A review of the migration of food-contact organotin stabilizers from poly(vinyl chloride)*

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The migration of di-n-octyltin-bis(2-ethylhexyl thioglycolate) and di-n-octlytin maleate polymer, two organotin heat-stabilizers approved by the US Food and Drug Administration, FDA, for poly(vinyl chloride) (PVC) used in food packaging, from PVC into foods and food simulants, is reviewed. The effects of other additives to PVC on organotin migration are considered. Methods of detecting organotins in foods and simulants are discussed. Two areas for further inquiry emerge from the review: (1) whether the intact organotin stabilizers or their degradation products migrate into simulating solvents; and (2) whether the bulk polymer or its surface is the more likely source of the stabilizer available for extraction. A bibliography of recent references is given.

Keywords Diffusion; extraction; food packaging; heat stabilizers; migration; octyltins; poly(vinyl chloride)

INTRODUCTION

Incorporation of heat stabilizing materials into poly(vinyl chloride) (PVC) is necessary in order to limit thermal degradation and prevent discolouration at the high temperatures at which the PVC melt is normally processed. These stabilizers are thought to react with HCl evolved from the polymer and to prevent it from causing further degradation. The chemical reaction mechanisms underlying the stabilizing ability of organotins in PVC have been reviewed in detail elsewhere (Ayrey and Poller, 1980). A recent review on the performance of many tin stabilizers under actual processing conditions is also available (Cooray and Scott, 1980).

ORGANOTIN MIGRATION INTO FOODS AND FOOD SIMULANTS

Two organotin stabilizers for PVC and vinyl chloride copolymers, di-n-octyltin-bis(2-ethylhexyl thioglycolate) (I) and di-n-octyltin maleate polymer (II), have been approved by the US Food and Drug Administration for food packaging applications [21 CFR § 178.2650 (1981)]. These stabilizers, but primarily I, have been the subjects of numerous migration studies, with both foods and food simulants used as the extracting medium for stabilized, rigid PVC.

Long term migration studies of I from PVC bottles into liquid foods have been conducted by Carr (1969), who gave the concentration extracted after two months at 30°C. The quantity of tin extracted from the bottles as organotin was often found to be comparable to the amount of 'natural tin' or the background level of tin in the foods before extraction, indicating the low level of migration occurring and the importance of correcting for the background factor in experimental total tin determinations. After six months, the amount of I which had migrated from PVC bottles into sunflower oil was found to be less than or equal to 2 ppm (Woggon *et al.*, 1969). Beer stored in PVC bottles at 20°C for eight months contained 0.01 mg/l of I (Koch and Figge, 1971). Organotin stabilizers were readily extracted from PVC food containers by olive oil, orange, or lemon soft drink concentrate, and 50% aqueous ethanol (Brighton, 1968). Migration of I and II into a variety of liquid foods has been measured at 57°C over a period of eight weeks (Pinkasavage, 1970). Levels of organotins in these materials ranged from 0.01 to 0.24 μg organotin per gram of food. No additional changes in the level of migration were found when the study was extended at room temperature to a full year in duration.

Several studies have been conducted with food simulating solvents as the extracting medium. A brief review on the use of food simulating solvents in determining migration of dioctyltin stabilizers from PVC is available (Keller *et al.*, 1975). Impact resistant PVC containing about 1% I was extracted with seven simulants (Dostal, 1980). The stabilizer was eluted over the range of 0.004 to 0.045 mg/dm^2 polymer, the highest values occurring for extractions with heptane. Studies of extraction kinetics comparing liquid foods to their corresponding simulating solvents have been reported (Keller *et al.*, 1974). The total amount of stabilizer I extracted varied from 0.06 μg per gram of type II foods (those simulated by 3% acetic acid) to 0.44 μg per gram of type V foods (simulated by heptane). Stabilizer I could be readily detected in heptane and other organic solvents used to extract rigid PVC but could not be detected in coconut oil, triacetin, or triglyceride mixtures (Bergner and Berg, 1972).

Radiolabelling of the stabilizers or food simulants has proven to be a useful approach for studying organotin migration. A determination of the total amount of all components migrating, so-called 'global migration', has been made for rigid PVC stabilized with I (Figge, 1976). The radiolabelled fat simulant HB307-^{14}C, a complex synthetic triglyceride mixture, was used in these extractions. The total quantity of migrants extracted is equal to the weight lost by the polymer during storage in the simulant after correcting for the weight gain caused by the amount of radiolabelled simulant absorbed. The radiolabelled stabilizers methyltin-tri- (III), dimethyltin-di- (IV), and trimethyltin-thioglycolic acid-2-ethylhexyl ester (V), ^{14}C-labelled in both the methyltin or

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thioglycolate moiety, have been extracted with HB307 (Figge, 1975). The total amount of intact stabilizer migrating into fat-containing foods was found not to exceed 1 ng of III, 73 ng of IV, and 39 ng of V per gram of food.

EFFECTS OF OTHER ADDITIVES ON ORGANOTIN MIGRATION

Typical food-grade PVC formulations include not only a stabilizer but also processing aids, lubricants, and colourants. Impact modifiers and plasticizers are often added. These materials can each be present at levels of 1 to 10% by weight of the total moulding compound. The influence of these additional components on stabilizer migration has been studied by several investigators. The chemical nature of organotin stabilizers was reported to have little effect on their migration from compounded PVC into water (Sheftel, 1978). The migration of dibutyltin-bis(isooctyl thioglycolate) (VI) stabilizer into water was found to increase as stabilizer and plasticizer (dioctyl phthalate) content increased. A study on the influence of epoxidized soybean oil, a lubricant, on the migration of dioctyltin and dibutyltin compounds into 50% ethanol, 5% acetic acid, and sunflower oil at 45°C for ten days concluded that lubricant concentrations below 3% have no effect on stabilizer migration (Woggon *et al.*, 1967). Global migration from rigid PVC into water, 10% aqueous ethanol, and 3% acetic acid was found to be unaffected by the presence of up to 11% of this lubricant or by the absence or presence of up to 1% of I (Thomas, 1980).

METHODS OF ORGANOTIN DETECTION

Detection of tin in foods is typically accomplished by oxidative destruction of the food with a nitric and sulphuric acid mixture followed by addition of HBr and HCl to form a tin halide which is then distilled and determined quantitatively by colourimetry (Farnsworth and Pekola, 1961). The distillation step can sometimes be omitted when food simulants are used. The method is sensitive to 1 to 5 μg of tin depending on the reagent used in colourimetric determinations, either pyrocatecholsulphone phthalein (Corbin, 1973) or 3,4-dimercaptotoluene (Farnsworth and Pekola, 1954). An anodic stripping method for determination of organotin compounds has also been described and an analytical scheme proposed for detection of these compounds and their decomposition products migrating from PVC (Woggon, *et al.*, 1972). Radiolabelled stabilizer compounds have been used successfully as a sensitive method for quantifying migration, as discussed previously (Figge, 1975). Flameless atomic absorption spectroscopy (AA) has also been used in a recent study of organotins extracted from PVC by water and edible oils (Taleb *et al.*, 1979). The water extracts were injected directly while the oil samples required dilution with cyclohexane. The limit of detection was reported to be 1.8 μg Sn/g in PVC and approximately 10 ng Sn/g in the simulants. AA has been employed to detect octyltins extracted by water from PVC pipe (Dietz *et al.*, 1979). Their quantitative analysis of tin was complicated by adsorption of extracted tin and precipitation of insoluble tin compounds. The procedure was modified by acidifying the solutions with concentrated HCl before AA analysis, which resulted in an eightfold increase in the tin levels of the solutions.

UNRESOLVED QUESTIONS

There is a lack of consensus in the food-contact organotin migration literature on two issues: whether the intact stabilizers or their degradation products migrate into simulating solvents and the likely source of the stabilizer available for extraction. On the question of stabilizer degradation, the undegraded organotin compound was found to migrate from PVC into hexane and lipid-based extractants while the major component migrating into aqueous extractants was an organotin oxide in the form of the cyclic trimer, $(R_2SnO)_3$ (VII), with minor amounts of the undegraded compound and an alcohol form, $R_2Sn(OH)_2$, also thought to be present (Yen, 1970). Migration of di-n-octyltin esters and other organotins into aqueous and fatty foods has been studied (Woggon *et al.*, 1971). No chemical change in the octyltins was evident while for the other organotins studied mainly decomposition products were found to have been extracted. Experiments with I, radiolabelled at the ester or n-octyl group, migrating into edible oils showed that the stabilizer migrates either undegraded from rigid PVC or, following its hydrolysis, as two moieties which migrate at the same rate (Seidler *et al.*, 1971). The same material similarly radiolabelled has been the object of another study involving migration into edible oils and HB307 (Figge and Zeman, 1973). They concluded that the stabilizer, its three decomposition products 2-ethylhexyl thioglycolate (VIII), di-n-octyltin dichloride (IX), and oxide (X), and their decomposition products all migrate from PVC into fat-containing foods. In addition, free X was thought to form cyclic trimer VII and migrate into aqueous media. Further studies with this radiolabelled stabilizer (Figge *et al.*, 1979) showed that it did not migrate intact but IX and bis(2-ethylhexyloxycarbonylmethyl) disulphide (XI), the dimer of VIII, could be found in small amounts in aqueous or fat simulants. The quantities migrating (in μg/dm^2 polymer) for ten days at 40°C were given as follows: 0.04–0.17 IX and 0.14–0.47 XI into water and 3% acetic acid, 0.50–2.12 IX and 0.51–0.99 XI into HB307 and olive oil, and 0.88–5.48 IX and 3.63–3.81 XI into heptane. Assuming that the methyltin stabilizers III, IV, and V discussed previously are transformed into the corresponding methyltin chlorides and thioglycolates before or during migration, thought to be a likely possibility for migration from rigid PVC into fat-containing foods, their concentrations have been determined to be 0.5, 29, and 13 ng/g for the methyl tin chlorides of III through V, respectively (Figge, 1975). These conflicting results from the available literature suggest that no definitive conclusions can be drawn on the chemical nature of the migrating species of stabilizer I.

Several studies present evidence that organotin stabilizers are extracted primarily from the surface of rigid PVC and not from the bulk polymer, as is normally assumed. A rapid initial migration into heptane and 95% ethanol followed by a period of further migration at a decreased rate was evident for samples containing 2% of an organotin stabilizer of unspecified chemical composition (Downes and Gilbert, 1975, Downes, 1972). The initial amount of migration was greatly retarded when the PVC surface was cleaned with heptane prior to extraction. If the polymer was aged for two weeks following the surface cleaning, the retardation was no longer observed upon extraction. A study on migration of decomposition products of I into edible oils and HB307 described previously concluded that since PVC cannot be swelled by these liquids, stabilizers within the polymer cannot migrate from the samples and only free surface stabilizer is available for extraction (Figge and Zeman, 1973). This point was amplified in a later study (Figge *et al.*, 1979). Stabilizer I, some VIII, and a trace of XI could be found in the bulk polymer while only decomposition products IX and XI could be identified on its surface. The latter two compounds were the species determined to have been extracted by the simulating solvents. The PVC samples also showed a maximum amount of migration in the first aliquot of extracting solvent during long term extractions at 40°C with both HB307 and water.

An additional complication on the source of the stabilizer available for extraction could arise if some of the stabilizer, either on the surface or in the bulk material, is not free to migrate but has reacted with polymer molecules during melt processing of the material and become chemically bound to the PVC. This possibility has been mentioned previously but not thoroughly explored.

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