A STUDY OF KINETICS OF METAL LEACHING FROM POLYPROPYLENE MATRIX USING A HYPHENATED MASS SPECTROMETRIC TECHNIQUE

*S Stephen[1], T Shah[2], AE Pillay[1] and E Siores[2,3]
[1]Department of Chemistry, The Petroleum Institute, Abu Dhabi, UAE
[2]Institute of Materials Science and Innovation, Bolton University, UK
[3]TEI – Athens, Greece

ABSTRACT

In this study polypropylene samples doped with varying levels of Mg, Ti and Zn were subjected to leaching under different pH conditions for a period of six months. Laser ablation and SEM techniques were used to investigate the samples in order to verify the presence of metals in the matrix. The leachates were subsequently analyzed by ICP-MS and the data were processed to compute the reaction kinetics. It was found that for all three metals of interest the leaching process was governed by first-order kinetics. The rate constant for the leaching reaction was noticeably low denoting that metal migration from polypropylene is protracted and does not particularly constitute a potential hazard. Significant differences between the leaching behavior of Ti and Mg/Zn from the polypropylene matrix were observed. The mechanism of the leaching process was considered to be analogous to aqueous degradation of polymorphic crystal structures of the embedded dopants.

Keywords: ICP-MS, SEM, polymers, metal leaching, laser ablation.

INTRODUCTION

Polymeric materials (e.g. polypropylene) are commonly used for packaging fluids such as edible oil, water, fruit juices, medical implants and oral pharmaceutical solutions. These polymers often contain metal residues, which could migrate into the encapsulated product and affect its performance or increase its level of toxicity. Migration studies of this nature are known; however, the rates of such migration and evaluation of kinetic factors, such as reaction order, have not been previously explored in depth. Leaching of metals from polymeric materials has always been a subject of interest. It is known that metals leach out of polymers under various conditions (Cheng *et al.*, 2010). Sharp thermal changes and other physical and chemical factors are known to influence leaching of metals from polymers. Studies have been conducted on assessing leaching of individual metals, often those that are toxic (Keresztes *et al.*, 2009). Nakashima et al, have studied the extent of toxic metal leaching from macro plastic litter on the Ookushi beach in southwestern Japan (Nakashima *et al.*, 2012). Antimony is known to be used widely as a catalyst for poly-condensation reactions in the production of polyethylene terephthalate used to make PET bottles. A significant amount of antimony is known to leach into beverages stored in PET bottles, which is a genuine health concern (Doremus, 1895). Polymers are also finding wider applications in packaging industries, replacing most or all of the metal containers. Various metals, mostly of the toxic nature are added to polymers as plasticizers,

catalysts, stabilizing agents, processing aids and pigments (Takahashi *et al.*, 2008; Teuten *et al.*, 2009). Coe and Rogers (1997) investigated the effects of marine debris and leaching of toxic materials on marine life, which eventually led to toxins entering the food chain. A more recent study by Derraik (2002) has highlighted the fact that marine life is polluted by plastic waste which is seen widely dispersed in the oceans. A recent study was conducted by Nakashima *et al.* (2011) on heavy metals percolated from plastic litter washed on the shores. The study proved to be significant in revealing appreciable concentrations of Pb leaching out of pigments used in marine equipment widely employed in fishing vessels. Several biomedical applications employ polymeric metal complexes as implants and as aids for invasive techniques (Fraser and Fiore, 2008). Modified polymers also find their way into tissue engineering applications (He *et al.*, 2008).

Several heavy metals enter the human food chain after leaching from polymeric materials. Some of them have the potential to accumulate in specific target organs such as kidney and spleen and end up as the root cause of various diseases (Stemmer, 1976). Studies have also revealed that entire regions have been affected by heavy metal contaminations and large parts of the population in these areas have fallen victim to such environmental hazards (Chen *et al.*, 1994 ; Buschmann *et al.*, 2008).

Development of certain kinetic factors associated with percolation (leaching) of metal components from polymeric material is relatively unexplored. Studies on

*Corresponding author email: sstephen@pi.ac.ae

kinetics of leaching will provide a comprehensive insight into the effect of some variables, such as dopant level and pH of the fluid medium, on the rate of migration of metal species from polymeric materials. Significant parameters, such as the reaction order and rate constant, could be obtained to provide useful information in assaying any potential hazard that could be linked to such leaching processes. Much of the available literature documents trace metal levels in selected fluid samples arising from polymer material under ambient conditions without any valid consideration of kinetics. No serious record exists of kinetics of leaching as a function of pH and dopant level and a simulated study of this nature would be of considerable practical interest.

Our work entails a simulated study to determine kinetics of heavy metal leaching from a polymeric matrix. The primary objective of this research reported here is to use an inductively coupled plasma mass spectrometer to indirectly determine specific kinetic parameters, such as the rate constant and reaction order, for heavy-metal percolation of polypropylene as a function of dopant level and pH of aqueous medium.

MATERIALS AND METHODS

Preparation of polymer samples
The samples for this study were prepared using a base homopolymer (HE445FB), obtained from Borealis, Linz (Austria), with standard characteristics of melt flow rate 9.2 (g/10min) and molecular weight 42.08 (g/mol). In preparing the compounded materials, the melt flow rate was measured using a Zwick B4106 melt flow rate machine employing the ISO1133 method (Pillay *et al.*, 2010). A Prism TSE 24 twin screw extrusion machine was employed to prepare the compounded material, maintaining the extrusion conditions of 230°C; the material was further dried and pelletized (Pillay *et al.*, 2010). Three different mineral fillers (dopants) were used individually in samples (titanium oxide; zinc oxide; and magnesium oxide). These metal dopants were selected because they are common components in catalysts and reagents linked to polymer synthesis (Williams *et al.*, 2003; Manzi-Nshuti *et al.*, 2009). For our study we used samples loaded with 3 and 10% zinc (II) oxide, titanium (IV) oxide and magnesium (II) oxide. Finally, tiles of 60x60x2mm of the different compounded materials were prepared using a Ferromatic Milacon FM60 injection molding machine. Each tile was cut into four thin slices measuring 60x14x2 mm, approximately, prior to submerging in the leaching medium. The tiles were also washed thoroughly and rinsed in de-ionized water to get rid of surface contaminants, prior to the leaching process.

Leaching Study
Aqueous media of pH 3, 7 and 10 were prepared using Type 1 de-ionized water (Siemens Ultraclear). 50mL polypropylene tubes with screw caps (VWR Scientific) served as sample jars to hold doped polypropylene samples immersed in the relevant medium. Jars were pre-washed using 6M HNO_3 and further rinsed with de-ionized water to purge them of any possible metal contamination. Each sample was kept individually in the leaching solvent of pH 3, 7 and 10 for 24 weeks. Samples were handled using non-metallic forceps to avoid metal contamination. The solvent media were maintained at room temperature (between 20 and 24°C) and the tubes were shaken for a period of two hours in a flask shaker, once every two days. At the end of each designated time span, the polymer samples were removed from the leaching solvent. Leachates were stored under refrigerated conditions prior to analysis.

Instrumentation
An ICP-MS (Perkin Elmer SCIEX DRC-e) with an integrated reaction cell (Fig. 1) was used to analyze the polymer samples and to quantify the leached metals. A New Wave UP-213 laser ablation system operating at a wavelength of 213nm was used as the front end of the ICP-MS for the surface characterization of the polymer. While analyzing the leachates, an aqueous sample introduction system fitted with a Scot spray chamber was employed as the front end of the mass spectrometer. The polymer plaques were cut to fit into a special sample holder with dimensions 5cm x 5cm. No serious pre-treatment was necessary prior to irradiation. Samples were subjected to 213-nm laser irradiation along a 16-point grid, each point separated by a distance of 1.0mm. The level of the beam energy was 30%, with a fluence of approximately 3 J/cm^2. The laser was programmed to scan the grid 5 times, recording measurements after each ablation. The analytical performance of the instrument was satisfactory producing relative standard deviations (RSD) <5% for repeated measurements on a certified standard (Table 1). Surface characterization of the polymer samples was carried out using a scanning electron microscope (FEI Quanta 200 fitted with Inca x-sight SEM detector from Oxford Instruments, UK) to confirm surface profiles of metals.

RESULTS AND DISCUSSION

Surface characterization / Laser ablation / SEM
Characterizing polymer surfaces in terms of metal distribution could be used to evaluate homogeneity (Pillay *et al.*, 2010) and also to establish where the embedded metals are located in the polymer itself. They may be concentrated on the surface or are they ingrained within the polymer matrix? In some cases high surface purity is necessary to obviate the possibility of extraneous ingrained metals migrating into the environment associated with the polymer – especially if it is used to encapsulate solutions, such as jet-oil and body fluids. In this respect the metal impurity (dopant) could itself play an intricate role in its distribution. As the polymer
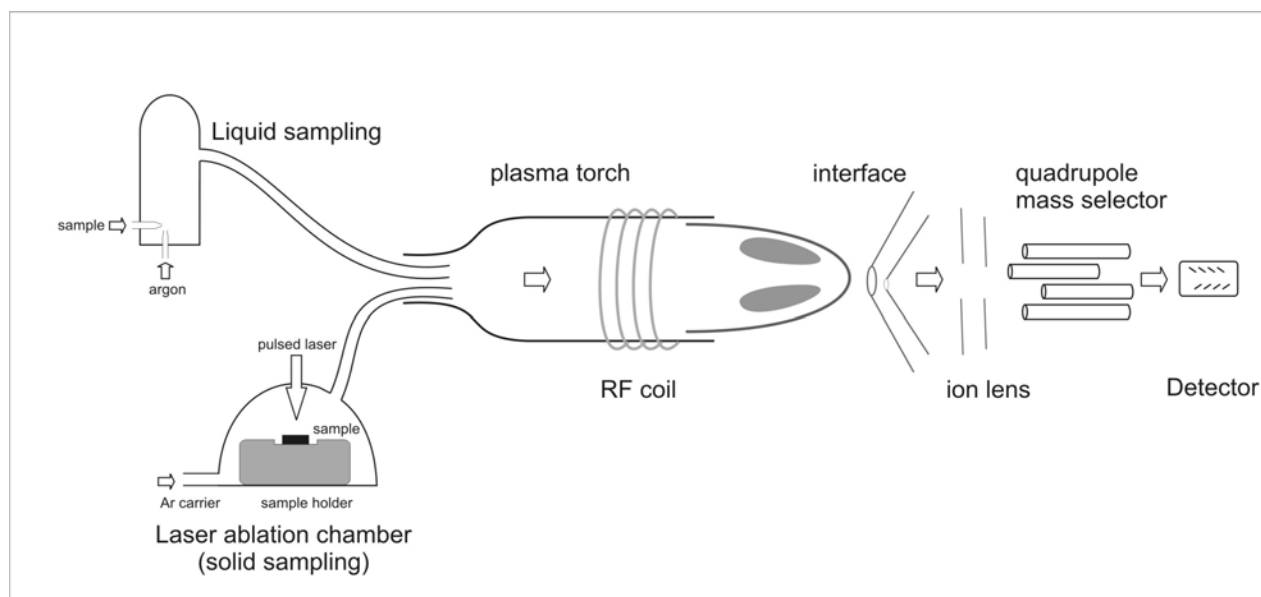
Fig. 1. Schematic of the ICP-MS depicting the laser ablator.

Table 1. Instrumental precision (μg/L) using a multi-elemental quality control sample (20ppb) [Fluka 70007].

Measurement	Be	V	Cr	Mn	Ag	Cd	Ba	Tl	Pb	U
1	20.04	20	18.63	20.01	20.76	19.77	21.11	20.91	20.06	20.23
2	20.78	21.4	20.08	20.35	19.92	20.18	21.5	20.6	19.99	20.87
3	21.75	19.82	18.82	18.78	19.92	18.6	20.46	20.44	20.76	21.01
Mean ± RSD	20.9 ± 4.1%	20.4 ± 4.2%	19.2 ± 4.1%	19.7 ± 4.2%	20.2 ± 2.4%	19.5 ± 4.2%	21.0 ± 2.5%	20.7 ± 1.2%	20.3 ± 2.1%	20.7 ± 2.0%

solidifies, some metals with greater mobility and affinity for the matrix could find themselves bound within the matrix. Others with fewer predilections to remain ingrained could migrate to the surface. The location of metal particles, therefore, depends not only on mixing but the potential of some metals with the capacity to remain ingrained. Laser technology has the unique capability of scanning micro-surfaces in polymer material to locate impurities. The laser technique had been successfully employed by the authors in an earlier study (Pillay *et al.*, 2010). It is not possible for the matrix to be completely devoid of metal impurities, therefore, the laser could be useful for developing surface profiles.

In this work, the SEM and laser ablation studies were conducted in order to establish the random existence and distribution of metals on the surface. When dopant is mixed in the polymer, the mixing itself could be imperfect and may lead to depleted surface levels, or no metals on the surface - which is unlikely. This study is an attempt to establish this premise scientifically using SEM /laser ablation techniques. Figure 2 portrays the spectral trends in metal distribution (for Ti, Mg and Zn) across the polymer surface. Strong and weak lines in figure 2 delineate corresponding elevated and diminished

metal levels on the surface, underscoring the point that these dopants are arbitrarily dispersed. Paper-thin slivers (10μm) of the three samples were subsequently examined using a scanning electron microscope (SEM), to re-confirm the irregular distribution of the selected metals (Fig. 3). Analysis of the results presented in figures 2 and 3 shows that the SEM images support the laser ablation study. The uneven heights of the peaks in the ablation spectra (Fig. 2) and the speckled SEM frames in figure 3 clearly establish the random distribution of metals on the surfaces of the samples of interest.

Kinetics of leaching
Tables 2a and 2b present the metal concentrations of the samples subjected to progressive leaching activity over the designated period of 24 weeks. These values (obtained by ICP-MS) show sharp differences – by more than a factor of 5 in some cases - for Mg and Zn compared individually at the 3 and 10% dopant level. This indicates that the rate of leaching rose markedly with increased dopant level. Such pronounced differences were not observed with Ti, with leaching levels remaining about the same for both the 3 and 10% samples. This anomaly may be attributed to polymorphism as discussed below; or possibly due to cluster formations that coalesced Ti and
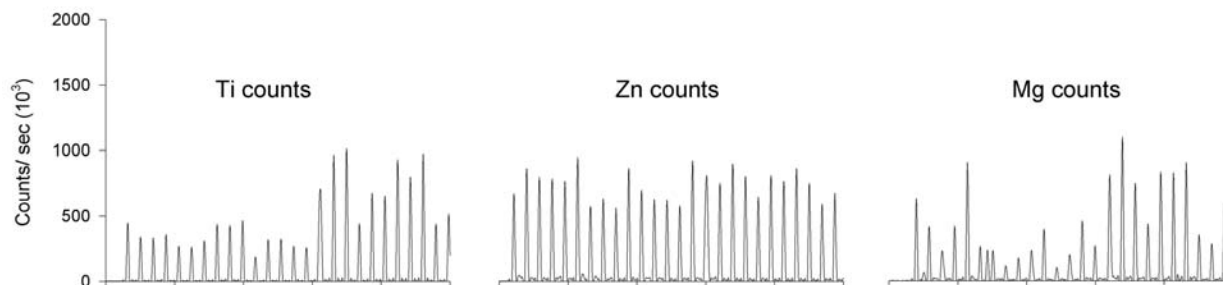
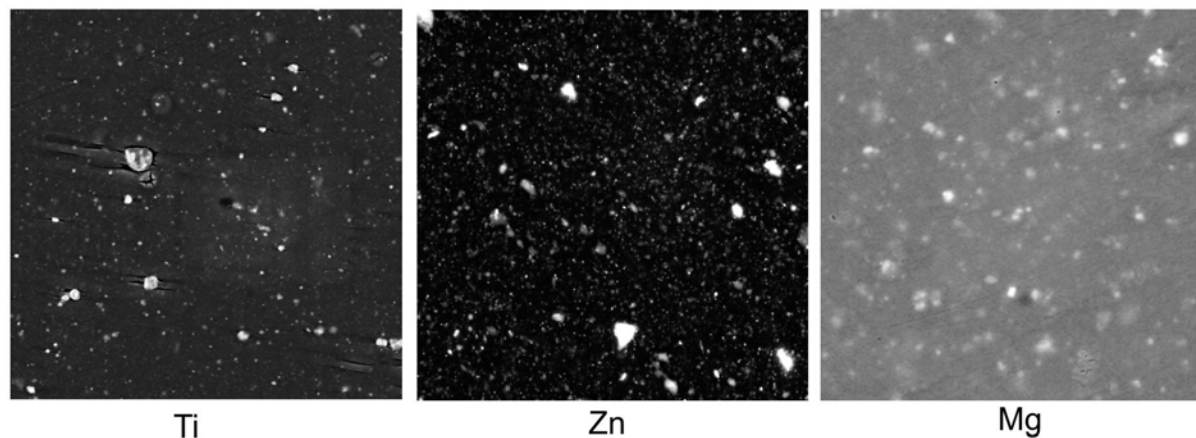Fig. 2. Spectra of metal distribution at points on the polymer surface (using laser ablation).

Fig. 3. SEM images of metal distribution on polymer surface.

Table 2a. Metal concentration in the leachate during a span of 24 weeks (3% doping).

Weeks	Ti (ppb)			Zn (ppb)			Mg (ppb)		
	pH 3	pH 7	pH 10	pH 3	pH 7	pH 10	pH 3	pH 7	pH 10
4	3.28±0.07	2.66±0.10	3.19±0.13	651±15.5	207±2.45	18.6±0.44	616±21.0	269±10.8	426±17.6
8	4.31±0.13	2.84±0.08	3.23±0.13	767±25.2	316±13.6	18.2±0.59	637±26.5	353±11.6	563±24.2
12	4.69±0.19	3.08±0.09	4.09±0.13	823±33.1	313±9.75	22.5±0.96	711±23.7	370±8.3	673±23.4
16	4.92±0.14	3.96±0.17	4.36±0.10	910±34.1	498±14.2	37.9±1.56	777±39.0	441±15.2	704±19.9
20	4.87±0.17	4.33±0.10	4.68±0.19	968±37.0	560±7.90	182.8±7.72	820±30.5	452±5.52	739±17.2
24	4.77±0.11	4.62±0.17	4.82±0.11	895±28.7	599±16.3	233.1±9.49	876±24.3	477±15.1	752±18.6

Table 2b. Metal concentration in the leachate during a span of 24 weeks (10% doping).

Weeks	Ti (ppb)			Zn (ppb)			Mg (ppb)		
	pH 3	pH 7	pH 10	pH 3	pH 7	pH 10	pH 3	pH 7	pH 10
4	3.7±0.12	2.28±0.05	2.60±0.08	2671±107.6	745±24.8	20.03±0.56	2447±85.2	2094±84.2	823±35.2
8	4.31±0.17	2.95±0.10	3.48±0.15	3404±112.0	1333±55.4	28.99±0.84	2578±110.6	2250±70.2	937±30.2
12	4.53±0.10	3.38±0.11	3.69±0.10	3641±116.8	1585±43.9	79.78±2.97	2947±72.9	2495±55.1	1202±49.0
16	4.66±0.10	3.39±0.12	4.13±0.12	4083±152.8	2213±110.9	534±22.8	3110±88.3	2607±72.0	1303±53.7
20	4.97±0.21	3.86±0.05	3.93±0.06	4129±157.8	2599±96.7	1300±29.1	2883±67.2	2745±94.7	1393±58.8
24	5.01±0.21	4.13±0.17	4.27±0.05	4098±97.2	2666±90.9	1655±61.6	3527±145.2	2955±65.0	1544±36.6

the polymer chain, thus hindered leaching. The general trends associated with leaching of the metals of interest are illustrated in figures 4-6. It is clear that in each case the process is more pronounced with progressive decreases in pH values. As mentioned earlier, the data show evidence of a higher percolation rate with increased dopant level. Among the selected metals, plots for Mg and Zn (10%) displayed the most prominent rates of leaching (Figs. 5 & 6) suggesting that magnesium and zinc bearing catalysts and reagents should be used sparingly for preparation of polymers. The plots for Ti were interesting and reflected percolation levels about an order of magnitude lower than those recorded for Mg and Zn. This unexpected outcome for Ti suggested complex

crystal structures that hindered degradation; or the possibility that the metal itself could be tightly entrenched within the polymer matrix (Smolensky *et al.*, 2005; Ulrich, 2001) which played a role in inhibiting the leaching process. Titanium resembles the electron configuration of carbon ([Ar] $3d^2$ $4s^2$) and this feature could have contributed to "melding" the metal within the matrix leading to inorganic-organic hybrid cluster formations. Earlier studies also point to the possibility of this metal-melding phenomenon (Smolensky *et al.*, 2005 ;Ulrich. 2001). However more extensive studies are required to establish this particular hypothesis.

The mechanism of the leaching process was considered to be analogous to the degradation of crystal structures in aqueous media (Koutsoukos *et al.*, 2007). The dopants used in this study were in the form of metal oxides, which contain the very reactive O^{2-} ion that is highly attracted to the metal ions in crystal lattice structures. Magnesium oxide, for example, consists of a structural arrangement of Mg^{2+} ions and O^{2-} ions held together by ionic bonding in an octahedral geometry (Zhu *et al.*, 2013). Zinc oxide exists in dual polymorphic structures: hexagonal and cubic symmetries (Fierro, 2006). Titanium oxide exists in multiple polymorphic structures: hexagonal,
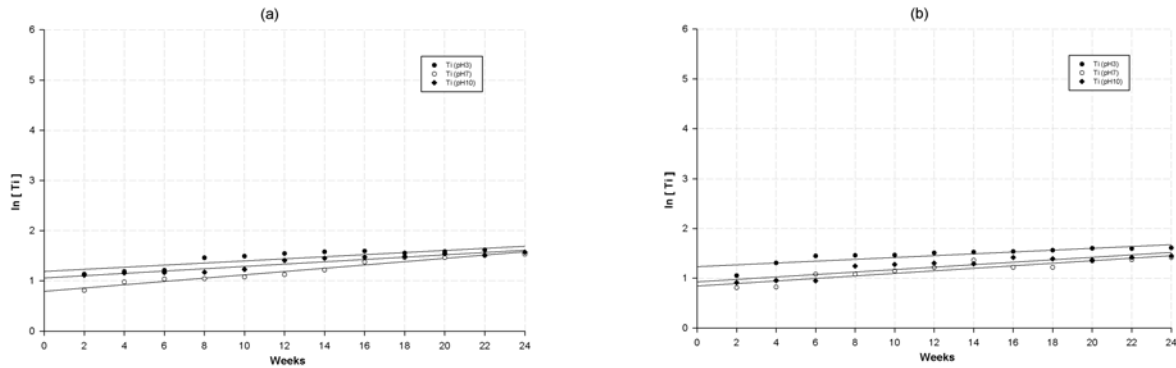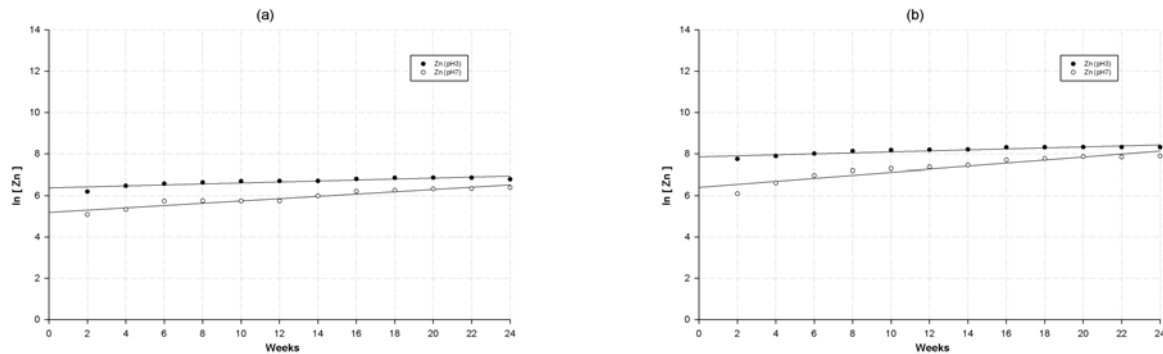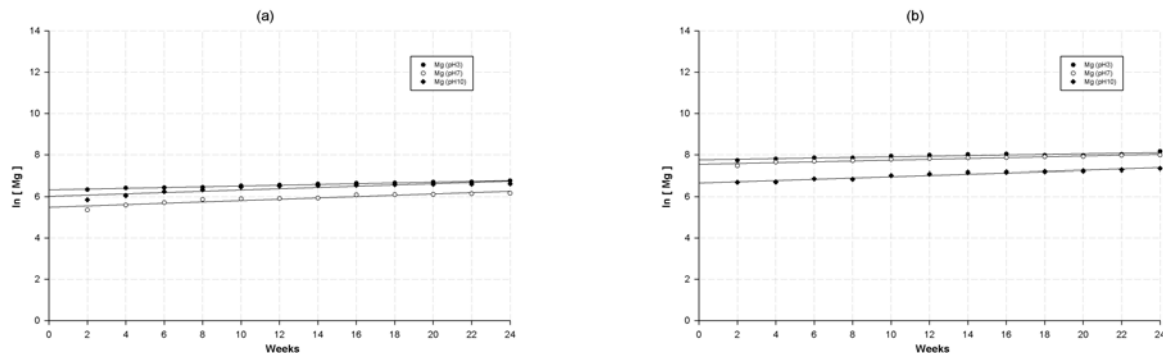

Fig. 4

Fig. 5

Fig. 6

Figs. 4-6. Concentration-time plots of metal levels in leachates conforming to first-order kinetics.
(a), (b) = 3%, 10% dopants, respectively.

orthorhombic and monoclinic arrangements (Marchand *et al.*, 1980; Latroche *et al.*, 1989; Akimoto *et al.*, 1994). Degradation (or leaching) of crystals in acidic media is related to the complexity of the structure and its polymorphic forms (Fierro, 2006). Leaching levels tend to be lower in the presence of more complex polymorphic structures (Fierro, 2006). This phenomenon agrees with our data in figures 4-6 where Mg levels in leachates were highest, and Ti lowest, reflecting the trend in polymorphism. This also accounted for the differences in the recorded data between Ti and the other metals. Clearly, in acidic media affinity of O^{2-} for H^+ will increase with decreasing pH of the medium, resulting in elevated leachate levels, as reflected in the plots in Figs 4-6. Hence the mechanism is pH-dependent, leading to enriched leachates as a function of pH.

For metals complexed within the solid matrix (Smolensky *et al.*, 2005; Ulrich, 2001) an interesting mechanism advanced by Abbu *et al*. (2000) proposes displacement of the metal ion by H^+, leading to augmented leachate levels with decreasing pH as depicted in figures 4-6. Again, according to this proposed mechanism, the leaching process is pH dependent. And, for highly charged metal ions tightly coalesced within the solid matrix (e.g. Ti^{4+}), displacement will be harder, thus leading to corresponding diminished leachate levels, as is the case for Ti (Fig. 4) which is significantly different from Mg/Zn data.

Within experimental limits the plots in figures 4-6 are linear, thus fulfilling first-order kinetics (Chang, 2010). The rate constants were determined from the corresponding slopes, and are roughly 0.01 wk^{-1} for all samples. This rate constant is particularly low indicating that the process is distinctly protracted for polypropylene, the polymeric material investigated in this study. It is important to point out that the dopant levels used in this study had to be high and distinct enough to determine the order of the leaching reaction. Therefore these levels were deliberately kept high, with appreciable differences in concentrations, so that significant data could be generated to establish the order of the metal leaching process. If the dopant levels were in the ppm range (for example) the effect would not have been sufficiently pronounced and perhaps not even observable. This is why kinetic studies of this nature remain underexplored.

CONCLUSION

Our study has established that metal leaching from polymeric material is pH dependent and of the first order. This has implications for liquids and food products encapsulated in polymer containers. Lower pH values tend to induce accelerated rates of percolation. The observed leaching trends for Mg/Zn impregnated samples were similar and could be representative of most heavy metals. However, Ti doped samples did not leach easily suggesting that either its multiple polymorphic structures inhibited the leaching process; or Ti could be intrinsically bound to the polymer chain. This latter phenomenon was considered anomalous and could form an interesting subject for future study, especially if titanium as a dopant forms inorganic-organic hybrid clusters. This suggests that the use of additives and catalysts based on Mg and Zn should be avoided for the production of this type of polymers, especially if such materials are intended for use in critical applications such as liquid food packaging and medical applications.

REFERENCES

Abbu, R., Moodley, KG. and Pillay, AE. 2000. A study of ICP-AES of sorption phenomena in aqueous solutions containing medium-weight and heavy trace metals. J Trace and Microprobe Techniques. 18:15-21.

Akimoto, J., Gotoch, Y., Oosawa, Y., Nonose, N., Kumagai, T., Aoki, K. and Takei, H. 1994. Topotactic Oxidation of Ramsdellite-Type $Li_{0.5}TiO_2$, a New Polymorph of Titanium Dioxide: $TiO_2(R)$. Journal of Solid State Chemistry. 113:27-36.

Buschmann, J., Berg, M., Stengel, C., Winkel, L., Sampson, ML., Trang, PTK. and Viet, PH. 2008. Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population. Environment International. 34:756-764.

Chang, R. 2010. Chemistry. Mcgraw-Hill. pp570.

Chen, SL., Dzeng, SR. and Yang, MH. 1994. Arsenic Species in Groundwaters of the Blackfoot Disease Area, Taiwan. Environmental Science & Technology. 28:877-881.

Cheng, XL, Shi, HL, Adams, CD. and Ma, YF. 2010. Assessment of metal contaminations leaching out from recycling plastic bottles upon treatments. Environmental Science & Pollution Research. 17:1323-1330.

Coe, JM. and Rogers, DB. 1997. Marine Debris: Sources, Impacts and Solutions. Springer-Verlag, New York, USA.

Derraik, JGB. 2002. The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. 44:842-852.

Doremus, CA. 1895. The Chemical History of a case of Combined Antimony and Aresenic Poisoning. Journal of the American Chemical Society. 17:667-682.

Fierro, JLG. 2006. Metal Oxides: Chemistry & Applications. CRC, Taylor Francis.

Fraser, CL. and Fiore, GL. 2008. Polymers for Biomedical Applications. American Chemical Society. 95-115:

He, W., Feng, Y., Ma, Z. and Ramakrishna, S. 2008. Polymers for Biomedical Applications. American Chemical Society. 310-335.

Keresztes, Szilvia., Tatár, E., Mihucz, GV., Virág, István, Majdik., Cornelia, Z. and Gyula. 2009. Leaching of antimony from polyethylene terephthalate (PET) bottles into mineral water. Science of The Total Environment. 407:4731-4735.

Koutsoukos, PG., Kofina, AN. and Kanellopoulou, DG. 2007. Solubility of salts in water: Key issue for crystal growth and dissolution processes. Pure Appl. Chem. 79:825-850.

Latroche, M., Brohan, L., Marchand, R. and Tournoux, R. 1989. New hollandite oxides: $TiO_2(H)$ and $K_{0.06}TiO_2$. Journal of Solid State Chemistry. 81:78-82.

Manzi-Nshuti, C., Songtipya, P., Manias, E., Jimenez-Gasco, MM., Hossenlopp, JM. and Wilkie, CA. 2009. Polymer nanocomposites using zinc aluminum and magnesium aluminum oleate layered double hydroxides: Effects of LDH divalent metals on dispersion, thermal, mechanical and fire performance in various polymers. Polymer. 50:3564-3574.

Marchand, R., Brohan, L. and Tournoux, M. 1980. A new form of Titanium dioxide and the potassium octatitanate $K_2Ti_8O_{17}$. Materials Research Bulletin. 15:1129-1133.

Nakashima, E., Isobe, A., Kako, SI., Itai, T. and Takahashi, S. 2011. Toxic Metals Derived from Plastic Litter on a Beach. Inter Disciplinary Studies on Environmental Chemistry-Environmental Pollution and Ecotoxicology. 2012. pp321-328.

Nakashima, E., Isobe, A., Kako, SI., Itai, T. and Takahashi, S. 2012. Quantification of Toxic Metals Derived from Macroplastic Litter on Ookushi Beach, Japan. Environmental Science & Technology. 46:10099-10105.

Pillay, AE., Vukusic, S., Stephen, S. and Abd-Elhameed, A. 2010. Rapid Ablative Laser Technique (ICP-MS) for Monitoring Material Homogeneity in Polypropylene. Chemical Sciences Journal. 2010:1-9.

Smolensky, E., Kapon, M., Woollins, JD. and Eisen, MS. 2005. Formation of Elastomeric Polypropylene Promoted by a Dynamic Octahedral Titanium Complex. Organometallics. 24:3255-3265.

Stemmer, KL. 1976. Pharmacology and toxicology of heavy metals: antimony. Pharmacol. Therapeut A. 1:157-160.

Takahashi, Y., Sakuma, K., Itai, T., Zheng, G. and Mitsunobu, S. 2008. Speciation of Antimony in PET Bottles Produced in Japan and China by X-ray Absorption Fine Structure Spectroscopy. Environmental Science & Technology. 42:9045-9050.

Teuten, EL., Saquing, JM., Knappe, DRU., Barlaz, MA., Jonsson, S., Bjorn, A., Rowland, SJ., Thompson, RC., Galloway, TS., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, PH., Tana, TS. and Predent, M. 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Phil. Trans. Roy. Soc. Biol. Sci. 364:2027-2045.

Ulrich, S. 2001. Polymers Reinforced by Covalently Bonded Inorganic Clusters. Chemistry of Materials. 13:3487-3494.

Williams, CK., Breyfogle, LE., Choi, SK., Nam, W., Young, J., Victor. G., Hillmyer, MA. and Tolman, WB. 2003. A Highly Active Zinc Catalyst for the Controlled Polymerization of Lactide. J. Am. Chem. Soc. 125:11350-11359.

Zhu, Q., Oganov, AR. and Lyakhov, AO. 2013. Novel stable compounds in the Mg-O system under high pressure. Phys. Chem. Chem. Phys. 15:7696-7700.