

Aqueous leaching of di-2-ethylhexyl phthalate and “green” plasticizers from poly(vinyl chloride)

Joshua Kastner, David G. Cooper, Milan Marić, Patrick Dodd, Viviane Yargeau
McGill University, Department of Chemical Engineering, 3610 University, Montreal, Quebec,
Canada, H3A 2B2

Corresponding Author: Milan Marić
Wong Building, Rm 4160, 3610 University, Montreal, QC, Canada, H3A 0C5
E-mail: milan.marić@mcgill.ca
Tel: 514.398.4272
Fax: 514.398.6678

Abstract

A method was developed to assess leaching of several poly(vinyl chloride) (PVC) plasticizers in aqueous media using gas chromatography (GC), and compared to a gravimetric standard test method (ASTM Method D1239). The GC method was a more direct measurement of plasticizer concentration in the aqueous phase. The leaching of commercial plasticizers, as well as several series of “green” candidate plasticizers, were assessed as a function of their

molecular characteristics and compared to the industry standard PVC plasticizer, di-2-ethylhexyl phthalate (DEHP). It was found that plasticizers containing longer alkyl chains or non-polar branching emanating from polar structural units, increased the hydrophobicity of the molecule and reduced its aqueous leaching rate. Several “green” plasticizer candidates were found to minimize aqueous leaching to rates ten times below that of DEHP; notably dioctyl succinate (DOS), dihexyl maleate (DHM), methyl cyclohexyl diester (MCDE), diethylhexyl succinate (DEHS), hexanediol dibenzoate (C6), and the commercially available Hexamoll® DINCH.

Keywords: Leaching; Plasticizer; Di-2-ethylhexyl phthalate; Poly(vinyl chloride); DINCH

1. Introduction

The use of phthalate ester plasticizers for poly(vinyl chloride) (PVC) dates from the 1930s (Graham, 1973) and, as of 2004, they account for 80% of all plasticizer production

(Wypych, 2004). Di-2-ethylhexyl phthalate (DEHP) is responsible for over 50% of worldwide phthalate production, and remains the most widely used PVC plasticizer (Carlson, 2010; Wypych, 2004). A 2008 market survey predicted a 2% increase in PVC demand per year, with production exceeding 40 million tons globally by 2016 (Ceresana, 2008). Added to PVC in concentrations of up to 40% by weight (Ono et al., 1975), plasticizers are used to impart flexibility and processability to rigid, unplasticized PVC by lowering its glass transition temperature (Sears and Darby, 1982). Plasticized PVC containing DEHP is used industrially in piping, roofing, flooring, wire insulation, and other building materials (Horn et al., 2004; Shea, 2003). Plasticized PVC is also used in commercial products such as medical tubing, blood and intravenous bags, food packaging, clothing and children's toys, which has brought phthalate esters into direct contact with humans (Shea, 2003).

DEHP and most other PVC plasticizers are categorized as external plasticizers; they do not form chemical bonds with the polymers they are dispersed in, but rather form weaker physical interactions in the amorphous regions of the polymer. Therefore, external plasticizers leach out of PVC and enter the surrounding environment (Koch et al., 2006). The leachability of external plasticizers coupled with the high production and widespread use of PVC has led to the occurrence of DEHP in soils, wastewater, air and sewage media (Helm, 2007; Staples et al., 1997). DEHP has shown recalcitrance to biodegradation once it is in the environment, bonding strongly to organic matter in deep soils and in aqueous environments (Aboul-Kassim, 2001). Despite the presence of microorganisms capable of biodegrading DEHP in soils and sludge, strong bonding to suspended solids makes mineralization of the plasticizer an extremely slow process. A study tracing mineralization of DEHP in activated sludge from wastewater treatment plants found only 40% mineralization of DEHP after 1 year (Roslev et al., 1998). Wastewater

treatment sludge with remaining concentrations of DEHP as high as 120 mg/kg (Madsen et al., 1999) was recycled as a fertilizer for the agriculture industry, effectively putting large quantities of DEHP back into the environment. Furthermore, in the presence of the common soil bacterium Rhodococcus rhodochrous the biodegradation of DEHP produces metabolites of 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid; compounds which have been shown to be acutely toxic (Cooper et al., 2006).

The extensive use of DEHP in industrial and commercial products has led to significant public interest and scientific research on the toxicity of this plasticizer, with results supporting the need for non-toxic DEHP alternatives. Several papers published in the 1980s proposed DEHP as a possible carcinogen in rats and mice (Kluwe et al., 1983; Warren et al., 1982), which led to the U.S. Environmental Protection Agency labelling of the plasticizer as a dangerous substance and possible carcinogen in 1992 (EPA, 1992). Furthermore, it has been shown that the ingestion of DEHP produces toxic effects in the organ systems of adult and developing animals; particularly, high levels of testicular toxicity and endocrine disruption (Tickner et al., 2001). These concerns have led to the banning of DEHP in children's toys across the European Union. As of 2007, a commercial phthalate-free plasticizer, 1,2-cyclohexane dicarboxylic acid diisononyl ester (sold under the trade-name Hexamoll[®] DINCH, BASF), has replaced DEHP as the predominant plasticizer in children's toys (Grob et al., 2008). DINCH has been shown to have low environmental persistence and high biodegradability compared to DEHP, as well as no acute toxicity after oral or dermal uptake (Wadey, 2003).

The toxicity of DEHP has led to the search for a “green” alternative that would minimize the environmental impact of plasticized PVC production. Many alternatives have been proposed

but not all combine the desirable properties required of the plasticizer during use and after disposal. Our group has investigated the synthesis and design of alternative PVC plasticizers (Erythropel et al., 2012), the biodegradation of alternative plasticizers (Pour et al., 2009), as well as the polymer processing and mechanical properties of alternative plasticizers in PVC (Firlotte et al., 2009). The ideal alternative to DEHP must satisfy many criteria but one crucial criterion is to minimize the plasticizer leaching rate from PVC mixtures into the environment. The research presented in this paper aims to quantify and compare the leachability of potential “green” alternative plasticizers to that of DEHP. The leaching experiments presented in this paper were performed in de-ionized water rather than in organic solvents like methanol or hexane (Messori et al., 2004; Messadi et al., 1981), since an aqueous medium is more representative of the common leaching environments of PVC (i.e. leaching into the human body from medical equipment, toys and clothes, from construction materials into storm water, from piping systems in water, and from PVC waste disposal sites into groundwater). An essential first step was to develop a reliable test method to quantify the leaching of plasticizers from PVC into water. This method, which uses gas chromatography (GC) analysis of the aqueous leachate solution, was compared to a standard test method (ASTM, 1998) based on the gravimetric analysis of the plasticized PVC before and after leaching. The GC analysis method was then used to test the leaching of several series of potential “green” plasticizers and to suggest favourable structural characteristics of the plasticizer to minimize leaching. The combination of gravimetric analysis of PVC and GC analysis of migration product has been previously used in the analysis of polyadipate-plasticized PVC in medical tubing (Wang and Storm, 2005), and GC analysis of DEHP has been previously used to investigate migration of the plasticizer from child articles into saliva (Steiner et. al., 1998). This research differs in that the goal is not only to identify or

quantify the leachate compounds from one type of plasticized PVC, but rather to compare the leaching of potential alternatives to DEHP in several series of prepared PVC/plasticizer mixtures and determine the effect of a plasticizer's structure on aqueous leaching.

2. Materials and Methods

2.1. Plasticizers

DEHP, three other commercially available plasticizers and 18 potential green plasticizers were tested for their leachability from PVC into de-ionized water. The chemical structures of the commercial plasticizers are presented in Scheme 1. DEHP was used as the reference plasticizer. DINCH, marketed as a less-toxic alternative to DEHP, was among the commercially available plasticizers tested. The other two were commercial dibenzoate plasticizers; diethylene glycol dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB), which are also marketed as “environmentally-friendly” alternatives to DEHP due to their relatively low volatility and low toxicity (Suguang, 2009) .

The potential green alternatives to DEHP tested were synthesized using a method previously published (Erythropel et al., 2012). These 18 compounds are organized into four classes of potential green plasticizers: dibenzoates, succinates, maleates and fumarates. The compounds selected in each class, along with their molecular structures, are presented in Scheme 2. The dibenzoate series of plasticizers has a varying hydrocarbon chain length as its middle group. The succinates, maleates and fumarates have an alkyl chain varying in length as their end groups. By comparing the succinate, maleate and fumarate series of plasticizers, the effect of the middle functional group on plasticizer leaching rate can be studied in addition to the effect of

alkyl chain length on the end groups of these plasticizers. These alternative plasticizers were selected for leaching tests based on their ability to lower the glass-transition temperature of PVC, as well as for their plasticization, biodegradation and mechanical testing results which have been shown to be comparable to that of DEHP (Erythropel et. al, 2012; Firlotte et al., 2009).

A subgroup of the succinate plasticizers (DHMS, DHCHS, MCDE), having increasingly hydrophobic branching of the middle group of the plasticizers, was also studied. These structures are shown in Scheme 3.

2.2. Preparation of test samples

The samples used for the leaching tests were PVC disks containing plasticizer, which were prepared at a concentration of 40 parts per hundred resin (PHR) (approximately 28.5 wt. %), measuring 25 mm in diameter by 1 mm in thickness and weighing 0.7g. This concentration was achieved in two steps. (1) Blends with a 20 PHR concentration were obtained by mixing 2.41g of PVC pellets (Solvay Benvic, France, Catalogue #1H014GH045AA) with 0.48g of a plasticizer, 0.10g of stearic acid and 0.10g of epoxidized soybean oil in a co-rotating twin-screw extruder (Thermo Scientific Haake Minilab, U.S.A.) operated at 140°C and 100 RPM. The PVC pellets provided by Solvay Benvic contained a calcium-zinc heat stabilizer and an unspecified colorant in small quantities. (2) The resulting disks were concentrated to 40 PHR concentration obtained by mixing 2.58g of the extrudate from (1) with 0.42g of a plasticizer, in the extruder operated at 120°C and 100 RPM. Stearic acid was added as a heat stabilizer to prevent degradation of the PVC and plasticizer while epoxidized soybean oil served as a secondary plasticizer and co-stabilizer. After each mixing step, the extrudate was passed back through the

extruder to ensure uniform mixing. Once the desired concentration was achieved, the extrudate pellets were placed in a mold in a hydraulic hot-press (Carver Hydraulic Press 3925, USA) at 170°C and 7000 psi for 50 minutes, then quickly cooled down to room temperature. Disks were then left in a desiccator for 3 days to ensure no plasticizer was volatilized prior to the leaching experiments. The disks were then weighed prior to setting up the leaching experiments. Since the boiling points of the plasticizers are well above the processing temperatures of the extruder and hot-press, it is unlikely that significant amounts of plasticizer were lost due to evaporation. Small losses of plasticizer were expected in the extruder. However, the leaching results are intended to be comparative so as to contrast the leaching of each plasticizer against DEHP and plasticizers of slightly altered functional groups. The extrusion and processing steps were reproduced carefully in the preparation of each sample to ensure that any small source of error due to loss of plasticizer could be considered consistent across all samples.

2.3. ASTM Leaching Test

The American Society for Testing and Materials (ASTM) Method D1239, “Resistance of Plastic Films to Extraction by Chemicals” was used as the basis for a gravimetric analysis method to measure plasticizer leaching (ASTM, 1998). This ASTM method measures the weight loss due to chemical extraction from the immersion of plastic into a solvent. The method can be applied to a range of solvents (oils, alcohols, soap solutions, water) (ASTM, 1998), but for this paper only leaching into de-ionized water will be studied. The method has been slightly adapted here for these leaching experiments to ensure the collection of reliable data: it was necessary to extend the time frame of the leaching experiments from the recommended time of 24h to times

of 1 and 3 weeks, because of the slower leaching rates observed for many of the plasticizers. While in some cases 3 weeks may not be long enough for plasticizer leaching to reach steady state, this leaching time frame proved to be long enough to allow for an adequate amount of plasticizer to be detected in the leachate solution using gas chromatography, and allowed for an adequate amount of leached plasticizer to compare the leaching rates of different plasticizers with certainty.

The modified method is as follows. For each sample, two PVC disks of known weight, containing plasticizer at a concentration of 40 PHR, were suspended in a 500mL Erlenmeyer flask containing 200mL of de-ionized water with a piece of stainless steel wire. The flask was then covered in aluminum foil to prevent photo-transformation of any leachate compounds, and set in a shaker at 100 RPM at room temperature. For each plasticizer studied, triplicate experiments were run with leaching times of 1 week and 3 weeks. At the end of the time period, the disks were removed from the flasks, rinsed with 70% ethanol and left in a desiccator for 3 days before being weighed. Weight gain in the disks was measured as the percent deviation from the dry weight of the disks, which was measured prior to leaching. Aqueous leachate samples were retained in a fridge at -5°C for further analysis using gas chromatography, in order to compare against the gravimetric data obtained from the ASTM leaching test.

2.4. Gas Chromatography Analysis

The 200mL of leachate solution from each sample was added to a 250mL separatory flask from the leaching flask. The flask was then rinsed with 20mL of chloroform containing an internal standard of pentadecane at a concentration of 2 g/L. This chloroform solution was then

added to the sample in the separatory flask. The organic phase was separated, diluted 10-fold with chloroform containing the internal standard at 2 g/L, and placed in a 1 mL vial to be analyzed using the gas chromatograph (Thermo Scientific TRACE GC Ultra, Montreal, QC, Canada). This dilution was necessary so as not to overload the GC column. The resulting peaks outputted from the gas chromatograph provided an area ratio of plasticizer to the internal standard of known concentration. These area ratios were converted to plasticizer concentration from calibration curves, which were constructed using standard samples of each plasticizer. Results are presented in the following section as the percent of plasticizer leached from the disks, based on the amount of plasticizer extruded into the disks prior to leaching to achieve a concentration of 40PHR.

3. Results

Data collected from the ASTM gravimetric analysis of the PVC/plasticizer disks following the leaching experiments showed weight gains in the disks in over half of the experiments run. Figure 1 shows DEHP disks exhibiting a weight loss after leaching, while DINCH disks exhibit a weight gain. It was hypothesized that this weight gain was due to water absorption. PVC disks containing DINCH plasticizer were then subjected to an experiment to determine whether the disks were capable of absorbing water into the plastic matrix, which would remain even after 3 days of desiccation. Dry disks were left suspended in de-ionized water for a week, desiccated for 3 days and weighed, then left in an oven at 80°C for 1 week and weighed once more. This cycle was then repeated, and the results are presented in Figure 2, with

initial point at time '0' representing the weight of the dry disk. The oven temperature of 80°C was used so as not to melt the PVC disks or evaporate the plasticizer.

The problem of weight gain during the standard gravimetric analysis thus was avoided by measuring plasticizer concentration in the leachate solution using a gas chromatograph method following leaching experiments. The results for the commercial series of plasticizers are shown in Figure 3. The change in plasticizer concentration is measured as the percent of plasticizer leached out of the disks, based on the amount of plasticizer extruded into the 40 PHR disks prior to leaching experiments. The GC analysis technique was then used to analyze the leaching of dibenzoate plasticizers from PVC in order to study the effect of varying hydrocarbon chain lengths of the plasticizer's middle group (corresponding to the diol) (Figure 4).

Figure 5 shows the GC analysis results for succinate, maleate and fumarate plasticizers. Unlike the dibenzoate series of plasticizers, these series have hydrocarbon chains of varying lengths emanating from their end groups instead of their middle group. The results are presented in terms of plasticizer leaching as an effect of the length of the longest chain in the plasticizer molecule. The chain as defined here spans from the end of one hydrocarbon chain, through the middle group, to the end of the second hydrocarbon chain. These series of plasticizers allow the study of the effect of chain length, via the end groups, as well as the effect of polarity of the middle group, on leaching.

To further investigate the effect of polarity of the middle group on plasticizer leaching in the maleate/succinate/fumarate series, the GC analysis technique was used to measure the leaching of succinate plasticizers with increasingly hydrophobic branching in the middle groups

(DHS, DHMS, DHCHS and MCDE). The results are presented in Figure 6 while GC analysis data for the leaching of all the plasticizers tested are compiled in Table 1.

4. Discussion

Initial leaching experiments run using the ASTM gravimetric analysis on DEHP and DINCH plasticized disks revealed a problem with extending this procedure for use in aqueous media, as shown in Figure 1. The disks containing DEHP lost weight in the first week of leaching and a bit more after three weeks. However, in other experiments, such as the data for disks containing DINCH, there were weight gains. The ASTM gravimetric analysis presumes that disks should only change weight due to plasticizer leaching but it is not this straightforward with the aqueous tests.

Data in Figure 2 is typical of that from another series of tests that involved cycles of first soaking the disks in water followed by heating the disks to remove the moisture. The data shown is for disks containing a DINCH concentration identical to that of the disks in Figure 1. These experiments show that the problem with adapting the ASTM test was that the disks absorbed water while the plasticizer was also being leached out from the disks into the water. Further leaching tests using the ASTM method with other plasticizers also exhibited similar inconsistent data. In the cases such as for DEHP shown in Figure 1, the loss of plasticizer was large enough that the effect due to uptake of water was not apparent. However, it was clear that the data did not reflect the total loss of plasticizer. To overcome the problem of the original tests, the rest of the measurements were done with a method that specifically measured the concentration of a plasticizer leached into the water by GC. In this way, the problem of the weight of the water uptake became irrelevant since the plasticizer concentration in the water is measured directly,

and the leaching of extrusion additives or impurities from the PVC does not bias the data. An added benefit was that this approach avoided any other possible weight loss due to the leaching of minor components in the PVC/plasticizer formulation.

The accuracy of the direct measurement approach is shown in Figure 3. The data for all four of these plasticizers are reproducible and the standard deviations (based on at least three different measurements for each) are all smaller than the differences being observed. As expected, the amount of leaching increases from the first week to the third week. The initial rates appear to be higher and then decrease, suggesting the weight loss was non-linear. The results also show that this is an effective way to compare plasticizer leaching as there are significant differences among the four compounds. The least likely compound to migrate from the PVC into water is the DINCH. This compound has a very low water solubility, estimated at less than 0.020 mg/L at room temperature (Babich, 2010). However, to look at the effects of structure on the rates of leaching, it is necessary to consider series of closely related compounds.

The distribution of polarity in the chemical structures of the polymer and plasticizer molecules is of great importance in determining their compatibility and the degree of flexibility imparted to the polymer (Wypych, 2004). For a plasticizer to be compatible with a relatively polar polymer such as PVC, and provide the desired flexibility, it requires both polar and non-polar parts. The plasticizer molecules must have a polar part to effectively dissolve the plasticizer into the PVC. The non-polar part of the plasticizer serves to attenuate the attractive forces between PVC chains, thus increasing the free volume and imparting flexibility to the polymer (Wypych, 2004). For plasticizer leaching to occur, there must first be movement of the plasticizer molecules to the interface of the plastic and the medium, and then there must be

adsorption of the plasticizer into the medium. Thus, the polarities of the medium and plasticizer molecules are of great importance in determining the rates of leaching.

When surrounded by an aqueous medium, the highly hydrophobic nature of the plasticizers leads to surface-controlled leaching rates, whereas PVC/plasticizer diffusivity-controlled leaching rates have been observed for more non-polar media (Wilkes et al., 2005). Therefore, the higher the hydrophobicity of the plasticizer, the slower the leaching rate into an aqueous medium. For example, the middle group of the DINCH plasticizer is polar enough to be miscible in PVC (Nexant, 2009), but the nonyl chains on the end groups are so hydrophobic that no leaching was observed within the three week experimental time frame (Figure 3). In contrast, the relatively high leaching rate of DEHP can be attributed to the saturated ring system increasing the polarity of the molecule, while the shorter hydrocarbon chains reduce hydrophobicity compared to the DINCH/PVC system. The differences in hydrophobicity and leaching rates of these two plasticizers are reflected in their solubilities in water at room temperature; 0.285 mg/L for DEHP compared to 0.020 mg/L for DINCH (Babich, 2010).

Figure 4 provides a dramatic demonstration of the importance of the structural features of a series of dibenzoate-based plasticizers. There was a significant decrease in leaching rate as the length of the central chain increased from C3 to C6. This decrease in leaching is not due to entanglement effects brought on by an increase in molecular size, as it has been shown that plasticizer molecules containing longer hydrocarbon chains actually lead to increased diffusion due to an increase in free volume within the polymer matrix (Wypych, 2004). Rather, this reduction in leaching is due to the increasingly hydrophobic nature of the compounds as the length of the alkyl chain is increased. For all but the shortest member of this series, the amount

of plasticizer lost was markedly less than that of DEHP. Therefore, the dibenzoates with longer hydrocarbon chain middle groups were superior to the commercial plasticizers for the leaching criterion, with the exception of DINCH. C6 is of particular interest as a potential “green” plasticizer not only due to its slow leaching rate, but also since it has been shown to biodegrade quickly without leaving persistent metabolites in the environment (Pour et al., 2009).

Figure 5 demonstrates another way to vary the hydrophobicity of a series of plasticizers for three different types of compounds. In these cases, the central group was kept constant – it was one of the succinate, maleate or fumarate diesters. Because the part of the compound being varied is the alcohol that reacts with the diacids from the anhydride, the data are plotted against the total number of atoms in the longest chain of the molecule from one end to the other. For all three series of compounds, the trend is the same. As the number of carbon atoms was increased, the rate of leaching decreased. The reduction in the rate of leaching can be attributed to the increase of hydrophobicity brought on by the increase in alkyl chain length of the capping groups. Again, the graphs contain lines indicating the leaching rate of DEHP for comparison. For most of these compounds, the persistence of the plasticizer inside the PVC matrix was much better than that observed for DEHP. DOS, DHM and DEHS all showed no leaching within the three week time frame.

The final set of compounds was not a series of plasticizers with increasing length in some aspect of the structure, but with a change in polarity by varying structural aspects of the central part of the molecule. The four compounds in Figure 6 are DHS and three similar compounds with modifications to the central structure. One modified plasticizer adds methyl branching to DHS, another adds a cyclohexyl branch, and the final modified succinate has a methyl

cyclohexyl group as the middle group (Scheme 3). Each of these modifications increases the hydrophobicity of the middle group of the succinate plasticizer, while the hydrocarbon chain lengths of the end groups are kept at a constant length. While the addition of a methyl branch (DHMS) did not show an observable change in leaching rate compared to DHS, the addition of a cyclohexyl structure (DHCHS, MCDE) reduced the leaching rate to less than a third of DHS. MCDE was so hydrophobic that no leaching was observed after three weeks. These results suggest the same effect as the tests involving an increasing alkyl chain length: as the plasticizer's structure becomes more non-polar, the plasticizer is less likely to leach out into a polar solvent. Since leaching of a plasticizer into an aqueous environment is surface-controlled, and less controlled by diffusivity of the plasticizer inside the PVC matrix, it makes sense that the leaching rate decreases as a plasticizer becomes more hydrophobic through the addition of non-polar groups. The results in Figures 3 through 6 show that this reduction of leaching through the addition of non-polar groups is not site-specific in the plasticizer's structure. The trend was seen in the increase of length of alkyl chains, on end groups and middle groups of the plasticizer molecules, as well as through the addition of non-polar branching from the polar segments of the plasticizer molecules.

5. Conclusion

It is important that a “green” plasticizer imparts flexibility and processability comparable to that of DEHP, that the plasticizer is non-toxic and does not biodegrade into toxic by-products. Further, the PVC/plasticizer mixture must maintain its mechanical properties during the working life of the material. However, reduced leachability from PVC is the most desirable criterion of a

“green” plasticizer for one important reason: the problems of high plasticizer toxicity, slow biodegradation and reduced mechanical properties due to plasticizer loss are all contingent on the plasticizer leaving the polymer matrix. The method developed and the trends presented in this paper can be used as a tool in designing a “green” plasticizer with favourable leaching properties. Not only did plasticizers containing a longer hydrophobic hydrocarbon chain or containing a less polar functional group show a drastically reduced leaching rate compared to DEHP, but the DINCH, DOS, DHM, DEHS and MCDE plasticizers showed no leaching at all within the three week time frame of the leaching experiments. In terms of the criterion of reduced leachability, these are ideal candidates for a “green” PVC plasticizer. The C6 plasticizer also exhibited a very slow leaching rate, and the fast degradation of its metabolites in the environment show previously, makes it also worthy of consideration as a replacement to DEHP.

Acknowledgements

This research was supported by grants from the Canadian Institutes of Health Research (CIHR) and the National Sciences and Engineering Research Council of Canada (NSERC). Financial support was provided by the Eugenie Ulmer Lamothe (EUL) Fund for Kastner and Dodd, through the Department of Chemical Engineering at McGill University.

References

- Aboul-Kassim TS, B. Organic Pollutants in Aqueous-Solid Phase Environments: Types, Analyses and Characterizations. The Handbook of Environmental Chemistry 2001; 5E: 1-105.
- ASTM. Standard Test Method for Resistance of Plastic Films to Extraction by Chemicals. In: D-1239. The American Society for Testing and Materials, West Conshohocken, PA, 1998, 268-269.
- Babich M. Review of Exposure and Toxicity Data for Phthalate Substitutes. In: Commission USCPS, editor Bethesda, MD, 2010.
- Carlson K. Toxicity Review of Di(2-ethylhexyl) Phthalate (DEHP). In: Commission USCPS, editor Bethesda, MD, 2010.
- Ceresana. Market Study: Polyvinyl Chloride http://www.ceresana.com/en/market-studies/plastics/polyvinyl_chloride/polyvinyl-chloride-market-share-capacity-demand-supply-forecast-innovation-application-growth-production-size-industry.html, Ceresana Research, 2008.
- Cooper DG, Nalli S, Nicell JA. Metabolites from the biodegradation of di-ester plasticizers by *Rhodococcus rhodochrous*. Science of the Total Environment 2006; 366: 286-294.
- EPA US. Hazard Summary, Bis(2-ethylhexyl) phthalate (DEHP). In: Radiation DoA, editor 1992.
- Erythropel HC, Maric M, Cooper DG. Designing green plasticizers: Influence of molecular geometry on biodegradation and plasticization properties. Chemosphere 2012; 86: 759-766.
- Firlotte N, Cooper DG, Maric M, Nicell JA. Characterization of 1,5-Pentanediol Dibenzoate as a Potential "Green" Plasticizer for Poly(vinyl chloride). J Vinyl Addit Technol 2009; 15: 99-107.

- Graham PR. Phthalate ester plasticizers--why and how they are used. *Environ Health Perspect* 1973; 3: 3-12.
- Grob K, Biedermann-Brem S, Biedermann M, Pfenninger S, Bauer M, Altkofer W, Rieger K, Hauri U, Droz C. Plasticizers in PVC toys and childcare products: What succeeds the phthalates? Market survey 2007. *Chromatographia* 2008; 68: 227-234.
- Helm D. Correlation between production amounts of DEHP and daily intake. *Sci Total Environ* 2007; 388: 389-391.
- Horn O, Nalli S, Cooper D, Nicell J. Plasticizer metabolites in the environment. *Water Res* 2004; 38: 3693-3698.
- Kluwe WM, Haseman JK, Huff JE. The Carcinogenicity of Di(2-Ethylhexyl) Phthalate (Dehp) in Perspective. *J Toxicol Env Health* 1983; 12: 159-169.
- Koch HM, Preuss R, Angerer J. Di(2-ethylhexyl)phthalate (DEHP): human metabolism and internal exposure-- an update and latest results. *Int J Androl* 2006; 29: 155-165; discussion 181-155.
- Madsen PL, Thyme JB, Henriksen K, Moldrup P, Roslev P. Kinetics of di-(2-ethylhexyl)phthalate mineralization in sludge amended soil. *Environ Sci Technol* 1999; 33: 2601-2606.
- Messadi D, Vergnaud JM, Hivert M. A New Approach to the Study of Plasticizer Migration from Pvc into Methanol. *J Appl Polym Sci* 1981; 26: 667-677.
- Messori M, Toselli A, Pilati F, Fabbri E, Fabbri P, Pasquali L, Nannarone S. Prevention of plasticizer leaching from PVC medical devices by using organic-inorganic hybrid coatings. *Polymer* 2004; 45: 805-813.

Nexant. PERP Program - Developments in Non-Phthalate Plasticizers

http://www.chemsystems.com/about/cs/news/items/PERP%200708S4_Plasticizers.cfm,
2009.

Ono K, Tatsukawa R, Wakimoto T. Migration of plasticizer from hemodialysis blood tubing.
Preliminary report. *Jama* 1975; 234: 948-949.

Pour AK, Cooper DG, Mamer OA, Maric M, Nicell JA. Mechanisms of biodegradation of
dibenzoate plasticizers. *Chemosphere* 2009a; 77: 258-263.

Pour AK, Mamer OA, Cooper DG, Marica M, Nicell JA. Metabolites from the biodegradation of
1,6-hexanediol dibenzoate, a potential green plasticizer, by *Rhodococcus rhodochrous*. *J*
Mass Spectrom 2009b; 44: 662-671.

Roslev P, Madsen PL, Thyme JB, Henriksen K. Degradation of phthalate and di-(2-
ethylhexyl)phthalate by indigenous and inoculated microorganisms in sludge-amended
soil. *Appl Environ Microb* 1998; 64: 4711-4719.

Sears JK, Darby JR. The technology of plasticizers. SPE monographs, Wiley, New York, 1982,
xi, 1166 p. pp.

Shea KM. Pediatric exposure and potential toxicity of phthalate plasticizers. *Pediatrics* 2003;
111: 1467-1474.

Staples CA, Peterson DR, Parkerton TF, Adams WJ. The environmental fate of phthalate esters:
A literature review. *Chemosphere* 1997; 35: 667-749.

Suguang. Environmentally Friendly Non-Toxic Plasticizers

[http://www.chemsuguang.com/cgi/search-](http://www.chemsuguang.com/cgi/search-en.cgi?f=company_en_1_+product_en+product_en_1_&t=product_en_1_&id=644339)
[en.cgi?f=company_en_1_+product_en+product_en_1_&t=product_en_1_&id=644339](http://www.chemsuguang.com/cgi/search-en.cgi?f=company_en_1_+product_en+product_en_1_&t=product_en_1_&id=644339),
2009.

- Steiner I, Scharf L, Fiala F, Washüttl J. Migration of di-(2-ethylhexyl) phthalate from PVC child articles into saliva and saliva stimulant. *Food Additives and Contaminants* 1998; 15:7, 812-817.
- Tickner JA, Schettler T, Guidotti T, McCally M, Rossi M. Health risks posed by use of di-2-ethylhexyl phthalate (DEHP) in PVC medical devices: A critical review. *Am J Ind Med* 2001; 39: 100-111.
- Wadey BL. An innovative plasticizer for sensitive applications. *J Vinyl Addit Techn* 2003; 9: 172-176.
- Wang Q, Storm BK. Migration of additives from poly(vinyl chloride) (PVC) tubes into aqueous media. *Macromol Symp* 2005; 225: 191-203.
- Warren JR, Lalwani ND, Reddy JK. Phthalate-Esters as Peroxisome Proliferator Carcinogens. *Environ Health Perspect* 1982; 45: 35-40.
- Wilkes CE, Summers JW, Daniels CA, Berard MT. *PVC handbook*. Hanser, Munich ; Cincinnati, 2005, xxvi, 723 p. pp.
- Wypych G. *Handbook of Plasticizers*. ChemTec Publishing, Toronto, 2004, 687 p.