Determination of inorganic constituents and polymers in metallized plastic materials

E. P. Soares,[1,2] M. Saiki,[1]* H. Wiebeck[3]

[1] *Neutron Activation Analysis Laboratory, IPEN/CNEN-SP, Avenida Lineu Prestes, 2242, Cidade Universitária,*
CEP 05508-000, São Paulo, SP, Brazil
[2] *Escola SENAI "Fundação Zerrenner", Rua Serra de Paracaina, 132, Cambuci, CEP 01522-020, São Paulo, SP, Brazil*
[3] *Chemical Engineering Department, Escola Politécnica, USP, Caixa Postal 61548, CEP 05424-970, São Paulo, SP, Brazil*

This work presents results obtained in the analyses of metallized plastics by neutron activation analysis (NAA) and results of polymer identification by infrared spectroscopy (IR) and differential scanning calorimetry (DSC). Metallized plastics of packagings, automobile accessories, toys, house wares, cards and compact discs were selected for these analyses. Toxic elements such as As, Cd, Cr, Ni, Sb and Sn as well as Ba, Br, Ca, Co, Fe, Sc, Se, and Zn were determined and their concentrations presented great variability. IR and DSC assays indicated that polyethylene, polypropylene, poly(ethylene terephthalate), polycarbonate, acrylonitrile-butadiene-styrene terpolymer are main types of polymers used in metallized plastics.

Introduction

In the past years, polymers have been applied in several fields of state of art technology, such as civil constructions, automotive industries, electro-electronic productions and packagings.[1] There is also an increasing use of metallized plastics, since they cost less than casting metals and present light weight, high resistance to corrosion, and versatility.[2,3]

Although many improvements in life quality can be attributed to plastics, it seems to be considerably less attractive as the accumulation of solid waste becomes a major environmental issue because of problems associated with its disposal. Plastic products could contain heavy metals originated from both additives used as polymer stabilizers, coloring agents, catalysts or filling materials and from contamination during manufacturing and recycling. Plastics are becoming an environmental issue regarding solid waste incineration.

At present, solid waste disposal is an increasing problem all over the world and in order to solve the problem, incineration and recycling are being proposed as a feasible solution to reduce the great quantity of urban solid waste. Besides, plastics are being extensively used in food, drink, blood, and medicine packaging storage. As toxic compounds may migrate from plastic to stored materials, there is also great concern regarding health hazards.

Consequently, toxic element determination and polymer identification in plastic materials are of great interest. From the environmental monitoring point of view, elemental analyses of plastics may contribute to the identification of possible sources of heavy metals present in incinerated solid waste and its gas emission. Polymer identification is also vital for selecting types of plastics to be recycled.

In a previous work, plastic materials originated from household and hospital wastes were analyzed.[4] This work presents results obtained in the analyses of metallized plastics by neutron activation analysis (NAA) and in the identification of polymers by infrared spectroscopy (IR) and differential scanning calorimetry (DSC).

Experimental

Samples of metallized plastics

Samples of metallized plastics were from food (appetizers, fried potatoes, smoke-dried meat), cosmetics (lipsticks, perfumes) packagings, automobile accessories (headlights, horn ornaments, wheel hub and logotypes), toys, house wares, identification and phone cards and compact discs. For NAA, these samples were cut or smashed into chips or strips smaller than 10 mm × 10 mm and then they were wiped with a cotton pad soaked with hexane p.a. grade and distilled water and finally dried at room temperature. For IR and DSC analyses, the samples were cleaned the same procedure used for NAA.

Standards

Standard solutions of As, Ca, Ba, Co, Cr, Fe, Ni, Sb, Sc, Se and Sn from Spex Certiprep Chemical were used to prepare synthetic standards of elements for comparative neutron activation analysis. The standard stock solutions of Br, Cd and Zn were prepared dissolving the element in the metallic form or its salt of high purity with adequate reagents. Concentrations of all this elements in the stock solutions were higher than

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* E-mail: mitiko@curiango.ipen.br

1.0 mg·ml^{-1}. Some of these stock solutions were diluted and used to prepare single or multielemental standards. 50 or 100 μl of these solutions were pipetted onto sheets of Whatman No. 41 filter paper and after drying at room temperature in a desiccator, these sheets were placed in clean polyethylene bags and irradiated with the samples. The quantity of each element in the standards varied from 0.06 to 500 μg.

Procedure for NAA

About 120–180 mg of the sample weighed and heat-sealed in polyethylene bags were irradiated at the IEA-R1 research nuclear reactor for a period of 16 hours and under a thermal neutron flux of $5 \cdot 10^{12}$ n·cm^{-2}·s^{-1}, with elemental synthetic standards. After about five days of decay time, samples and standards were fixed onto stainless steel planchets for the gamma-ray measurements. The measurements were carried out using a Canberra system, consisting of a Model GX2020 hyperpure detector, which is connected to a Model 1510 integrated processor and S100 card. The resolution of the system (FWHM) used was of 0.80 keV for 121.97 keV of ^{57}Co photopeak and 1.80 keV 1331.49 keV of ^{60}Co photopeak. Counting times varied from 6,000 to 50,000 seconds, depending on the half-lives or activities of the radioisotopes considered. The gamma-spectra were processed using VERSAO2 computer program.[5] The radioisotopes measured were identified according to their half-lives and gamma-ray energies. The radioisotopes and their respective gamma-ray energies (in keV) utilized were: ^{76}As (559.1), ^{31}Ba (383.2); ^{82}Br (776.5); ^{47}Ca (1297.5); ^{115}Cd (336.2 and 527.9); ^{60}Co (1332.2); ^{51}Cr (320.0); ^{59}Fe (1099.2); ^{58}Co (810.8); ^{122}Sb (564.2); ^{46}Sc (889.3); ^{76}Se (264.7); ^{113}Sn (391.7) and ^{65}Zn (1115.5).The elemental concentrations were calculated by comparative method.

Quality control of the results was evaluated by analyzing certified reference materials NIST-1577b Bovine Liver of National Institute of Standards and Technology and IMEP-10 Polyethylene of the Institute for Reference Materials and Measurements, Commission of the European Communities (IRMM).

Procedure for IR analysis

First, the plastic was isolated from the metal excepting in the case of plastic films samples that were measured directly. Plastic samples free of metal part were obtained by immersing them in concentrated nitric or hydrochloric acid for a time enough to dissolve the metal without affecting the polymer according to the

procedure described in Reference 6. These samples without metallic surface were washed with deionized water, dried at room temperature before the measurements. Some metallized plastics were dissolved using organic solvent, such as chloroform, ethyl methyl ketone or ethyl acetate or some of them were also submitted to a pyrolysis. The organic solvent was evaporated and a film was obtained for IR measurements. When the pyrolysis process was applied, the vapor formed was collected on a surface of KBr crystal and analyzed, afterwards. The equipment used was a Fourier transform infrared spectrophotometer, Nicolet IR 550 series II, with a resolution of 4.0 cm, beamsplitter of KBr and DTGS/KBr detector. The function "find peaks" was used to obtain absorption bands. The polymers identification was carried out comparing a sample spectrum with standard spectra,[7] and then the interpretation of absorption bands was performed.

Procedure for DSC analysis

Samples were cut in small pieces to be analyzed in a thermal analyzer model DSC 910 from TA Instruments and using a heating rate of 10 °C·min^{-1} for temperatures ranging from 20 to 350 °C. For peak identification, the DSC curves obtained for the samples were compared with those presented by BRANDUP.[8]

Results and discussion

Table 1 presents the concentration ranges of As, Ba, Br, Ca, Cd, Co, Cr, Fe, Ni, Sb, Sc, Se, Sn and Zn determined in metallized plastics of computer discs, telephone and identification cards and automobile accessories. As can be seen in this table, not all the elements were detected in some samples and the range of elements is varying from few ppb to percentage levels in samples of same type. The compact discs presented the lowest concentrations of most elements presented in this table, and in metallized plastics of telephone and identification cards were found toxic elements such as As, Cd, Sb and Sn. In metallized plastics of telephone cards, the highest concentration of Ni found was of 0.1% and for Sn was of 7.8% and in identification cards the concentration of Cd found was 761 μg·g^{-1}. The high concentrations of these elements are due to a thin layer of metal present inside these cards. High concentrations of Ca were detected in some metallized plastics from automobile accessories since compounds of this element are used to improve their properties and make it cheaper.

Table 1. Range of elemental concentrations obtained in metallized plastics of compact discs, telephone and cards and automobile accessories

Element	Compact discs	Telephone cards	Identification cards	Automobile accessories
As, $\mu g \cdot kg^{-1}$	1.3 ± 0.5[a]	747 – 775	195 – 678	60 – 258
Ba, $\mu g \cdot g^{-1}$	2.3 – 379[b]	613 – 23874	338 – 383	4.5 – 51
Br, $\mu g \cdot g^{-1}$	0.28 – 0.45	0.73 – 2.18	1.00 – 4.38	0.33 – 14.8
Ca, $mg \cdot g^{-1}$	0.031 – 0.068	7.9 – 9.4	6.2 – 18.95	0.085 – 272.4
Cd, $\mu g \cdot g^{-1}$	ND[c]	37.2 ± 0.3	2.6 – 761.0	0.064 – 0.410
Co, $\mu g \cdot g^{-1}$	0.016 – 0.022	0.67 – 1.43	0.15 – 0.84	0.017 – 3.7
Cr, $\mu g \cdot g^{-1}$	0.166 – 0.45	7.3 – 8.6	0.27 – 0.50	2.01 – 24.6
Fe, $\mu g \cdot g^{-1}$	1.7 ± 0.4	9 – 11	10 – 21	10 – 203
Ni, $\mu g \cdot g^{-1}$	ND	1033 – 1115	ND	1.8 ± 0.3
Sb, $\mu g \cdot kg^{-1}$	3.8 – 155.2	430 – 457	1775 – 21693	5.2 – 5538
Sc, $\mu g \cdot kg^{-1}$	0.06 – 0.82	166 – 177	156.1 – 176	10.7 – 150.8
Se, $\mu g \cdot g^{-1}$	ND	4.4 – 9.6	1.4 – 6.5	0.41 ± 0.04
Sn, $mg \cdot g^{-1}$	0.001 – 0.0029	69.2 – 78.6	2.0 – 3.8	ND
Zn, $\mu g \cdot g^{-1}$	5.3 – 5.8	3.5 – 5.3	4.2 – 5.5	5.1 – 1068

[a] Results with uncertainties indicate that the element was found only in one sample.
[b] Range of elemental concentrations. Number of samples analyzed varied from 2 to 4.
[c] Not detected.

Table 2. Range of element concentrations obtained in metallized plastics of food and cosmetic packagings, toys and house wares

Element	Food packagings	Cosmetic packagings	Toys	House wares
As, $\mu g \cdot kg^{-1}$	122 – 191[a]	1.4 – 386	96 ± 3	17 – 811
Ba, $\mu g \cdot g^{-1}$	35 – 280	14 – 908	ND	13 ± 2
Br, $\mu g \cdot kg^{-1}$	552 – 1752	95 – 3039	298 – 436	163 – 2685
Ca, $\mu g \cdot g^{-1}$	306 ± 77	134 – 675	67 ± 27	246 – 1872
Cd, $\mu g \cdot g^{-1}$	0.98 ± 0.14	0.029 – 518.2	ND	21.3 – 28.0
Co, $\mu g \cdot kg^{-1}$	14 – 3922	18 – 8458	1715 – 12390	45 – 4541
Cr, $\mu g \cdot g^{-1}$	0.17 – 163	0.08 – 54.9	0.024 – 0.67	1.8 – 9.3
Fe, $\mu g \cdot g^{-1}$	10 – 918	7 – 58	5 – 135	44 – 852
Sb, $\mu g \cdot kg^{-1}$	7.2 – 44346	3.8 – 5888	4.4 – 35	19.0 – 3898
Sc, $\mu g \cdot kg^{-1}$	2.1 – 135.5	0.45 – 114	10.2 ± 0.3	2.3 – 107.5
Se, $\mu g \cdot kg^{-1}$	38 – 3591	36 – 33006	ND	64 – 5673
Zn, $\mu g \cdot g^{-1}$	10.1 – 1088	4 – 593	113.3 – 154.1	37.1 – 124.3

[a] Range of elemental concentrations. Number of samples analyzed varied from 2 to 8.

Table 2 presents concentration ranges of the elements As, Ba, Br, Ca, Cd, Co, Cr, Fe, Sb, Sc, Se, and Zn determined in metallized plastics of food and cosmetic packagings as well as of toys and house wares. Elements Sb and Cr were detected in all samples analyzed and their contents varied from 0.004 to 44.3 $\mu g \cdot g^{-1}$ for Sb and from 0.02 to 163 $\mu g \cdot g^{-1}$ for Cr. Elements As and Cd were detected in some metallized plastics and their concentrations were lower than 0.8 and 520 $\mu g \cdot g^{-1}$, respectively. The high concentrations of Cd found in cosmetic packagings probably are originated from a compound of this element used as pigment and the high concentration of Sb in some food and cosmetic packaging are probably originated from the catalyst used in plastic manufacture. Some metallized plastics of cosmetic packagings presented the highest concentrations of most elements analyzed. Metallized plastics of toys did not present high concentrations of toxic elements.

The detection limits of the elements were evaluated according to CURRIE[9] in different metallized plastic samples and these values are presented in Table 3. As can be seen in this table, these values are lower than 280 $\mu g \cdot g^{-1}$ and dependent upon the sample composition.

In Table 4 are presented results obtained in the analysis of reference materials and certified values for comparison. The results obtained indicate a good agreement with certified values. The relative error were lower than 10.2% and the relative standard deviations varied from 0.2 to 14%.

Table 3. Detection limit values obtained for metallized plastic analysis

Element	Metallized plastics of			
	Food packaging	Phone card	Lipstick packing	Mirror holder
As, $\mu g \cdot kg^{-1}$	13.4	422.8	3.1	529.7
Ba, $\mu g \cdot g^{-1}$	29.3	12.9	–	6.9
Br, $\mu g \cdot kg^{-1}$	271.2	199.5	8.3	242.2
Ca, $\mu g \cdot g^{-1}$	$-^a$	270.4	70.9	280.7
Cd, $\mu g \cdot kg^{-1}$	423.3	790.5	–	792.9
Co, $\mu g \cdot kg^{-1}$	18.4	15.1	19.6	17.4
Cr, $\mu g \cdot g^{-1}$	0.2	0.2	0.06	0.1
Fe, $\mu g \cdot g^{-1}$	–	7.3	8.1	10.1
Ni, $\mu g \cdot g^{-1}$	5.2	3.5	–	2.7
Sb, $\mu g \cdot kg^{-1}$	13.2	11.7	1.4	11.0
Sc, $\mu g \cdot kg^{-1}$	1.4	1.5	1.2	1.4
Se, $\mu g \cdot kg^{-1}$	147.4	270.2	–	99.9
Sn, $\mu g \cdot g^{-1}$	44.8	18.3	3.5	–
Zn, $\mu g \cdot g^{-1}$	0.7	0.6	0.7	0.6

[a] Indicates that the detection limit was not evaluated.

Table 4. Concentrations (in $\mu g \cdot g^{-1}$) obtained for certified reference materials

Element	1577b Bovine liver			Polyethylene IMEP-10		
	M ± SD	RSD, %	Ref. 10	M ± SD	RSD, %	Ref. 11
As				9.45 ± 0.08	0.8	9.61 ± 0.57
Br	9.51 ± 0.04	–	(9.7)	308.4 ± 0.5	0.2	280 ± 24
Ca	105 ± 14	13	116 ± 4			
Cd	0.49 ± 0.07	14	0.50 ± 0.03	108.9 ± 1.0	8.9	119.72 ± 6.29
Co	0.297 ± 0.003	–	(0.25)			
Cr				95.6 ± 1.7	1.8	100.9 ± 5.7
Fe	181 ± 2	1.1	184 ± 15			
Zn	125.8 ± 0.3	0.2	127 ± 16			

[a] M±SD – arithmetical mean and standard deviation from 3 to 8 determinations.
[b] RSD: Relative standard deviation.
[c] Data in parentheses are informative numbers.

Table 5. Identification of polymers in the metallized plastic samples

Metallized plastic sample	Method of analysis	
	IR	DSC
Food packagings	PE;[a] PET; PA; PP	PE; LDPE; HDPE; PET; PA6; PP
Cosmetic packagings	ABS; PP; PS	ABS; PP; PS
Automobile accessories	PMMA; ABS, PC	PMMA; PE; ABS; PC
Computer discs	PC	PC
Telephone cards	ABS	ABS
Identification cards	EVA; PVC	PVA; PVC; EVA
Toys	ABS; PS; BR	ABS; PS
House wares	PP; ABS; PA	PP; ABS; PA6.6

[a] PE – Medium density polyethylene; PET – poly(ethylene terephthalate); PA – polyamide; PP – polypropylene, LDPE – low density polyethylene; HDPE – high density polyethylene; PA6 – polyamide 6; ABS – acrylonitrile-butadiene-styrene terpolymer; PS – polystyrene; PMMA – poly(methyl methacrylate); PC – polycarbonate; EVA – poly(ethylene vinyl acetate); PVC – poly(vinyl chloride); PVA – poly(vinyl acetate); BR – polybutadiene; PA6.6 – polyamide 6.6.

Results obtained in IR and DSC analyses presented in Table 5 indicate that several types of polymers are being metallized. By applying IR and DSC tests it was possible to identify polyethylene, polypropylene, poly (ethylene terephthalate), polycarbonate, poly(methyl methacrylate), acrylonitrile-butadiene-styrene terpolymer, polybutadiene, poly(vinyl chloride), poly(vinyl acetate), poly(ethylene vinyl acetate), polyamide, polystyrene in metallized plastic materials.

Conclusions

NAA could be successfully applied for the determination of toxic elements found in metallized plastics. IR and DSC analyses also indicated that several types of polymers are being metallized. Consequently, these techniques can supply important information to select plastics for its recycling or incineration so that the contamination of the environment does not occur. Elements found in samples indicated that toxic metals were also used in the metallization.

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