Title

Designing green plasticizers: Influence of molecular geometry on biodegradation and plasticization properties

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Abstract

The plasticizer di (2-ethylhexyl) phthalate (DEHP) and its metabolites are considered ubiquitous contaminants, which have a range of implications on the environment and human health. This work considered several alternative compounds with structural features similar to DEHP. This added to the understanding of why DEHP is so poorly biodegraded once it enters the environment. These alternative compounds were based on 2-ethylhexyl diesters of maleic acid (cis-isomer), fumaric acid (trans-isomer) and succinic acid (saturated analogue). The rates of biodegradation by the common soil bacterium *Rhodococcus rhodocrous* were shown to be dependent on the structure of the central unit derived from the diacid used to make the ester. The diacid components of DEHP and the maleate both had a cis orientation and they were the two that were slow to biodegrade. Plasticizing properties were also compared and, because the ester of the saturated succinic acid was degraded quickly and also had good plasticizing properties, it was concluded that the succinic esters of straight chain alcohols would make the best green plasticizers. The maleate ester had excellent plasticizing properties but this is mitigated by a significant resistance to biodegradation.

Keywords

Green Plasticizer, Phthalates, Biodegradation, Succinate, Maleate

Introduction

Plasticizers have recently received significant negative attention. For example, several types of phthalate compounds were banned in children's toys in the European Union, the United States and Canada (EU/2005/84/EC, 2005; CPSIA, 2008; HPA, 2010). Plasticizers are additives to polymers that serve to improve their workability and flexibility but, while they are mixed into the polymer, they are not chemically bound, and can leach out during use or after disposal of the material (Sears and Darby, 1982). The majority of plasticizers, about 80% (Stevens, 1999; Murphy, 2001), are used for poly (vinyl chloride) (PVC). Worldwide, about 90% of all PVC plasticizers (Murphy, 2001) were based on phthalic acid and 51% of the material used was di (2-ethylhexyl) phthalate (DEHP) (Murphy, 2001), which is shown in Fig 1. In 2006, worldwide production of DEHP was approximately 6 Mt, accounting for $9.5\text{x}10^9$ USD (AgPU, 2006). The majority of plasticized PVC is used in applications such as medical equipment (hospital tubing, blood bags, etc.), food wrapping, wire and cable insulation and automobile parts (Rahman and Brazel, 2004).

Plasticizers can leach out of the PVC products over time after disposal. This is particularly noticeable at landfill sites (Öman and Hynning, 1993; Marttinen et al., 2003). Twenty years ago, the presence of phthalate plasticizers was already considered to be ubiquitous in the environment (Wams, 1987). Other studies have identified phthalates in soils (Bauer and Herrmann, 1997; Cartwright et al., 2000), surface water (Taylor et al., 1981; Staples et al., 2000; Horn et al., 2004) and as pollutants in indoor air (Butte et al., 2001; Edwards et al., 2001; Becker et al., 2004) and in the atmosphere (Thuren and Larsson, 1990). They were also found to accumulate in the tissue of mammals (Staples et al., 1997) as well as in several aquatic species such as oysters, brown shrimp and several types of fish (Wofford et al., 1981). DEHP is also believed to disrupt the endocrine system in laboratory rats (Fukuwatari et al., 2002) and has been proven to be weakly estrogenic (Jobling et al., 1995).

The breakdown pattern of DEHP and other plasticizers by bacteria (Nalli et al., 2002) has been studied and identified stable metabolites such as mono (2-ethylhexyl) maleate , 2-ethyl hexanol, 2-ethyl hexanal (as a volatile organic compound (VOC)) and 2-ethyl hexanoic acid (Nalli et al., 2006b; Nalli et al., 2006c). These compounds have been found to be more toxic than their parent compounds (Horn et al., 2004).

Because of all of the above problems, there is a strong incentive to develop "greener" plasticizers. Several workers have proposed alternative plasticizers such as those based on lactic esters and dibasic acids (Rehberg et al., 1952; van Veersen and Meulenberg, 1967) as well as modified dibenzoate plasticizers (Firlotte et al., 2009). Recent work has focussed on succinic acid as a base for plasticizers because of the potential to produce it by fermentation (Stuart et al., 2010). Most of these studies have been concerned with the plasticization properties. There has been less emphasis on biodegradability and toxicity of these compounds and/or their metabolites. To design greener plasticizers, emphasis must also be placed on the degradability of the plasticizer and on avoiding a build-up of concentrations of metabolites. The goal of this work has been to relate both plasticizing and environmental considerations to simple structural features of the plasticizers. Earlier work has determined that small diesters are particularly suitable as plasticizers (van Veersen and Meulenberg, 1967). Our work considered diesters of three small organic acids. They were succinic acid and fumaric acid (both components of the citric acid cycle) and their structural isomer maleic acid. The properties of these compounds were compared to the two common conventional plasticizers DEHP and di (2-ethylhexyl) adipate (DEHA).

Materials and methods

The plasticizers DEHP and DEHA, both with 99% purity, were purchased from Sigma-Aldrich. The other plasticizers studied were synthesized in our laboratories and the components used to make them are identified in the relevant sections below.

Synthesis of di (2-ethylhexyl) maleate (DEHM)

A mixture of maleic anhydride (10.1 g, 77.4 mmol, 99%, Sigma Aldrich) and 2-ethyl hexanol (18.4 g, 141.4 mmol, 99.6%, Sigma Aldrich) were dissolved in 200 mL of benzene (ACP Chemicals) with 1.0 mL (18.0 mmol) conc. sulphuric acid (Fisher Scientific) and heated at 95° C over night in a 150 mL-flask fitted with a Dean-Stark trap attached to a reflux condenser. The white suspension in the flask gradually became clear and a total of 1.4 mL of water was collected in the Dean-Stark trap. After cooling this mixture, 50 mL of a concentrated aqueous solution of sodium bicarbonate (Fisher Scientific) was added while stirring. Once the evolution of carbon dioxide ceased the phases were separated using a separatory funnel and the aqueous phase was extracted with three aliquots of 50 mL dichloromethane (Fisher Scientific). The combined organic phases were washed with deionized water, dried with sodium sulphate (Anachemia) and then the solvents were removed on a rotatory evaporator at 95° C and a pressure of 1.2 kPa (Büchi RE III with Heidolph Rotavac Valve Control). A colorless, oily liquid was obtained. Yield: 20.4 g (59.9 mmol) = 84.7%.

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [m, 12H, $C\underline{H}_3$], δ (ppm) = 1.20 -1.40 [m, 16H, $CH(C\underline{H}_2CH_3)((C\underline{H}_2)_3CH_3)$], δ (ppm) = 1.60 [m, 2H, $OCH_2C\underline{H}$], δ (ppm) = 4.08 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.20 [s, 2H, $CO(C\underline{H})_2CO$].

Synthesis of di (2-ethylhexyl) fumarate (DEHF)

Fumaric acid (10.0 g, 86.2 mmol, 99.5%, Fisher Scientific) and 2-ethyl hexanoic acid (21.5 g, 165.1 mmol, 99.6%, Sigma Aldrich) were dissolved in 150 mL of benzene (99%, ACP Chemicals) with

1.0 mL (18.0 mmol) conc. sulphuric acid (Fisher Scientific) and heated at 95° C for 24 h in a 250 mL-flask with a Dean-Stark trap attached to a reflux condenser. A total of 2.8 mL of water was collected in the Dean-Stark trap. Following the same procedure as described above, a colorless, oily liquid was obtained.

Yield: 13.8 g (40.6 mmol) = 49.2%.

^{1}H-NMR (500.1 MHz in CDCl3): δ (ppm) = 0.92 [t, 12H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 12H, $CH(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.40 [dd, 4H, $CH(C\underline{H}_2CH_3)$], δ (ppm) = 1.60 [m, 2H, $CH_2C\underline{H}$], δ (ppm) = 4.20 [m, 4H, $OC\underline{H}_2CH$], δ (ppm) = 6.81 [s, 2H, $CO(C\underline{H})_2CO$].

Synthesis of di (2-ethylhexyl) succinate (DEHS)

Succinic anhydride (10.0 g, 100.0 mmol, 99%, Fisher Scientific) and 2-ethyl hexanol (40.3 g, 309.1 mmol, 99.6%, Sigma Aldrich) were dissolved in 150 mL of toluene (Sigma Aldrich) with 1.0 mL (18.0 mmol) conc. sulphuric acid (Fisher Scientific) and heated at 125° C over night in a 250 mL-flask with a Dean-Stark trap attached to a reflux condenser. A total of 1.5 mL of water was collected in the Dean-Stark trap. Following the same procedure as described above, a colorless, oily liquid was obtained.

Yield: 27.7 g (80.9 mmol) = 80.9%.

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 12H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 12H, $CH(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.40 [dd, 4H, $CH(C\underline{H}_2CH_3)$], δ (ppm) = 1.60 [m, 2H, $CH_2C\underline{H}$], δ (ppm) = 2.62 [s, 4H, $CO(C\underline{H}_2)_2CO$], δ (ppm) = 4.00 [m, 4H, $OC\underline{H}_2CH$]

Biodegradation Study: Microorganism, Growth and Sample preparation

The microorganism used was *Rhodococcus rhodocrous*, American Type Culture Collection 13808. All biodegradation experiments were performed using 500 mL Erlenmeyer flasks with foam caps. Each flask contained 100 mL Minimum Mineral Salt Medium (MMSM), 10 mM plasticizer, 2 g L^{-1} hexadecane and 0.1 g L^{-1} yeast extract. The MMSM medium contained in g L^{-1}: Na_2HPO_4, 6, NH_4NO_3, 4, KH_2PO_4, 4, $MgSO_4 \cdot 7H_2O$, 0.2, Na_2EDTA, 0.014, $CaCl_2 \cdot 2H_2O$, 0.01 and $FeSO4 \cdot 7H_2O$, 0.01 (Fisher Scientific). The flasks were autoclaved at 121 °C and 100 kPa for 15 min (AMSCO, Model 3021-S), allowed to cool and then inoculated with 1 mL of cell broth from a previously grown culture in a laminar fumehood (Baker Company, Model VBM600) using sterile techniques. The flasks were then put into an incubator-shaker (innova44, New Brunswick Scientific or Multitron II, Infors AG) at 30 °C and 140 rpm for the duration of the experiment.

Because the plasticizers were only slightly soluble in water, it was impossible to take representative samples of the mixture. Thus, the entire contents of a flask were extracted for each set of measurements. Nine flasks were prepared for each compound. The first was extracted at day 0 as a control and the rest, one at a time, every third to fifth day. A tenth flask was also prepared, but not inoculated, as an abiotic control, and this was extracted at the same time as the last flask in the series.

Before a flask was extracted, the pH of its contents was adjusted to pH 2–3 using sulphuric acid. Then the flask was extracted using 20 mL of chloroform containing 2 g L^{-1} of pentadecane, which served as an internal standard for quantification of the GC analysis. The contents of each flask were added to a separatory funnel and the organic phase was recovered and stored at 4 °C until analysis.

Gas Chromatography (GC)

A GC was used to monitor plasticizer concentrations as well as to detect and quantify metabolites. The samples were diluted to an appropriate concentration for the GC (Trace GC Ultra with AI3000 Autosampler, Thermo Scientific) and then 1.0 µL was injected using a syringe. The column used was a Restek RTX-5 (length 30 m, id 0.32 mm, 0.25 µm film), and a flame ionization detector. Calibration curves were prepared in order to calculate concentrations from the ratios of peak areas of the compounds to those of the internal standard pentadecane.

Extrusion of PVC blends containing plasticizers

Unplasticized PVC was obtained from Solvay Benvic, France. A conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation, screw diameter 5/14 mm conical, screw length 109.5 mm) was used to create plasticized blends of PVC. The extruder was operated at a batch feed size of

3 g, a rotation speed of the screws of 60 min^{-1} and an operating temperature between 110 and 130 °C, depending on the amount of plasticizer in the blend. Because unplasticized PVC is a solid and all of the compounds tested were liquids, the extrusions had to be carried out in several steps to ensure homogeneity of the resulting blends. In a first step, a blend of 20 phr (16.6 wt%) was prepared, which also incorporated 4 phr of epoxidized soy bean oil (Chemtura Corporation) as heat stabilizer and 5 phr of stearic acid (Fisher Scientific) as lubricant. (The unit phr is often used in the polymer blends and additives industry and stands for parts per hundred rubber.) After the desired number of batches was collected, all the material was chopped into small pieces and recycled through the extruder again to ensure homogeneity. This blend of 20 phr could then be used to prepare blends of higher plasticizer content by simply adding more of the plasticizer to the masterbatch.

Differential Scanning Calorimetry

A temperature modulated differential scanning calorimeter was used (TA Instruments Q100). Thin slices of about 1-2 mg were cut from the blend while avoiding contamination of the surface of the freshly cut slices. Four or five of these freshly cut slices were placed in a standard DSC pan (TA Instruments, model #070221). The top was crimped on and the total weight of the loaded pan was recorded (Sartorius CP225D). The pan was then placed in the autosampler of the instrument, along with an empty pan for calibration. The samples were quenched at -90 °C, held at this temperature for 5 min, then heated with a rate of 2 °C min^{-1} to +100 °C and again held at this temperature for 5 min. The constant heating rate was superimposed by a sinusoidal modulation of 1.27 °C with a period of 60 s. A first cycle served to erase the sample's previous thermal history and a second cycle was used for the actual glass transition temperature (Tg) measurement. Using the software "TA Universal Analysis" the reversible heat flow of the second heating cycle was plotted against the temperature and, using the half height method, the glass transition temperature Tg was determined according to ASTM D-3418 (ASTM D-3418, 2003).

Production of Tensile Strength Test Bars

The plasticized PVC blends were pressed into tensile strength test bars using a hot press (Carver Manual Hydraulic Press with Watlow Temperature Controllers, Carver). The appropriate mold was filled with small cut pieces of PVC blend, wrapped in aluminum foil to prevent direct contact of the platens with the polymer, and inserted into the hot press between two steel plates. The applied pressure was calculated from the force of the press over the area of the mold. The apparatus was allowed to heat up to 180 °C for 10 min at an applied pressure of 1 MPa, degassed three times and the mold was turned upside down. Following this, the samples were pressed at an applied pressure of 2 MPa for 10 min after which the mold was turned upside down once again. Finally the samples were pressed for two times at an applied pressure of 3 MPa for 15 min from each side. The cooling water was turned on and the cooled test bars were carefully removed from the mold and placed in a desiccator until testing (Drierite, Fisher Scientific, Montréal, QC). The dimension of the test bars are shown in Fig. 2 and correspond to those used for the method ASTM D-638 (ASTM D-638, 2003).

Tensile Strength Testing

All tensile testing was done on a Yamazu Easy Test with a load cell of 500 N after the test bars had spent at least 2 d in the desiccator. The exact thickness and width of the middle section of the test bar were recorded (Electronic Outside Micrometer, Fowler Tools & Instruments) after which the test bars were clamped by their wider section into the apparatus and were then exposed to a strain rate of 5 mm min^{-1}. Both elongation distance and force imposed on the test bar were automatically recorded by a computer until rupture of the test bar. Using these data, a stress-strain curve was generated using equations 1 and 2.

$$\%EL = \frac{L - L_0}{L_0} x100 \left(\frac{mm}{mm}\right) \qquad \text{(Eq. 1)}$$

$$\sigma(MPa) = \frac{F}{\left(T_0 \times W_0\right)} \left(\frac{N}{mm^2}\right) \qquad \text{(Eq. 2)}$$

Equation 1 was used to calculate the tensile strain, which is generally reported in percent elongation. L_0 represents the initial separation of the grips (32.5 mm), and L the elongation distance as recorded by the machine. Equation 2 was used to calculate the tensile stress, which is usually reported in units of MPa. T_0 and W_0 represent the thickness and width, respectively, of the inner section of the test bar resulting in its cross sectional area. F is the force that is recorded at any moment by the machine (Callister, 2005). Stress and strain were calculated for every recorded point and plotted to give a typical stress-strain curve.

The parameters extracted from the stress-strain curve were elongation at break, which is the strain at the point of rupture of the test bar, as well as the secant modulus, which is the slope of a straight line from the slack-corrected origin to a given point on a stress-strain curve. In this work, all secant moduli were calculated for a stress of 2 MPa. In tensile strength measurements, usually the modulus of elasticity is calculated, but if no Hookean behaviour was observed, the ASTM standard D-368 demands the calculation of the secant modulus as explained above. The only blend exhibiting Hookean behaviour was the fumarate samples, so that for these, the modulus of elasticity was reported. All reported data is the average of 3–5 samples. The procedure was adapted from the ASTM standard for tensile testing (ASTM D-638, 2003).

Results

Biodegradation Properties

Figure 3 shows the results for a typical biodegradation experiment. The compound being tested here is di (2-ethylhexyl) succinate. This compound disappears within a period of approximately 14 d. Almost immediately, there is the appearance of the monoester, 2-ethylhexyl succinate and the alcohol 2-ethylhexanol. The concentration of the monoester never increases to more than a trace amount but the concentration of the alcohol first increases and then starts to decrease. The metabolite with the highest observed concentration is 2-ethylhexanoic acid. This is the last of the metabolites to appear. It reaches a significant concentration just as the parent compound has disappeared and then degrades only very slowly by the end of the experiment.

Table 1 shows the results for all of the biodegradation experiments. The table contains values for the half-life of each of these estimated using a first order, initial rate approximation. There was almost no biodegradation observed for either DEHP or di (2-ethylhexyl) maleate. All of the other compounds were biodegraded rapidly but none as quickly as the succinate. Table 1 also indicates the types of metabolites observed and the maximum amounts. It can be seen that, except for 2-ethylhexanoic acid, in some cases, none of these were observed in appreciable amounts.

Plasticizer Properties

The glass transition temperatures of the PVC blends with the compounds of interest as well as with the commercial plasticizers are shown in Fig. 4. Each of the compounds was tested at three different concentrations that covered the range of normal usage. Both the succinate and the maleate were shown to be more efficient in lowering the Tg compared to the commercial plasticizer DEHP, and as efficient as DEHA. The fumarate was the poorest at lowering the Tg at the lowest concentration of plasticizer added. It improved at higher concentrations but was not quite as good as the other compounds tested.

Further analyses done by tensile testing measurements show the succinate to be performing as well as the commercial plasticizers in terms of elongation at break once a threshold of about 30 wt% is reached, while also being more malleable then DEHP and as malleable as DEHA, using the secant modulus at 2 MPa (see Fig. 5a for graphs of strain at break ordered by central molecule and within these by concentration of plasticizer; and Fig. 5b for graphs of Young's modulus/secant modulus ordered in the same manner).

Neither the maleate nor the fumarate blends reach values as high as those of the commercial plasticizers in terms of elongation at break; especially the fumarate, which seems to fracture at much lower strains. Meanwhile for a secant modulus at 2 MPa, the fumarate is even less malleable than the phthalate but the maleate is as malleable as the succinate and adipate.

Discussion

Plasticizers are used in formulations to make many inexpensive plastic products. Usually this is with PVC, a relatively cheap polymer. Thus, the plasticizers must also be inexpensive. The general structure of diesters has been proven to be ideal for plasticizers for PVC (van Veersen and Meulenberg, 1967; Stuart et al., 2010) and these can be easily synthesized using a Dean-Stark esterification that forces the reaction almost to completion by removing the water released from the reaction in a trap attached to a reflux condenser. A simple washing step with a solution of sodium bicarbonate was shown to remove excess catalyst and unreacted reagents as well as any monoester produced from incomplete esterification.

For both maleate and succinate esters, the starting material was an anhydride, which made the production even easier because only one equivalent of water needed to be removed instead of two from the diacid. Overall, the production of all of these compounds was simple, as the small amounts of contaminants could be removed cheaply and the overall process would be easy to scale up. However, it is also essential to show that any diester candidate has the appropriate plasticization properties. In order to design a green plasticizer, its biodegradation properties have to be considered because, inevitably, it will end up in the environment.

The biodegradation pattern for all of the diesters tested in this study is consistent with the pattern presented in Fig. 6. This pattern is analogous to those reported for other diesters (Nalli et al., 2002; Horn et al., 2004; Nalli et al., 2006c). The first step was the hydrolysis of one of the ester groups yielding one equivalent each of alcohol and monoester. Both types of metabolites were observed for all of the compounds tested but often only in trace amounts. Subsequent steps were the hydrolysis of the second ester bond and the further biodegradation of both molecules of alcohol released after the two hydrolysis steps. The alcohols were oxidized to the corresponding carboxylic acids. The carboxylic acids were always observed in the highest concentrations of any of the metabolites and were only slowly removed from the media. This type of behaviour has been observed before (Nalli et al., 2006a, 2006b; Kermanshahi et al., 2009), and the slow degradation has been related to the pathway of β-oxidation being blocked due to the 2-ethyl branch in the β-position to the acid function.

In these experiments, the release of succinic acid or fumaric acid can be inferred after the second hydrolysis step. However, both compounds are part of the Krebs cycle and would be expected to be quickly metabolized by the bacteria. This is an obvious example of the advantages of basing new compounds on natural products that can be considered as safe when entering the environment.

The slow degradation of di (2-ethylhexyl) maleate is particularly interesting. Only very small amounts of even the initial metabolites released by the first hydrolysis step were observed in the time scale of the experiments. The geometry of the two ester functions with regard to the double bond are in the cis orientation and this is essentially the same orientation as the two ester functions in the commercial plasticizer, DEHP, which is well known to be difficult to biodegrade and persistent in the environment (Horn et al., 2004). The ester functions in the fumarate analogue are in the trans orientation. Thus, the stability of both the maleate and the phthalate could be attributed to steric hindrance interfering with the enzymatic hydrolysis. Another contribution to the stability could be due to the delocalization of the ester functional groups with the aromatic ring of the phthalate or with the double bond of the planar core of the maleate ester. However, this same delocalization would be present for the analogous fumarate diester, which was biodegraded relatively quickly. Furthermore, the half-life of the fumarate diester was not that much longer than that of the unsaturated succinate diester. Therefore, a significant amount of the resistance to biodegradation in the commonly used phthalate esters must be due to these steric effects and not to the aromatic nature of these compounds. As rapid biodegradation is important for a green plasticizer, this makes the maleate less desirable even though it is lacking the aromatic component of the phthalates.

There is another possible factor in the relative rates of biodegradation and that is the solubility of the compounds in water. The more soluble compounds could be expected to degrade more quickly. However, this does not seem to be a factor in the data presented here. No data are available on the solubility of these diesters but the relative solubilities in water for a series of closely related compounds will be related to their relative polarities. For example, data is available for the solubility of the three diacids used to make diesters: maleic acid: 788 g L^{-1} (Sigma Aldrich Canada, 2010); succinic acid: 80 g L^{-1} (Fisher Scientific, 2009); fumaric acid: 6 g L^{-1} (Acros Organics, 2009). These values for solubility of the acids can be used to suggest the relative polarities of their esters. The cis isomer would be held in the most polar configuration and the trans isomer would be in the least polar orientation. The order of polarities for the diesters would be the same so the maleate structure should lead to the most water-soluble diester. As this was by far the most stable structure with regard to biodegradation, it makes it clear that relative solubility in water is not a relevant factor in the stability of the esters with the cis orientation.

The two esters based on the saturated diacids (succinic and adipic acids) were both degraded very quickly. This is consistent with the above arguments because the freedom of rotation around the saturated bonds between the two ester groups would allow structures with the most favourable arrangements for interaction with the appropriate enzymes. However, the small differences in the rate of biodegradation of these two saturated compounds could show that, as expected, relative solubility does have some effect on biodegradation. The larger adipate ester would be expected to be less soluble in water than the succinate ester because it has a longer central hydrocarbon chain. This would explain the fact that the half-life of the adipate ester is about twice that of the succinate ester.

An important consideration for a green plasticizer is that when it does start to biodegrade, there should not be an accumulation of metabolites. In all of the examples studied here, the only problematic compound was 2-ethylhexanoic acid. As discussed above, this is stable because of the ethyl branch (Nalli et al., 2002; Horn et al., 2004; Nalli et al., 2006a) but the problem is easily removed by using a straight chain alcohol to make the diesters.

In some of the earlier examples, the most toxic metabolites were considered to be the monoesters (Tomita et al., 1982; Richburg and Boekelheide, 1996; Nalli et al., 2002; Horn et al., 2004). Small amounts of the various monoesters were observed (see Table 1) in this work but there were never more than trace amounts of any of the monoesters, which implies that they were removed relatively rapidly by a second hydrolysis step.

There were small amounts of 2-ethylhexanol in all of these biodegradation studies but, in every case, this was quickly oxidized to 2-ethylhexanal. The presence of this aldehyde been shown in previous work (Nalli et al., 2002) but it was not observed in this work. This compound is quickly oxidized to the stable acid. Overall, there is little concern about an accumulation of toxic metabolites for any of these compounds except for 2-ethylhexanoic acid and earlier work has shown that this problem could be avoided by using a linear alcohol (Nalli et al., 2006a).

In general, all of the di-2-ethylhexyl esters tested were found to be as good as or better at plasticizing PVC than the commercial plasticizers DEHP and DEHA. This can be seen in the trends for glass transition temperature, strain at break, Young's modulus and secant modulus. For example, at the highest concentrations tested, the succinate had the lowest Tg values –comparable to those for the adipate and these were both better than the data for the phthalate.

Again, there were noticeable affects due to the orientation of the two ester functions. The trans fumarate consistently had the highest Tg values as well as the poorest data for the tensile testing such as the lowest elongation and the highest stiffness, meaning that is was not a suitable candidate as a plasticizer. The other two had similar properties and both were good but the unsaturated succinate was slightly better than the cis maleate isomer.

Earlier work concluded that the polarity of a plasticizer is an important consideration in its effectiveness, improving the compatibility of the plasticizer with the PVC resin (Würstlin and Klein, 1952; Leuchs, 1956). The cis orientation of the maleate diester would be significantly more polar than the trans fumarate and this would explain the significantly superior plasticizing properties of the former. The flexibility of the saturated succinate allows the two ester functions to be arranged in the most advantageous manner with respect to polarity of the compound in the polymer matrix. This results in the succinate having better properties than the maleate.

Conclusions

The esters made with either succinic acid or maleic acid would be suitable plasticizers for PVC because their plasticizing properties are comparable to DEHP. The fumarate esters had the poorest properties of all of the compounds studied. All of these compounds were made with simple procedures using relatively cheap starting materials.

The biodegradation of the various esters was very dependent on the structure of the central diacid used to make them. The succinate ester was rapidly removed from the growth medium and the only stable metabolite was 2-ethylhexanoic acid. This problem could be avoided by changing the alcohol used in the synthesis to a straight chain compound. The fumarate had a very similar biodegradation pattern but this took a bit longer to degrade.

The biodegradation of the maleate diester was as slow as that of the important plasticizer DEHP. Both compounds have a similar arrangement of the ester bonds. It was concluded that the cis orientation resulted in a stable compound that was resistant to enzymatic hydrolysis – probably due to unfavourable steric interactions. There were small amounts of metabolites observed for the maleate so it is reasonable to assume that this compound would slowly degrade in the environment in a manner similar to that of the phthalate.

Overall, the results for di-2-ethylhexyl succinate show the best potential for the development of a green plasticizer to replace the phthalate analogue. Despite its slow biodegradation, the di-2-ethylhexyl maleate might also have potential. It was slow to biodegrade but this may be of less concern because it does not contain an aromatic group such as that found in DEHP.

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