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PIXE Spectroscopy for Determination of Volatile Corrosion Inhibitor Concentration in Anticorrosion Polymer Films

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Summary. Anti-corrosion polymer films used for 0 to 6 years were investigated to determine the type and content of volatile corrosion inhibitors (VCI) and how long the films emit it to protect the metal surface encased by the film. By FTIR and DSC low density polyethylene (LDPE) was identified as the polymer carrier. Particle induced X-ray emission (PIXE) spectroscopy of anti-corrosion polymer films revealed significant concentration of molybdenum implying that corrosion inhibitor was molybdate based. The films were divided into three groups according to different rate of the VCI concentration decrease with increasing age. The division of films into groups and diffusion of VCI was confirmed by significant decrease of Mo content determined by PIXE spectroscopy after accelerated ageing in vacuum at 50°C. It was concluded that films with initial concentration of Mo above 6000 ppm emit VCI for at least 6 years while the films with less than 4000 ppm of molybdenum do not emit the VCI in the ambient conditions.

Keywords. IR spectroscopy; DSC; Diffusion; Molybdate; LDPE.

Introduction

Volatile corrosion inhibitors (VCI) or vapor phase corrosion inhibitors (VpCI) are chemical substances that, by evaporation from fluid or solid, create a monomolecular film on metal surface. Such film offers temporary corrosion protection, can easily be removed prior to the use of the metal item or even left untouched what is particularly beneficial in case of military equipment. One of the most important factors determining the efficiency of the VCI is its vapor pressure [1, 2] that has to be high enough to ensure the adequate VCI concentration to enable formation of the protective film on the metal surface and prevent corrosion. The vapor pressure is, among other factors, influenced by the form of VCI carrier. VCIs can be applied in number of forms such as powder, pellets, solutions in solvents or oils and, as in

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this case, can be coextruded in a polyolefinic film. Due to the simplicity of its application, such anti-corrosion polyolefinic films are being increasingly used in corrosion protection, from packaging of electronic products to protection of firearms of all sizes [1].

The anti-corrosion polymer films emit the VCI over a period of time thereby protecting the items encased by the film. To determine how long the films provide protection the first and very important step was to identify the VCI and determine its concentration and the rate of its evaporation, what was the goal of the presented investigation. In a further step the least concentration of VCI still providing anti-corrosion protection should be determined what will be objective of further research.

As a nondestructive method that at the same time provides qualitative and quantitative information about the sample, particle induced X-ray emission (PIXE) spectroscopy was chosen. It belongs to ion beam techniques because the sample is exposed to the ion beam of MeV energy range inducing different atomic and nuclear processes that lead to the emission of products. Each product carries information about the sample composition, or some other material property (Fig. 1).

When a charged particle (proton or heavier ion) enters the material, it encounters numerous inelastic collisions by sample atoms. From some of those numerous ionized atoms along the particle path, characteristic X-rays are emitted with a probability given by the X-ray production cross section. Advantages of PIXE spectroscopy stem from very high probability of X-ray emission – for most elements and sample types detection limits are of the order of 1 ppm, while simple X-ray spectra obtained by high energy resolution detectors make PIXE multielemental. Since the X-ray fluorescence yield and detector efficiency are lower for light elements, PIXE is most often used for the analysis of elements $11 > Z > 92$ so it can be employed for investigations of polymers or polymer containing samples. Some recent examples of application of PIXE to polymers follow. The diffusion of Se of $CuInSe_2$ absorber layers deposited into polyimide carrier foils of solar cells was detected by depth profiling with micro-PIXE method [3]. Diffusion of mono- and bifunctional monomers during and after photo-polymerization of acrylate based polymer gratings was monitored by PIXE and PIGE (particle induced γ-ray spectroscopy) [4, 5], and results were correlated to reactivity of monomers. *Tadić et al.* [6] measured distribution of Li, F, S, and Mn in gel-polymer, Li anode, and on the interfaces of gel-polymer, components of Li-ion battery, while *Moretto et al.* [7]

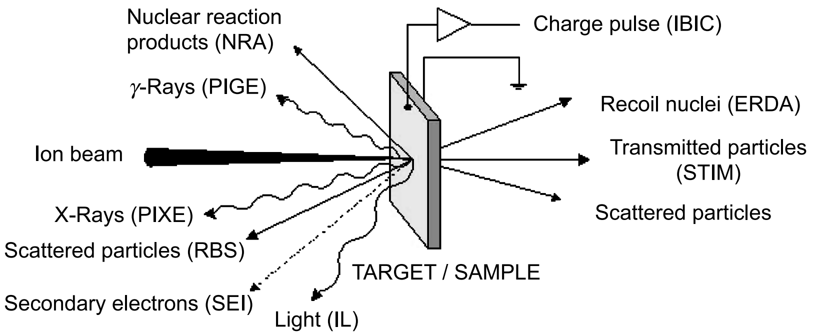

Fig. 1. The principles of ion beam analysis techniques

analyzed terthiophene porphyrin conducting polymers and found trapped cations and traces of water from the electrolyte in which the polymer was synthesized. Based on such evidence, PIXE was chosen as a particularly convenient method that could be applied for qualitative as well as for quantitative analysis of VCI of anti-corrosion polymer films without much sample preparation. Prior to that, identification of polymer carrier was performed by infrared spectroscopy and differential scanning calorimetry.

Results and Discussion

The Analysis of Polymer Carrier of the Anti-Corrosion Films

All the investigated anti-corrosion polymer films had the same FTIR spectrum shown in Fig. 2. The prominent absorptions at around 2900 cm^{-1}, out of the absorption range of the instrument because of film thickness, and absorptions at 1466 and 729 cm^{-1} indicate that the films are polyolefinic [8]. To identify the polyolefine, differential scanning calorimetry measurements on all anti-corrosion films were performed. The DSC thermograms had several characteristic patterns shown in Fig. 3, that are denoted so the thermogram type could be identified in Table 1 where the temperatures and total heats of melting are listed. In all cases an endothermic process between 100 and 120°C was present, what is the temperature range of low density polyethylene (LDPE) crystallite melting [9]. The onset of the melting process was just above 60°C what was important for setting the conditions for accelerated ageing of anti-corrosion films. No other processes at higher temperature were detected and taking into account the FTIR spectra, the polymer carrier of the anti-corrosive films was identified as LDPE.

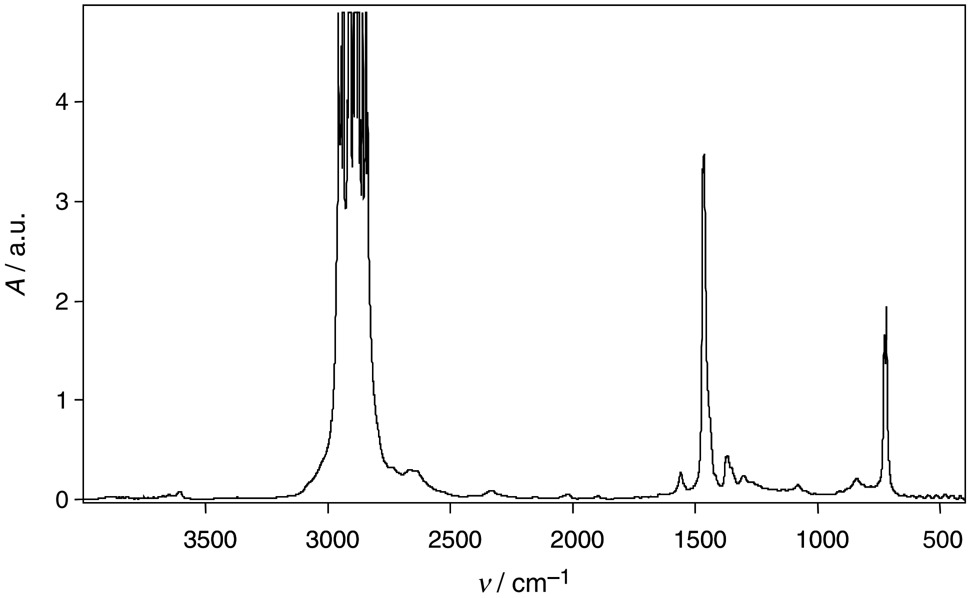

Fig. 2. FTIR spectra of analyzed anti-corrosion films

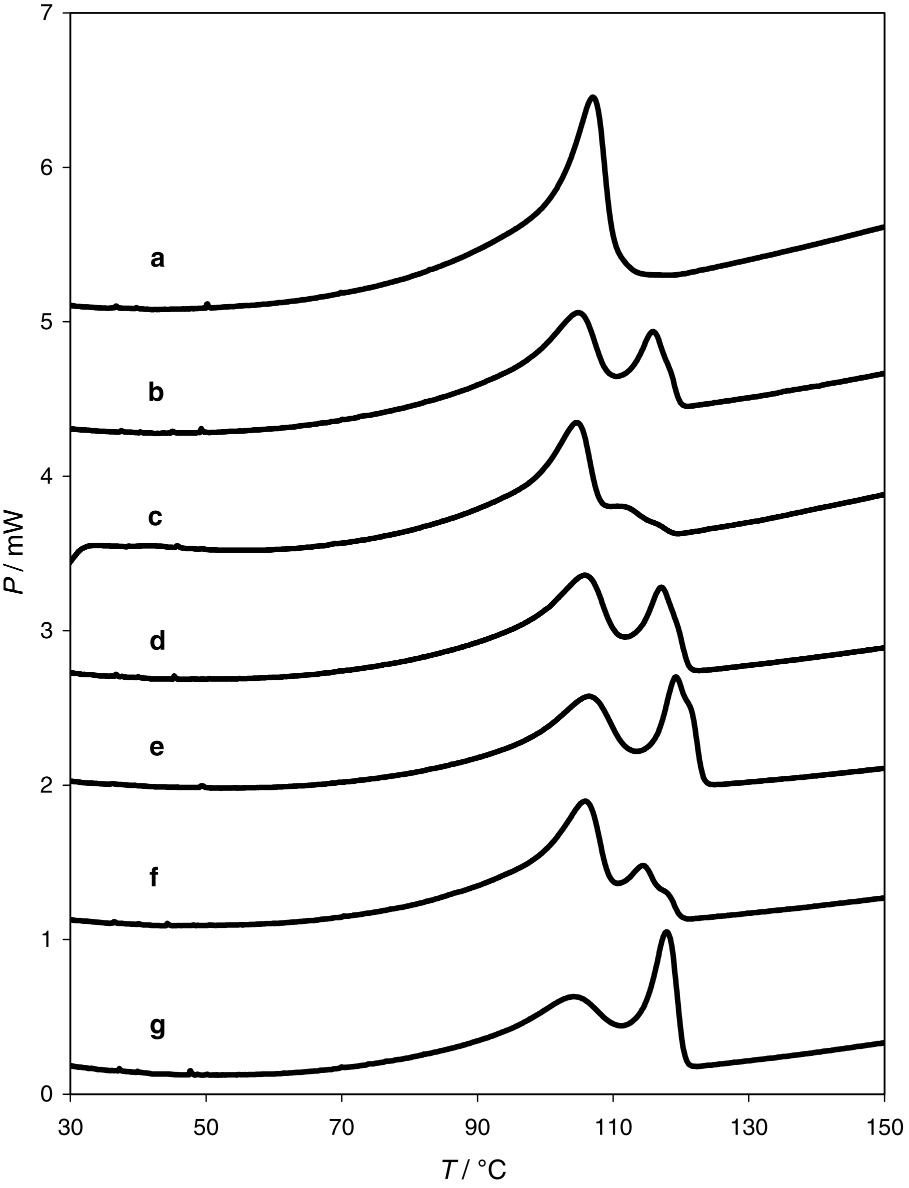

Fig. 3. Typical DSC thermograms of analyzed anti-corrosion films

In most cases the melting process was split into two maxima of different intensities at 105 and 118°C and in some cases the higher temperature peak had shoulder(s). Thermal history was excluded as the cause for double melting peaks since the same thermograms were obtained in the second heating run. The appearance of double peaks in most anti-corrosion films and even multiple processes in some samples stems from differences in branching of the corresponding LDPE because olefine chains of different length tend to crystallize separately [10]. The branching could not be further analyzed by FTIR because intensity of 2900 cm^{-1} absorptions was to high.

Table 1. The temperatures and heats of melting of investigated anti-corrosion films; thermogram types are shown on Fig. 3

Sample	Thermogram type	Peak 1 $T/°\mathrm{C}$	Peak 2 $T/°\mathrm{C}$	$\frac{\text{Total } \Delta H}{\mathrm{J\,g^{-1}}}$
19970	g	104.8	117.2	98.09
19971	f	105.8	114.6	83.49
19980	d	105.4	118.2	96.95
19981	d	104.8	117.2	99.45
19990	d	105.2	117.1	86.77
19991	d	105.8	117.2	83.24
19992	b	104.8	116.0	79.68
20000	g	104.8	117.8	88.61
20010	d	104.1	117.0	85.45
20011	c	104.6	/	94.41
20020	a	107.0	/	87.29
20021	e	104.8	117.0	85.45
20022	a	107.0	/	86.57
20030	e	106.2	119.2	86.45

VCI of the Anti-Corrosion Films

PIXE spectra of all anti-corrosion films, as received, were recorded. A typical PIXE spectrum is shown in Fig. 4, prominent Mo K_α peak was present in all cases and it is the most intense peak present in all films. After the correction for background, the molybdenum peak intensity was 1–2 orders of magnitude greater than any peak of other present elements. Such high concentrations of molybdenum

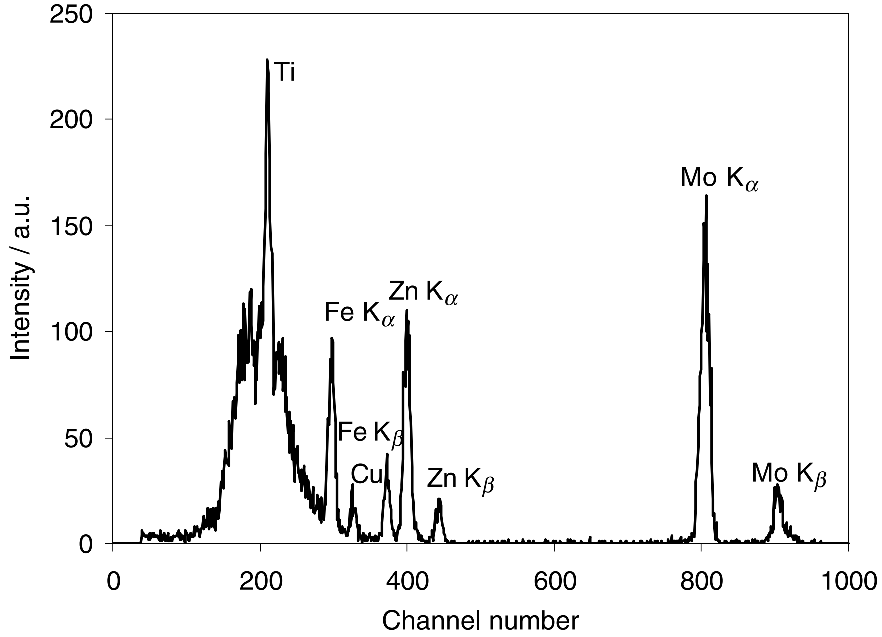

Fig. 4. Typical PIXE spectrum of an anti-corrosion film

imply that VCI in investigated anti-corrosion films was molybdate based. Molybdate anion, $MoO_4{}^{-2}$, is often used as corrosion inhibitor that is considered to be environment-friendly. It is classified as an anodic inhibitor without oxidizing properties, because of that oxygen has to be present for molybdate to provide corrosion inhibition. The mechanism of its anti-corrosion activity includes adsorption on the metal surface and incorporation into pre-existing oxide film. Based on temperature dependence of inhibition process, *El Din* and *Wang* [11] concluded that formation of bond is probable. There is no data on initial molybdate content of VCI in analyzed polymer films and its lowest concentration needed to provide anti-corrosion protection is also unknown. If the molybdate concentration in investigated polymer films was high enough, its characteristic absorptions at 915 and 460 cm^{-1} should be detected in FTIR spectra of the anti-corrosive films. As can be seen in Fig. 2 no such absorptions were detected so only highly sensitive PIXE spectroscopy could provide the information on concentration of molybdenum without introducing additional errors.

From the intensity of the Mo K_α the concentration of molybdenum in films was calculated as a measure of molybdate based VCI content in the anti-corrosion films under consideration. The concentrations of Mo plotted against the time passed from the beginning of use of each film are shown in Fig. 5.

The plot revealed that analyzed anti-corrosion films can be divided into three groups according to the molybdenum concentration that was the highest in group A films implying the highest initial concentration of VCI. Its concentration decreased with time faster than that of group B anti-corrosion films that had intermediate molybdenum concentration. In the group C are the films with lowest concentration of molybdenum that is apparently constant over time. No influence of LDPE structure (Fig. 3 and Table 1) on the rate of the VCI content decrease is seen for analyzed samples. The division of samples into groups and corresponding concentrations of Mo is listed in Table 2.

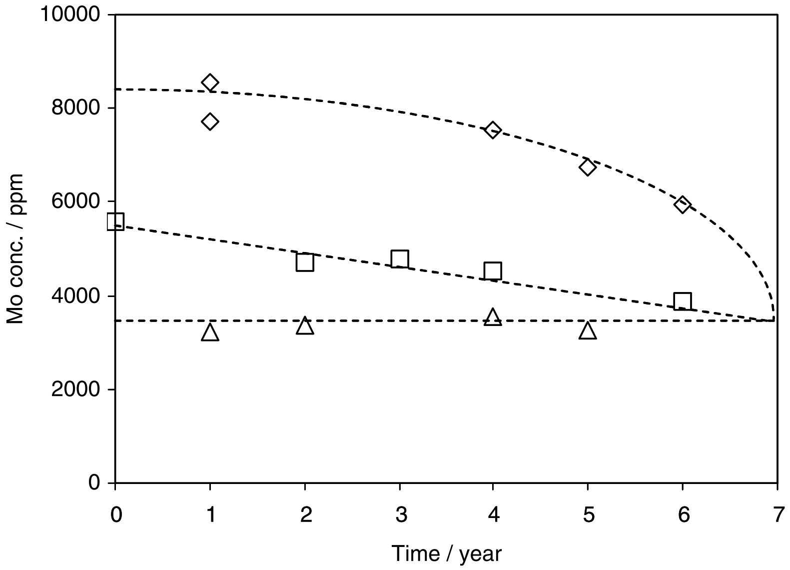

Fig. 5. The concentrations of molybdenum in analyzed anti-corrosion films of different age

Table 2. Three groups of anti-corrosion films differing in concentrations of molybdenum and in the rate of Mo concentration decrease

Year	A		B		C	
	Sample	Mo conc. ppm	Sample	Mo conc. ppm	Sample	Mo conc. ppm
1997	19970	5935	19971	3875		
1998	19981	6734			19980	3245
1999	19992	7522	19990	4542	19991	3553
2000			20000	4788		
2001			20011	4693	20010	3367
2002	20020	8534				
2002	20021	7715			20022	3220
2003			20030	5571		

In a group with the lowest molybdenum concentration the VCI content has obviously decreased to saturation level for the polyethylene film under ambient conditions. No further emission of VCI could be expected from films in group C and, consequently, no anti-corrosion protection could be expected of such films. Accordingly, the time at which concentration of VCI reaches 4000 ppm of Mo is set as end of life for the anti-corrosion polymer film. The concentration of molybdenum in anti-corrosion films of group A tends to reach that level in about 8 years, 7 years for films of group B. The lasting of anti-corrosion protection by protective

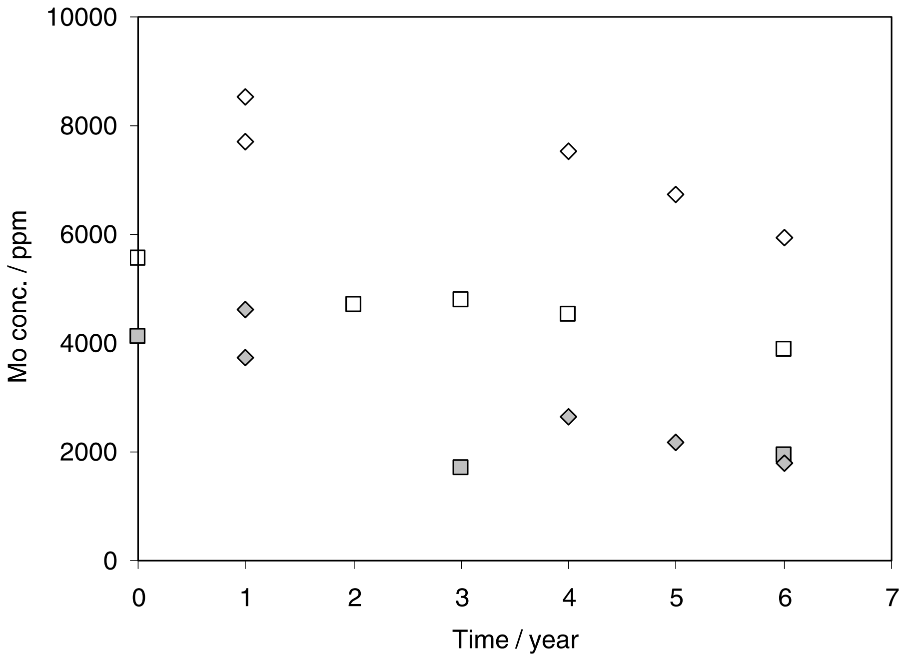

Fig. 6. The concentrations of molybdenum in selected anti-corrosion films of different age as received (white signs) and after accelerated ageing (grey signs)

layer formed during the period in which molybdate was emitted out of the anti-corrosion polymer film is not known and should also be investigated.

Anti-corrosion polymer films that showed molybdenum concentration decrease over time, *i.e.* those of group A and most of group B, were subjected to the accelerated ageing in vacuum at 50°C. The ageing temperature had to be below the start of the melting process because it could influence the diffusion of VCI and has been determined to begin at 60°C. After 223 days of the accelerated ageing PIXE spectroscopic determination of molybdenum content was repeated (Fig. 6). A significant decrease in molybdenum concentration occurred, more prominent for group A, confirming the evaporation of molybdate VCI out of the LDPE film. The differences between films of group A and group B were preserved after ageing, justifying the previous division of the samples into the groups. It should be noted that the final concentrations of Mo in aged films in most cases fell much below 4000 ppm what is a consequence of vacuum application during ageing so it is not possible to correlate the length of time of the accelerated ageing with ageing under ambient conditions.

Conclusions

PIXE analysis of characteristic X-rays revealed that VCI in the investigated anti-corrosion film samples of different age was molybdate based. The anti-corrosive polymer films can be divided into three groups that substantially differ in molybdate concentration and in the rate of its evaporation. Evaporation of molybdate based VCI and the division of films into groups was confirmed by repeated PIXE determination after accelerated ageing.

When the concentration of molybdenum in polymer films falls bellow 4000 ppm no emission of VCI can be expected under ambient conditions. For the anti-corrosion polymer films that showed molybdenum concentration decrease with time, it was estimated that significant VCI emission lasts up to 6 or 7 years, depending on the initial concentration of VCI.

Minimum concentration of molybdate based VCI in anti-corrosion polymer that is capable of formation of protective film on metal surface and how long that film, covered by the polymer no longer emitting VCI, remains on metal surface has yet to be determined.

Experimental

14 samples of new and used anti-corrosion films of age between 0 and 7 years, all produced by Cortec company, were analyzed. The samples were marked by the year of their application (first 4 numbers) and a number from 0 to 2 was added for multiple samples in a corresponding year. The samples were kept sealed at room temperature. Accelerated ageing of anti-corrosion films was performed in vacuum at 50°C for 223 days.

FTIR spectra of anti-corrosion films were taken on Bruker Tensor 27 with air as background, at room temperature.

DSC thermograms were recorded on Perkin Elmer DSC 7, in aluminum sample pans in nitrogen atmosphere. The temperature range was 0 to 200°C, scanning rate was 20°C/min, two heating and cooling cycles were recorded for each sample.

For recording of PIXE spectra anti-corrosion film samples were put into the vacuum chamber in which 3 MeV protons coming out of a 6 MV Tandem Van de Graaff accelerator induced X-ray emission that was detected by X-ray Silicon Drift Detector.

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