
23	0.0323	0.0328	101.6
24	0.0323	0.0341	105.6
25	0.0323	0.0330	102.2
26	0.0154	0.0155	100.6
27	0.0154	0.0160	103.9
28	0.0154	0.0144	93.5
29	0.0154	0.0168	109.1
30	0.0154	0.0175	113.6
		Average	101.0
		SD	5.9
		RSD	5.8

Table 3. Detection limit study of XRF phosphorus measurement

	Phosphorus measured (*ppm*)
	39
	26
	23
	4
	0
	28
	16
	10
	1
	3
Average	15
SD	13

Average recovery was 101.0% ranging from 90.6 to 110.3% with a relative standard deviation of 5.8%. The relatively large range in recovery can be attributed to the homogeneities of solid standards and the counting error of XRF readout system. However, the results show good agreement between the estimated concentration of phosphorus by the XRF method and the actual concentration of these fabricated samples.

Detection limit

Two phosphorus free polycarbonate films were used to examine the detection limit of this method and the results are shown in Table 3. The detection limit, defined as three times the standard deviation of the blank measurements, was 40 ppm. This is much lower than the typical phosphorus content of PBO film samples measured to date, in which the phosphorus content ranges from 200 to 5000 ppm.

Precision study

The precision of this method was determined by replicate analyses of two standard phosphorus

Table 4. Precision study of XRF phosphorus measurement

	Phosphorus measured	
	Film-1, % (0.24% P added)	Film-2, *ppm* (540 *ppm* P added)
	0.2400	572
	0.2400	535
	0.2300	536
	0.2400	517
	0.2400	539
	0.2400	539
	0.2400	518
	0.2400	549
	0.2400	550
	0.2400	539
Average	0.2390	539
SD	0.0030	16
RSD	1.32	2.97

Table 5. Comparison of phosphorus measurement by NMR and XRF

Sample number	Phosphorus content measured (*ppm*)	
	by XRF	by NMR
1	2500	2700
2	1600	1400
3	1500	1400
4	831	830
5	465	470
6	242	280

polycarbonate films. The results of this study are summarized in Table 4. For the 2400 ppm film, the relative standard deviation was 1.32% for 10 measurements. For the 540 ppm film, a relative standard of 2.97% was observed which is attributed to the increased background effect on the low concentration sample measurement.

Comparison of XRF and NMR analyses

The phosphorus content of several PBO film samples were first measured by the XRF technique and then dissolved in MSA/MSAA to check the results by NMR. In the NMR measurements, the concentration of residual phosphorus in the PBO film was calculated by the ratio of peak intensities of triphenylphosphine and H_3PO_4, where a known amount of triphenylphosphine had been added. This intercomparison is shown in Table 5, and the agreement between the two techniques is acceptable.

Inert species detection

There have been several elements found in the PBO film which are not directly related to the PBO processing, but appear to be a result of post processing and sample handling of the PBO thin film. The species found were Si, K, Ca, and S. Of these, the two with the most significant effect on the phosphorus determination are Si and S. This is important since silicate is often used as an antistatic agent in the plastic films and bags used to store PBO films. The Si and S peaks in XRF spectrum effect the phosphorus determination by skewing the background level, making it appear to be much higher than it actually is. In such cases, when background subtraction is done on the PBO film sample spectra the phosphorus level appears to be much lower than it actually is. It was found that this problem could be minimized by washing the PBO thin film with acetone or other solvents prior to XRF analysis.

CONCLUSIONS

A rapid and non-destructive XRF method with minimum sample preparation was developed and validated for the measurement of residual phosphorus in PBO thin films. Standard phosphorus polycarbonate thin films were used as a standard for quantitative analysis. A thin film computer program was used for quantitative analysis and to correct for the effect of film thickness variation in the measurements. In principle, this method could be used to measure the residual phosphorus or additives in any thin film.

The XRF method has been shown to be an accurate and reliable technique for measuring the phosphorus content of PBO thin films, and has been used successfully in the range of 100–5000 ppm. The detection limit was determined to be 40 ppm; however, the method has been used for analyzing samples down to 20 ppm using a longer preset time (200 sec). NMR spectroscopy was used to validate the results of this newly developed XRF method, and the agreement between the two techniques was considered to be excellent.

The non-destructive nature of the method is especially important when trying to examine the effects of residual phosphorus on other film properties, such as the dielectric constant, where the same film sample can be examined for both tests. The rapidity of the XRF measurement and the fact that it has been completely automated to handle up to 16 samples at a time, make it an ideal QA tool. It is currently being used on a routine basis to evaluate the effectiveness of different coagulating and leaching processes for residual phosphorus removal.

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