XPS Analysis of Plastic Resin Pellets

For

Dupont Canada Inc.
Research Centre
Kingston, Ontario

By

Surface Science Western
University of Western Ontario
London, Ontario

August, 1989

Prepared by:
Dr. R. Foerch
R.D. Davidson

NOTE: A FEW REFERENCES TO WORK ON NON-SPI SAMPLES HAVE BEEN REMOVED FROM THIS REPORT.

Introduction

Pellets of PVC, PE and ABS containing various levels of lead chromate ($PbCrO_4$) have been analyzed by X-ray photoelectron spectroscopy (XPS or ESCA) to determine the levels of lead actually on the surface of the pellets. Techniques such as IR and SEM have indicated high levels of Pb present on the surface, however both these techniques probe beyond depths of several hundred Angstroms into the sample, thus probing the bulk polymer as well as the surface. XPS, on the other hand probes the first few monolayers to an approximate depth of 30-50 Angstroms.

During XPS analysis a sample is irradiated with monochromatized X-rays of known energy causing the ejection of photoelectrons from all elements (except hydrogen) within the sample. The kinetic energy (E_{KE}) of the ejected electron is equal to

$$E_{KE} = E_{Al\ K\alpha} - E_B - \Phi$$

Where $E_{Al\ K\alpha}$ = energy of the incident photon and
E_B = binding energy of the electron / eV
Φ = work function (usually negligible)

Thus, by measuring E_{KE} of the photoelectron and knowing $E_{AlK\alpha}$, E_B can be calculated. XPS provides both qualitative and quantitative information on the elemental composition of the sample.

Experimental

X-ray photoelectron spectroscopy was performed on the polymer pellets using an SSX-100 Surface Science Laboratory X-ray photoelectron spectrometer which utilizes monochromatic Al Kα X-rays for excitation of the samples. The elemental broad scans were recorded using a pass energy of 148.00eV and an X-ray spot size of 1000μm or 600μm analyzing binding energies between 0 and 1000eV.

Samples A1, A2, B1, B2 and C2 were analyzed on the cylindrical, the end and on a fractured surface. On A1, A2 and B2 the cylindrical surface was sputtered for 2 minutes using Argon to probe deeper into the surface. B1 was sputtered on the fractured surface.

Results

XPS results have been tabulated in Table 1 and values are given in atomic %. They appear to indicate that when the bulk polymer is PVC, lead is detected even at a

concentration by weight of 2%. On the other hand if the bulk polymer was PE, lead is detected at a concentration level by weight of 50%, but is not detected if the concentration level is 2%. However, when the bulk polymer is ABS, no lead is detected.

Samples A1, A2, B1 and B2 show levels of Pb on the cylindrical surface ranging from 1.2% to 0.01% which represents the detection limit of XPS for Pb. Upon sputtering the cylindrical surface (A1, A2, B2) for 2 minutes using Argon (to roughly a depth of 100 Angstroms), the amount of Pb very noticeably decreases suggesting lesser amounts of Pb further into the surface. Other elements detected were chlorine, silicon and very low levels of chromium in B1. Barium and cadmium were detected in sample A2.

Analyzing the end surfaces of samples A1 and A2, similar levels of Pb were observed as on the cylindrical surfaces. B1 shows slightly more Pb on the end surface of the pellet, while B2 shows no Pb.

Fractured surfaces of A1, A2 and B2 show similar levels of lead compared to the cylindrical surfaces. B1 shows a similar level of Pb on the fractured surface as on the outside cylindrical surface. When sputtering the fractured surface, XPS indicates an increased level of both Pb and Cr being exposed from further inside sample B1. Chromium was also be detected on A1 (cylindrical surface) and B1 (end and sputtered fracture).

Sample C2 was extremely "clean", showing no Pb or Cr on any surfaces examined, even after sputtering. However, it was noticed that upon sputtering the relative % of N and O on the surface decreased. Otherwise all surfaces showed similar amounts of O and N.

SEM Results

A series of secondary electron SEM micrographs were obtained from samples B1 and B2. The micrographs are identified on an attached sheet, Table 4.

The micrographs clearly show the difference in the pigment loading levels between 2% and 50% $PbCrO_4$ in the PE samples. The pigment particle size is approximately 0.5 - 1.0µm. The different contrast levels for the particle (from bright white to a faint grey) suggest that the particles are at different depths within the matrix material. Pb X-ray

mapping was carried out on the 2% $PbCrO_4$ sample. The results show Pb, as expected, associated with the pigment particles.

Conclusion

The XPS results indicate that lead ($PbCrO_4$) is present in small amounts on the surface of $PbCrO_4$ doped PVC pellets. Upon sputtering deeper into the surface less Pb is detected. The concentration of Pb on the fractured surface is very similar to that on the cylindrical side, suggesting that the lead is present on the surface.

Pb is detected in very small amounts in the $PbCrO_4$ doped PE, even for the 50% doped pellets. The fractured surface shows similar amounts of Pb, yet upon sputtering, the concentration of Pb clearly increases. This indicates that even though some Pb is present on the surface, the majority is deeper inside the sample.

In the $PbCrO_4$ doped ABS, lead and chromium are not detected on any surface.

Recommendations

The objective of this preliminary study was to determine if $PbCrO_4$ pigment particles were exposed at the surface of the plastic resins. Intriguing XPS results, especially for the PVC samples, suggest that the pigment is concentrated at the surface. Further characterization with XPS and SEM may result in a better understanding of the location of the pigment particles in the PVC.

It may be possible to carry out further SEM examination using stereo imaging to determine whether or not the pigment particles are standing proud of the surface. Further XPS analysis on additional samples may aid in this study. For example, XPS analysis of freshly fractured (perhaps cooled to liquid N_2 temperatures) resin pellets would provide a good 'bulk' analysis to compare to the extruded cylindrical surfaces.

NOTE: THESE VALUES ARE IN ATOMIC %

Table 1. XPS analysis of $PbCrO_4$ containing polymer pellets.

sample	%C	%N	%O	%Cr	%Pb	%Cl	%Si	%Ba	%Cd	CALCULATED % WEIGHT Pb
A1 33% $PbCrO_4$ in PVC										
cylindrical side	82.7	-	10.1	0.2	1.2	5.0	1.0	-	-	15.4
cyl. side sputtered	91.5	-	8.1	-	0.1	0.4	-	-	-	1.7
endview	86.3	-	12.4	-	1.3	-	-	-	-	18.0
fractured	79.2	-	9.7	-	1.1	10.0	-	-	-	13.5
A2 2% $PbCrO_4$ in PVC										
cylindrical side	78.6	-	9.3	-	0.3	10.4	-	0.8	0.7	3.6
cyl. side sputtered	91.2	-	3.4	-	0.04	5.3	-	0.1	-	0.6
endview	84.3	-	9.1	-	0.2	5.4	-	0.5	0.5	2.7
fractured	72.2	-	4.7	-	0.1	22.9	-	0.2	0.1	1.2
B1 50% $PbCrO_4$ in PE										
cylindrical side	97.3	-	2.7	-	0.03	-	-	-	-	0.5
endview	96.1	1.2	2.2	0.05	0.1	-	0.35	-	-	1.7
fractured	98.7	-	1.3	-	0.05	-	-	-	-	0.9
frac. side sputtered	93.3	0.3	4.5	0.8	0.6	-	0.6	-	-	4.0
B2 2% $PbCrO_4$ in PE										
cylindrical side	99.2	-	0.85	-	0.01	-	-	-	-	0.2
cyl. side sputtered	98.2	1.1	0.75	-	-	-	-	-	-	<0.2 NOT
endview	99.2	-	0.8	-	-	-	-	-	-	<0.2 DETECTED
fractured	100	-	-	-	-	-	-	-	-	<0.2
C2 2% $PbCrO_4$ in ABS										
cylindrical side	90.3	4.9	4.3	-	-	-	0.5	-	-	<0.2 NOT
cyl. side sputtered	95.1	2.0	2.9	-	-	-	-	-	-	<0.2
endview	92.1	4.6	3.3	-	-	-	-	-	-	<0.2 DETECTED
fractured	89.1	5.0	4.2	-	-	-	1.8	-	-	<0.2