DESIGNING GREEN PLASTICIZERS

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Abstract

Plasticizers are additives in poly (vinyl chloride) (PVC) formulations that render the material flexible. This is important for many applications. Because these plasticizers are not bound to the polymer chemically, they will eventually leach out upon disposal. Considering also the widespread use of flexible PVC, it is not surprising that some plasticizers, such as di(2-ethylhexyl) phthalate (DEHP), are considered ubiquitous contaminants in the environment. Previous studies have shown that DEHP, upon degradation, forms stable, toxic metabolites. Because of this and other concerns, DEHP and other phthalates have already been banned in certain products in Canada and other countries. Hence, there is a strong incentive to develop new, green plasticizers.

A series of diesters based on maleic acid, which resembles a part of the phthalate chemical structure, was tested, along with other series based on the structural isomer of maleic acid, fumaric acid, and the saturated analogue, succinic acid. The alcohols used to form the ester bonds varied in length from ethanol to octanol and, also, included the branched 2-ethyl hexanol. Each of these diesters was incorporated into unplasticized PVC at about 30 weight-percent and then evaluated for plasticizer properties such as glass transition temperature Tg and tensile strength. These data were compared to each other and to results with DEHP. Pure samples of the diesters were tested for their biodegradability by the common soil bacterium *Rhodococcus rhodocrous* (ATCC 13808) while it was growing on hexadecane as a primary carbon source.

The results demonstrated that esters based on succinic and maleic acids performed at least as well as or were even superior to DEHP as plasticizers. In particular, the esters with the longer alcohols were very good plasticizers. There was little effect due to branching on the plasticizer properties. The experiments with *Rhodococcus rhodocrous* showed how important the structure of the central diacid is for the rate of biodegradation. In particular, the maleates, which have an orientation of the two ester groups very similar to that in DEHP, showed little to no susceptibility to biodegradation over the course of 30 days. The fumarates exhibited some degradation and the succinates were degraded very quickly. These results indicate that the orientation of the esters in DEHP, is responsible for the stability of this compound in the environment. The other factor in the rate of biodegradation was the length of the alcohol and the longest chains had the slowest rates. However, all straight-chained alcohols were biodegraded without the build-up of stable metabolites. The compounds made with the branched 2-ethyl hexanol did result in the formation of stable metabolites.

Consequently, several of the tested diesters could be considered as “green”. Yet, in terms of a middle molecule, the succinates should be considered as the best choice. As for side chain length, plasticizer properties improve with increasing alcohol length, and biodegradation properties improve with decreasing alcohol length. A potential candidate for a compromise would thus be dihexyl succinate.

Sommaire

Les plastifiants sont des additifs ajoutés au poly (chlorure de vinyle) (PVC) pour obtenir des plastiques souples; une propriété importante pour plusieurs applications. Ces plastifiants ne forment pas de liens covalents avec la matrice de polymères, ils peuvent donc graduellement migrer hors de celle-ci. Dû à la grande utilisation du PVC souple, il n'est pas étonnant que certains plastifiants, tel le di(2-éthyle hexyl) de phtalate (DEHP), soient considérés comme des polluants omniprésents dans l'environnement. Des études ont démontrées que la biodégradation du DEHP mène à l'accumulation de produits métaboliques toxiques. Ces considérations, entre autres, ont déjà conduit à l'abolition ou à la restriction, au Canada, aux États-Unis et dans l'Union Européenne, de l'utilisation de certains phthalates. Ainsi, il y a un intérêt prononcé pour le développement de nouveaux plastifiants « verts » complètements biodégradables.

Une série de composés diesters ayant l'acide maléique comme molécule de base et ressemblant partiellement à la structure chimique des phthalates, a été testée. De même, des séries basées sur l'isomère structurel de l'acide maléique, l'acide fumarique, et son équivalent saturé, l'acide succinique ont aussi été testées. L'estérification des ces acides a été réalisée avec des alcools de longueur variable allant de l'éthanol à l'octanol, incluant aussi le 2-éthyle hexanol. Tous ces diesters ont été incorporés à du PVC à une composition d'environ 30% de la masse du matériau. La température de transition vitreuse (Tg) et la résistance à la traction ont été mesurées pour déterminer l'efficacité de ces plastifiants potentiels. Ces données ont été comparées entre elles ainsi qu'avec des résultats obtenus avec le DEHP. Des échantillons de plastifiants potentiels ont été testés pour déterminer leur biodégradabilité par la bactérie *Rhodococcus rhodocrous* (ATCC 13808); l'hexadécane étant utilisé comme source principale de carbone.

Les résultats obtenus pour les diesters de l’acide succinique et de l’acide maléique ont démontrés qu’ils étaient d’aussi bons ou de meilleurs plastifiants que le DEHP. Dans le groupe des diesters de l’acide succinique, ceux contenant des alcools plus longs étaient de meilleurs plastifiants. Il a été déterminé que la présence d’une chaîne 2-éthyle dans certains diesters avait un effet significatif sur les propriétés des composés. Les expériences de biodégradabilité avec *Rhodococcus rhodocrous* ont démontré l’importance de la structure chimique de l’acide central des diesters. Les maléates en particulier, dans lesquels la position des deux groupes esters ressemble à celle du DEHP, n’ont démontré aucune susceptibilité à être biodégradés après 30 jours. Les fumarates ont été dégradés partiellement tandis que les succinates l’ont été très rapidement. Ces résultats indiquent que l’orientation des deux groupes esters, comme dans le cas du DEHP, est responsable de la stabilité de ces composés dans l’environnement. L’autre facteur influençant le taux de biodégradation est la longueur des alcools utilisés pour l’estérification: les molécules les plus longues avaient des taux plus bas. Toutefois, tous les alcools sans chaîne secondaire furent dégradés sans accumulation de métabolites stables. Inversement, tous les plastifiants potentiels contenant du 2-éthyle hexanol, ont démontrés une telle accumulation.

Plusieurs diesters testés pourraient être considéré comme « verts ». En ce qui a trait au choix de l’acide central, les diesters de l’acide succinique représente probablement le meilleur choix. Pour les alcools utilisés pour l’estérification, les alcools longs démontrent de meilleures propriétés plastifiantes, alors que pour la biodégradation, les alcools courts étaient meilleurs. Un candidat représentant un bon compromis entre ces propriétés est le dihexyl de succinate.

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1 Introduction

1.1 Overview

Plasticizers are a group of compounds that are added to polymeric materials to give them beneficial properties. The most important reason is to improve flexibility and processability by lowering the polymer-specific glass transition temperature Tg. The effectiveness of a plasticizer is evaluated by considering the increase in the polymer's flexibility and elongation at break, as well as the decreases in the tensile strength, hardness, density and melt viscosity. (Rahman and Brazel 2004)

According to the German society "Arbeitsgemeinschaft PVC und Umwelt e.V." 6 million tons of plasticizer, amounting to €7 billion, or C$9.5 billion, were produced and consumed worldwide in 2004. (Arbeitsgemeinschaft PVC und Umwelt e.V. 2006) Approximately 90% of these plasticizers belonged to the class of phthalate diesters and about 50% in this was accounted for by di(2-ethylhexyl) phthalate, as shown in Figure 1. (Rahman and Brazel 2004) For the European market, the fraction of phthalates out of the total amount of plasticizers increased from 92% to 93% between 1999 and 2004. (Arbeitsgemeinschaft PVC und Umwelt e.V. 2006)

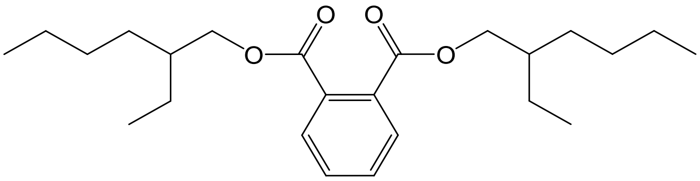


Figure 1 - Chemical Structure of di(2-ethylhexyl) phthalate (DEHP)

Most of the plasticizers (80-90%) are used in poly (vinyl chloride) (PVC), because of the high quantities of plasticizer needed to make PVC workable, which is a result of its high glass transition temperature, circa 80 °C. (Wilkes et al. 2005) Major end users of PVC include the automobile, construction, electrical and cable industries. (Arbeitsgemeinschaft PVC und Umwelt e.V. 2006) Other polymers that are usually plasticized are poly (vinyl acetate) (PVA), nylon, acrylics and polyamides. (Rahman and Brazel 2004)

There are two subcategories of plasticization: external and internal. External plasticizers are usually rather small molecules of low molecular weight compared to the polymer, and are often liquid. They are mechanically mixed into the polymer matrix, where they partly hinder polymer chains from interacting with each other, which results in a softer, more easily deformable mass. (Rahman and Brazel 2004) Internal plasticizers are themselves part of the polymer chain and thus chemically bound. Because of this they cannot leach from the final product. It should be noted that usually, in modern PVC applications, several plasticizers are needed. Thus it is necessary to add external plasticizers even when an internal one is present. (Sears and Darby 1982)

The reason for adding more than one plasticizer to a polymer system is usually to fine-tune certain properties. Generally, the main plasticizer is the primary plasticizer, while those added for fine-tuning are labeled secondary plasticizers. These secondary plasticizers are commonly added to improve properties like flexibility at lower temperatures or simply to lower costs. (Rahman and Brazel 2004)

Other additives to PVC include lubricants, heat stabilizers, polymeric flow aids, colouring agents or solvents. Often, the same additive might cover several of these effects including plasticization, and in these cases no clear differentiation can be made. (Sears and Darby 1982)

1.2 Plasticization Theory

The exact mechanism of plasticization by the inclusion of small molecules in large polymer chains has not been completely established. Several theories have been established, yet no theory has been able to give a complete explanation of plasticization. (Sears and Darby 1982; Matthews 1996)

The first theory called the lubricity theory, developed by a number of researchers (Kirkpatrick 1940; Mead et al. 1942), dates as far back as the 1940's and simply suggests the plasticizer acts as a lubricant between the large polymer chains. This model assumes no bonding between polymer molecules and only weak interactions between plasticizer and polymer. (Matthews 1996)

The free volume theory, which is somewhat more recent, is based on the concept of free volume – defined as the specific volume at a given temperature minus the specific volume at 0 K, as initially postulated by (Fox and Flory 1950). According to this theory, a rubbery material loses volume in a linear fashion until it hits its material-specific glass transition point, and turns into a glassy material. After this point, the material's density will still increase when cooled, but at a slower rate. The free volume is influenced heavily by the number of end groups in a material or blend (both on side chains as well as on the backbone of the polymer chain). The more end groups present, the higher will be the free volume as these end groups take up more space, usually lowering the density. The theory suggests that external plasticizers lower the Tg of a rubbery material because of their comparatively small size relative to the polymer, resulting in a higher proportion of end groups. (Matthews 1996; Wypych 2004)

A mathematical model was developed using the free volume theory to relate plasticizer structure and concentration to the change of glass transition temperature in blends with polymers. (Gordon and Taylor 1952) This method works fairly well in very narrow ranges of conditions, but limits have to be manually set. As this approach is solely based on numbers of end groups, it would, for example, attribute a large drop in Tg to small molecules, without accounting for boiling points or vapor pressures of the materials, and these factors could actually render these molecules unsuitable. On the other extreme, it would also predict very small effects to polymeric plasticizers simply because of their size. (Sears and Darby 1982; Matthews 1996; Wypych 2004)

The "generalized structure theories" have also been used to help explain plasticization. These include the distinction between regions of order and regions of disorder in polymeric materials. An ordered region is characterized as micelles or crystallites depending on their size and this is often related to substantial hydrogen bonding between polymer chains. These ordered regions contribute to the rigidity of the resin, while disordered regions contribute to flexibility and have higher free volumes. (Sears and Darby 1982; Matthews 1996)

Generally, a plasticizer is added to a resin to achieve a higher elongation at break along with a lower tensile strength, which in combination means a more flexible material. This cannot be explained by any one of the above mentioned theories alone. Usually a combination of several theories is required to predict plasticizer properties in a compound. When adding small amounts of plasticizer to a resin, a phenomenon called anti-plasticization is observed. This happens because the introduction of only small amounts of plasticizer molecules gives the polymer chains the possibility of greater movement, and this results primarily in the formation of more ordered regions. The result of this is that a small amounts of additive give an increased rigidity and, thus higher tensile strength. This phenomenon has been observed in several resins such as PVC, poly (methyl methacrylate), polycarbonate and nylon 6,6. Only as greater amounts of plasticizer are added, is the expected trend of higher elongation and lower tensile strength observed. (Sears and Darby 1982)

1.3 Toxicity and Environmental Concerns

For plasticization purposes, external plasticizers are preferred over internal plasticizers as they are cheaper to produce. As mentioned before, these external plasticizers are not bound to the polymer matrix and thus can leach out of the material over time. This is particularly noticeable at landfill sites where a lot of the disposed of PVC ends up. (Öman and Hynning 1993; Marttinen et al. 2003) Many studies have been conducted especially for the phthalate plasticizers as these are the most commonly used. Twenty years ago, their presence had already been considered ubiquitous in the environment. (Wams 1987) More recent studies have identified them in soils (Bauer and Herrmann 1997; Wang et al. 1997; Cartwright et al. 2000; Cartwright et al. 2000), surface water (Saeger and Tucker 1976; Taylor et al. 1981; Staples et al. 2000; Call et al. 2001) as well as pollutants of 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 several aquatic species such as oysters, brown shrimp and species of fish. (Wofford et al. 1981)

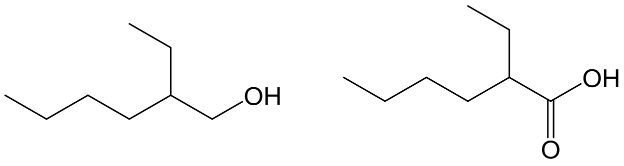
A big concern is that phthalate plasticizers are suspected of disrupting the endocrine system. This has been shown in laboratory rats. (Fukuwatari et al. 2002) They were also determined to be weakly estrogenic. (Jobling et al. 1995) Also, the International Agency for Research on Cancer classified di(2-ethylhexyl) phthalate (DEHP) as "possibly carcinogenic to humans". (Rahman and Brazel 2004)

Plasticized PVC is used in many day-to-day products resulting in a constant exposure to the plasticizers by humans. For example, in food which had been wrapped in plasticized film. (Castle et al. 1988; Petersen et al. 1995) Another major source for intake of plasticizers is from products made from PVC that are used in hospitals, for example blood bags or medical tubing. (Egestad et al. 1996; Tickner et al. 2001) This can be especially problematic for certain groups of patients with regular stays in hospitals, such as dialysis patients, (Tickner et al. 2001) or premature infants, that need intensive care in a hospital over a large period of time. (Calafat et al. 2004)

Canada, (Health Canada News Release 2011) the US (110th Congress 2008) and the European Union (European Union Press Release 2005) have passed legislation that bans several phthalates in children's toys and childcare articles "because of their carcinogenic, mutagenic and reprotoxic effects". (European Union Press Release 2005)

Biodegradation of several classes of plasticizers has been studied in the Department of Chemical Engineering at McGill, including degradation of DEHP, di(2-ethylhexyl) adipate (DEHA) and dibenzoate plasticizers by a variety of microorganisms including bacteria, yeast and fungi. (Nalli et al. 2002; Gartshore et al. 2003; Nalli et al. 2006; Kermanshahi et al. 2009) It was found that these plasticizers were only partially degraded leaving behind metabolites, which were more toxic than the plasticizer itself and which accumulated in the growth medium. For plasticizers containing the 2-ethylhexyl group like DEHP and DEHA, these compounds were found to be 2-ethyl hexanol and 2-ethyl hexanoic acid (Figure 2), and both were shown to be toxic by a number of assays. (Nalli et al. 2002; Horn et al. 2004)

The study by Horn et al. collected samples of water in various locations in the Montréal area in Québec, Canada, and documented that these metabolites could be identified in samples of surface water of the St-Lawrence river, river sediments, freshly fallen snow and tap water. (Horn et al. 2004) Another study found these metabolites in all of the streams of the physiochemical wastewater treatment plant of Montréal. (Barnabe et al. 2008) These results make a very convincing connection between the patterns of plasticizer degradation determined in the laboratory with pure culture and the actual fate of these plasticizers in the environment.



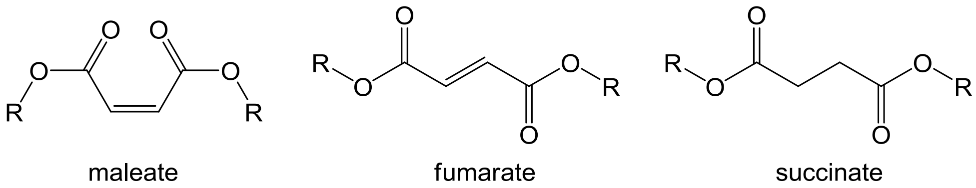
2-ethyl hexanol

2-ethyl hexanoic acid

Figure 2 - Chemical structure of metabolites 2-ethyl hexanol and 2-ethyl hexanoic acid, respectively

1.4 Objective

The goal of this project was to find plasticizers that had at least comparable plasticizing properties to those of DEHP, while showing faster biodegradation rates and not showing any metabolite buildup. In order to do so, it was decided to use diesters, because, like DEHP, they were easily synthesized. This is important because the cost of a plasticizer will be crucial, as it is added to a relatively “cheap” product – in this case PVC. This work looked at the effects of varying both the length of the side-chain as well as the middle molecule of these diesters. As DEHP is known to be a working plasticizer, a similar diacid, maleic acid, was chosen as the middle molecule, because it superficially mimics the rigidity of the aromatic group in DEHP. This could be compared to its geometric isomer fumaric acid, and the saturated analogue succinic acid. (Figure 3)



R = CH_2CH_3, $CH_2(CH_2)_2CH_3$, $CH_2(CH_2)_4CH_3$,
$CH_2CH(CH_2CH_3)(CH_2)_3CH_3$, $CH_2(CH_2)_6CH_3$

Figure 3 - Three different types of diesters and the side chains investigated

Both fumaric and succinic acid are natural products and play a role in the citric acid cycle, which is of central importance in all living cells that use oxygen as part of cellular metabolism (Horton 1996). Also, there have been studies looking at succinates as possible plasticizers due to the relative ease of producing succinic acid biochemically (Stuart et al. 2010). Maleic acid is a stereoisomer of fumaric acid, and gets converted to fumaric acid at temperatures above 150 °C. If any of these were observed as biodegradation products, they would not cause a threat to humans or the environment.

The specific objectives of this project were the following:

- To obtain a homologous series of diesters to test. Compounds that could not be obtained commercially would be synthesized.
- Incorporation of these compounds into unplasticized PVC at specific concentrations.
- Testing of the PVC-compound blends to determine their plasticization properties such as glass transition temperature Tg, elongation at break and Young's modulus and compare against DEHP/PVC blends.
- Determination of the biodegradability of these compounds by bacterial co-metabolism while monitoring for any possible accumulation of metabolites in the growth medium.

2 Materials and Methods

2.1 Materials

Unplasticized poly-(vinyl chloride) (PVC) was obtained from Solvay Benvic, France. It was essential that the PVC being used did not already contain plasticizer, in order to accurately test plasticizing properties of the compounds of interest. Table 1 gives an overview about other additives and selected properties of the material as reported by the supplier. The stabilizer is a heat stabilizer, composed of a mixture of calcium and zinc salts of fatty acids. No data was available on the colouring agent.

Table 1 - Properties of the unplasticized PVC as reported on the supplier data sheet

Property	Value
Supplier	Solvay Benvic, France
Catalogue number	IH14G045AA
Stabilizer	Calcium/zinc
Colour	Grey
Form	Pellets
Density at 20 °C	1.4 kg / dm3
Yield stress at 23 °C	41 MPa
Recommended extrusion temperature	160 – 180 °C

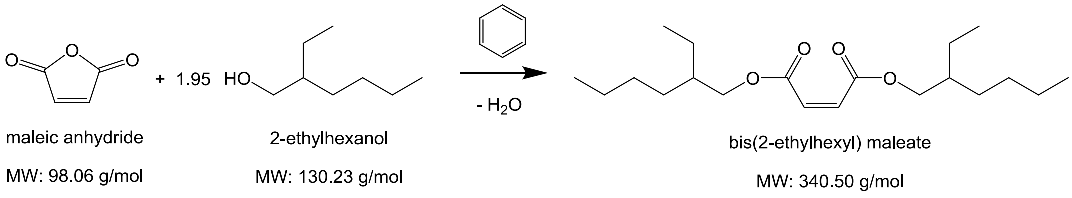
In the process of extrusion (see section XY) the plasticizer was mixed with the Unplasticized PVC (UPVC), and an additional heat stabilizer as well as a lubricant. Some of the chemicals used were available commercially but the majority of the compounds were synthesized. Table 2 gives an overview of the purchased compounds including the specific function, the purity and the supplier.

Table 2 - Chemicals, functions, purities and suppliers

Compound	Function	Purity	Supplier
Di (2-ethylhexyl) phthalate (DEHP)	Plasticizer	99 %	Sigma Aldrich, Oakville, ON, Canada
Bis (2-ethylhexyl) adipate (DEHA)		99 %	
Diethyl maleate (DEM)		97 %	
Diethyl fumarate (DEF)		98 %	
Diethyl succinate (DES)		99%	
Dibutyl maleate (DBM)		97 %	Fisher Scientific, Montréal, QC, Canada
Dibutyl fumarate (DBF)		-	Scientific Polymer, Ontario, NY, USA
Epoxidized soybean oil (ESO)	Heat stabilizer	-	Chemtura Corporation, Middlebury, CT, USA
Stearic acid	Lubricant	-	Fisher Scientific, Montréal, QC, Canada
Maleic anhydride	reactant for synthesis	99 %	Sigma Aldrich, Oakville, ON, Canada
Fumaric acid		99.5 %	Fisher Scientific, Montréal, QC, Canada
Succinic anhydride		99 %	
n-Butanol		99.9 %	
n-Hexanol		98 %	Sigma Aldrich, Oakville, ON, Canada
n-Octanol		99 %	
2-Ethyl hexanol		99.6 %	
Butyric acid	Standard for gas chromatography	99 %	
Hexanoic acid		99.5 %	
Octanoic acid		99 %	
2-Ethyl hexanoic acid		99 %	Fisher Scientific, Montréal, QC, Canada
Sulphuric acid	Catalyst	98 %	
Fumaryl chloride		95 %	Sigma Aldrich, Oakville, ON, Canada
Sodium sulphate	Drying agent	99 %	Anachemia, Lachine, QC, Canada
Sodium bicarbonate	pH regulator	100 %	Fisher Scientific, Montréal, QC, Canada
Hexanes	solvent	99.9 %	
Chloroform		99 %	
Toluene		99.9 %	Sigma Aldrich, Oakville, ON, Canada
Benzene		99 %	ACP Chemicals, Montréal, QC, Canada

2.2 Syntheses

2.2.1 Diesters derived from maleic anhydride



A mixture of 10.08 g (77.4 mmol) maleic anhydride and 18.41 g (141.4 mmol) 2-ethyl hexanol were dissolved in 200 ml of benzene with 1.0 ml (18 mmol) conc. sulphuric acid and heated at 95° C over night in a 250 ml-flask with a Dean-Stark trap attached to a reflux condenser (Figure 4). The white suspension gradually cleared 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 solution of sodium bicarbonate 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 three times with 50 ml aliquots of dichloromethane. The combined organic phases were washed with deionized water, dried with sodium sulphate and then the solvents were evaporated on the rotatory evaporator at 95° C and a pressure of 12 mbar. Yield: 20.39 g (59.9 mmol) = 84.7 %.

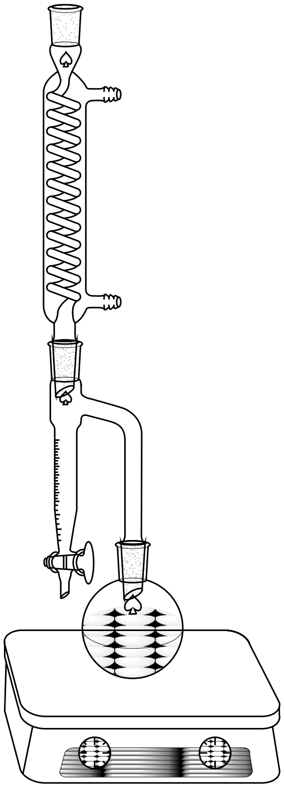


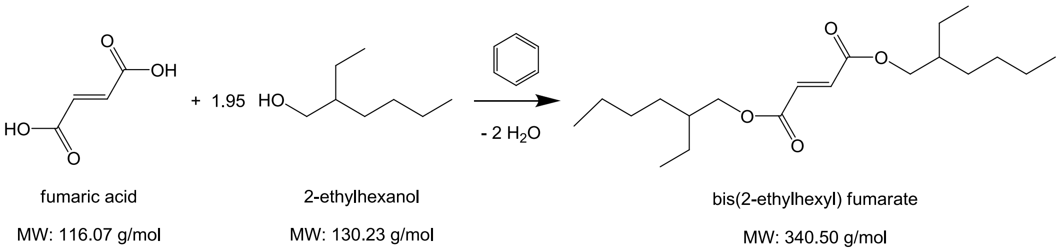
Figure 4 - Typical Dean-Stark setup

To synthesize all of the other maleate compounds, 10 g of maleic anhydride were used, and the ratio between educts was kept at 1:1.95 as above. Table 3 gives an overview of these syntheses. NMR data is provided in Appendix A.

Table 3 - alcohol used and yield for synthesized maleate compounds

Product	Reactant alcohol	Yield
Dihexyl maleate	n-hexanol	85.7 %
Dioctyl maleate	n-octanol	89.3 %
Di 2(ethylhexyl) maleate	2-ethyl hexanol	84.7 %

2.2.2 Diesters derived from fumaric acid



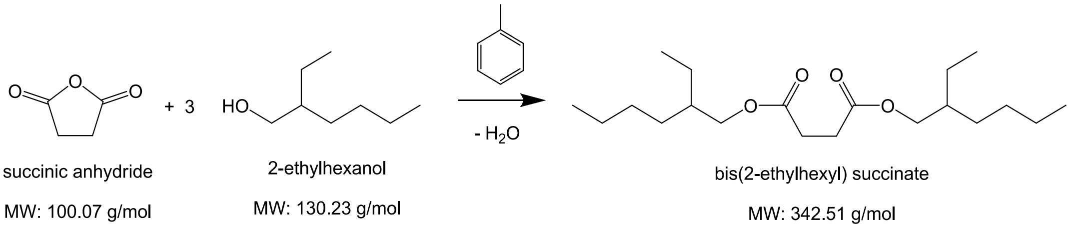
A mixture of 10.0 g (86.2 mmol) fumaric acid and 21.5 g (165.1 mmol) 2-ethyl hexanoic acid were dissolved in 100 ml of benzene with 1.0 ml (18 mmol) conc. sulphuric acid and heated at 95° C for 24 hours in a 250 ml-flask with a Dean-Stark trap attached to a reflux condenser. The white suspension gradually cleared and a total of 2.8 ml of water was collected in the Dean-Stark trap (Figure 4). After cooling this mixture, 50 ml of a concentrated solution of sodium bicarbonate 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 three times with 50 ml aliquots of dichloromethane. The combined organic phases were washed with deionized water, dried with sodium sulphate and then the solvents were evaporated on the rotator evaporator gradually at 95° C and a pressure of 12 mbar. Yield: 13.83 g (40.6 mmol) = 49.2 %.

To synthesize all other fumarate diesters, 10 g of fumaric acid were used, and the ratio between educts was kept at 1:1.95 as above. Table 4 gives an overview of educt alcohol used and the yield of product. NMR data is provided in Appendix A.

Table 4 - alcohol used and yield for synthesized fumarate compounds

Product	Reactant alcohol	Yield
Dihexyl fumarate	n-hexanol	90.9 %
Dioctyl fumarate	n-octanol	80.98 %
Di 2(ethylhexyl) fumarate	2-ethyl hexanol	49.2 %

2.2.3 Diesters derived from succinic anhydride



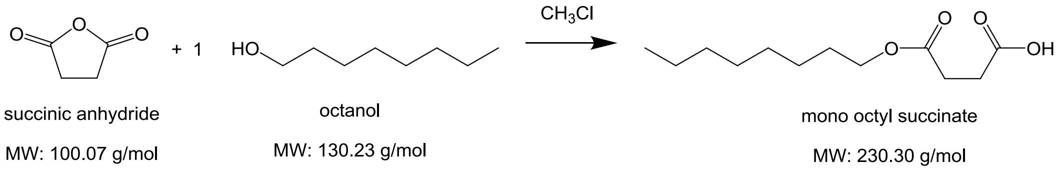
A mixture of 10.0 g (100.0 mmol) succinic anhydride and 40.26 g (309.1 mmol) 2-ethyl hexanol were dissolved in 100 ml of toluene with 1.0 ml (18 mmol) conc. sulphuric acid and heated at 125° C over night in a 250 ml-flask with a Dean-Stark trap attached to a reflux condenser. A total of 1.5 ml of water was collected in the Dean-Stark trap (Figure 4). After cooling this mixture, 50 ml of a concentrated solution of sodium bicarbonate 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 three times with 50 ml aliquots of dichloromethane. The combined organic phases were washed with deionized water, dried with sodium sulphate and then the solvents were evaporated in the rotatory evaporator at 120° C and a pressure of 12 mbar. Yield: 27.69 g (80.9 mmol) = 80.9 %.

To synthesize all other succinate diesters, 10 g of succinic anhydride were used, and the ratio between educts was kept at around 1:3 as above. Table 5 gives an overview of educt alcohol used and the yield of product. NMR data is provided in Appendix A.

Table 5 - alcohol used and yield for synthesized succinate diesters

Product	Reactant alcohol	Yield
Dibutyl maleate	n-butanol	90.3 %
Dihexyl maleate	n-hexanol	99.9 %
Dioctyl maleate	n-octanol	81.5 %
Di 2(ethylhexyl) maleate	2-ethyl hexanol	80.9 %

2.2.4 Monoesters derived from succinic anhydride



A mixture of 1.0 g (10.0 mmol) succinic anhydride and 1.29 g (9.9 mmol) n-octanol were dissolved in 5 ml of chloroform and heated at 70° C for 60 minutes in a hermetically sealed 16 ml-vial. The chloroform was evaporated on the rotatory evaporator at 70 °C and the product was recrystallized from n-hexane. Yield: 1.49 g (6.5 mmol) = 65.0 %. NMR data is provided for all synthesized compounds in Appendix A.

To synthesize all other succinate mono-esters, 1 g of succinic anhydride were used, and the ratio between educts was kept at 1:1 as above. Table 6 gives an overview of educt alcohol used and the yield of product. In the case of mono-hexyl succinate, no product could be crystallized, yet hexanoic crystallized, which was formed by oxidation of hexanol present. The remaining liquid was identified as ca. 90% pure product. NMR data is provided in Appendix A.

Table 6 - alcohol used and yield for synthesized succinate mono-esters

Product	Educt alcohol	Yield
Mono-butyl succinate	n-butanol	71 %
Mono-hexyl succinate	n-hexanol	38 %
Mono-octyl succinate	n-octanol	65 %

2.3 NMR Spectroscopy

^{1}H - Nuclear Magnetic Resonance spectroscopy was carried out in the department of chemistry at McGill on two spectrometers: Varian Mercury-300 (^{1}H = 300 MHz) and Varian Unity-500 (^{1}H = 500 MHz). The solvent used for all measurements was deuterated chloroform ($CDCl_3$), with tetramethylsilane (TMS) as internal standard. The chemical shifts δ are indicated in ppm.

2.4 Polymer Processing and Testing

2.4.1 Extrusion

The amount of plasticizer in a formulation is often reported in parts per hundred rubber (phr) in the plastic industry. This is also applied to formulations of PVC, although the resin is not a rubber. This unit is based on weight, e.g. a blend of 40 phr of commercially available DEHP in PVC means 40 parts of DEHP in 100 parts of PVC, totalling 140 parts. The resulting concentration in this case is ca. 28.6 weight-percent of plasticizer in the overall blend.

A conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation, speed range 10 - 360 min^{-1}, torque range 0-5 Nm, screw diameter 5/14 mm conical, screw length 109.5 mm) as used to create the plasticized blends of PVC (Figure 5). 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 °C and 130 °C, depending on the amount of plasticizer in the blend.

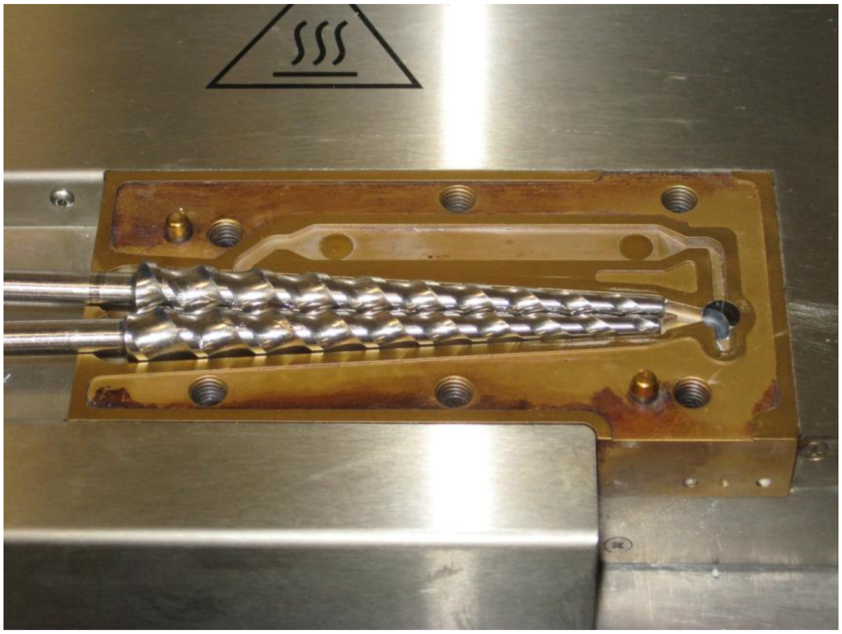


Figure 5 - conical intermeshing twin-screw extruder

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 was prepared, which also incorporated 4 phr of epoxidized soy bean oil as heat stabilizer and 5 phr of stearic acid as lubricant. After the desired number of batches were collected, all material was chopped into small pieces and – in batches of 3 g – run through the extruder again to ensure homogeneity. This blend of 20 phr could then be used to prepare blends of higher plasticizer content.

Table 7 gives an overview of the ingredients and parameters used to prepare a blend of 40 phr.

Table 7 - Ingredients per batch of 3 g depending on initial plasticizer concentration

Step	Ingredients per batch of 3 g
Step 1 (T = 130 °C) 20 phr blend	2.41 g Unplasticized PVC 0.48 g plasticizer 0.12 g stearic acid 0.096 g epoxidized soy bean oil
Step 2 (T = 110 °C) 40 phr blend	2.57 g plasticized PVC from step 1 0.43 g plasticizer

2.4.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a technique that enables the detection of thermally induced phase transitions (such as melting - or glass transition points), by heating a sample and measuring any changes in its heat capacity. Conventional DSC can be modified to do Modulated Differential Scanning Calorimetry (MDSC) which is used when phase transitions overlap. By superimposing a sinusoidal modulation on the constant heating rate used in conventional DSC, it was possible to differentiate between reversible (e.g. glass transition) and non-reversible phase transitions, for example melting or crystallization. (W.D. Callister 2005)

For this procedure, a temperature modulated differential scanning calorimeter was used (TA Instruments Q100). Thin slices of about 1-2 mg were cut from the blend while wearing gloves to avoid contamination or moisture on the surface of the freshly cut slices. Subsequently, four to five of these freshly cut slices were placed on the bottom part of a standard DSC pan (TA Instruments, model # 070221). The appropriate top was cramped on, and the total weight of the loaded pan was recorded (Sartorius CP225D). The loaded pan was then placed in the autosampler of the instrument, along with an empty pan for calibration.

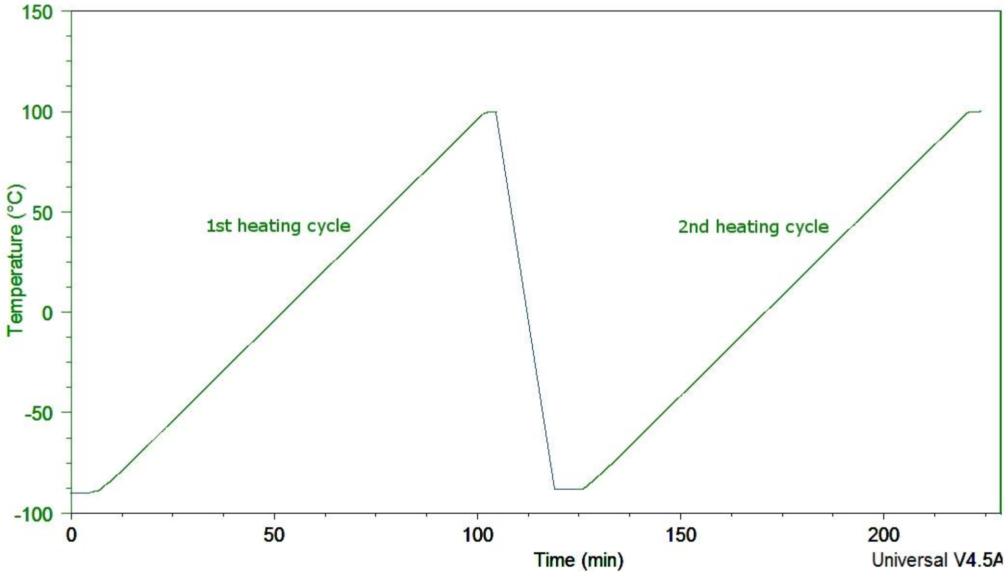


Figure 6 - Schematic heating and cooling rate during MDSC without superimposed sinusoidial signal

As shown in Figure 6 - Schematic heating and cooling rate during MDSC without superimposed sinusoidial signalFigure 6, the samples were quenched at -90 °C, held at this temperature for 5 minutes, then heated with a rate of 2 °C / min to +100 °C and again held at this temperature for 5 minutes. The constant heating rate was superimposed by a sinusoidal modulation of 1.27 °C with a period of 60 seconds. The first cycle served to erase the sample's previous thermal history and the second cycle was used for the actual 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. In order to do so, tangents were drawn to the three linear regions of the curve in Figure 7 and their intersection points labelled as extrapolated onset temperature T_{eig} and extrapolated end temperature T_{efg}. The midpoint between these two was taken as midpoint temperature T_{mg} which equals the glass transition temperature of the material. This method was adapted from the ASTM standard D 3418 for transition temperatures using DSC. (ASTM D-3418, 2003)

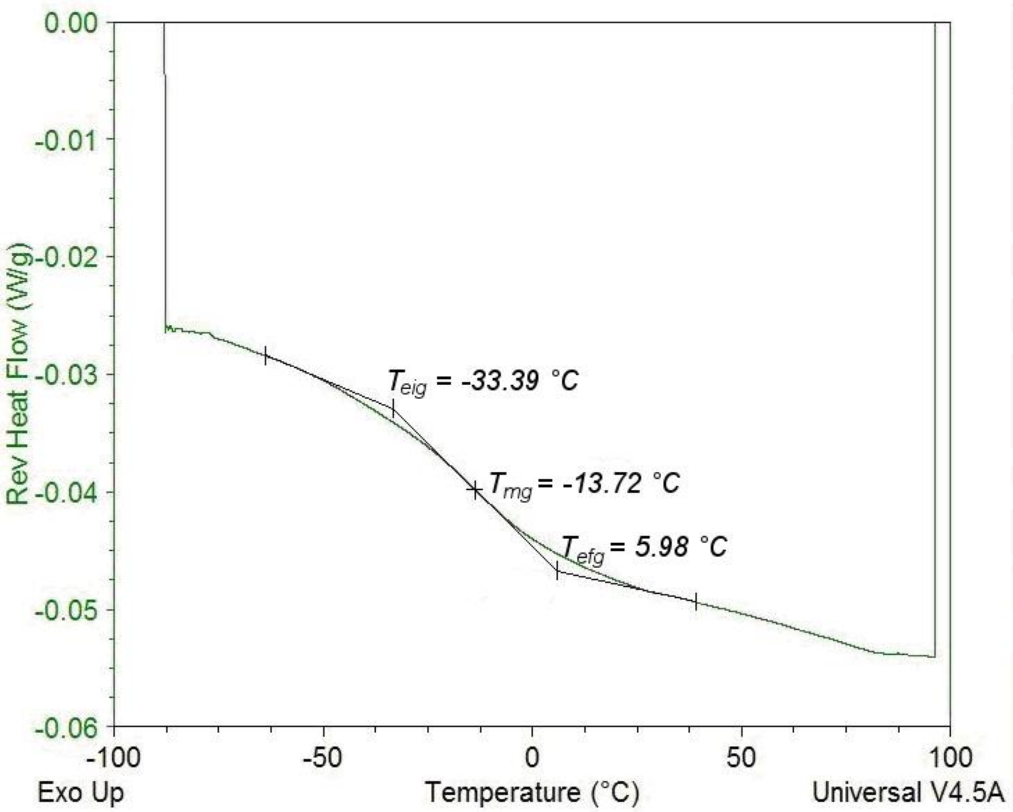


Figure 7 - MDSC thermogram of a blend of 40 phr of diethyl maleate in PVC.

2.4.3 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 Inc., Wabash, IN, USA). The appropriate mold, as depicted in Figure 8, was filled with small cut pieces of PVC blend, wrapped in aluminum foil and inserted into the hot press between two steel plates. The apparatus was allowed to heat up to 180 °C for 10 minutes at 5 tons of pressure, degassed three times and the mould turned upside down. Following this, the samples were pressed at a pressure of 10 tons for 10 minutes after which the mould was turned upside down once again. Finally the samples were pressed for two times at 15 tons for 15 minutes from each side. The cooling water was turned on, and the cooled test bars were carefully removed from the mould and placed in a desiccator on the same day (Drierite, Fisher Scientific, Montréal, QC). See Figure 9 for the dimension of the test bars, which correspond to (ASTM D-638, 2003).

Figure 8 - Mould for preparation of 5 tensile strength test bars

2.4.4 Tensile Strength Testing

All tensile testing was done on a Yamazu Easy Test with a load cell of 500 N (see Figure 10) after the test bars had spent two days 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. Both elongation distance and force imposed on the test bar were automatically recorded by a connected computer until rupture of the test bar. Using this data, a stress-strain curve was generated using Equations 1 and 2:

Equation 1:

$$\varepsilon\ (\%EL) = \frac{L-L_0}{L_0} \times 100\ \left(\frac{mm}{mm}\right)$$

Equation 2:

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

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 Megapascals. 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. The force F is the force that is recorded at any moment by the machine (W.D. Callister 2005). Stress and strain were calculated for every recorded point and plotted to give a typical stress-strain curve, as shown in Figure 11.

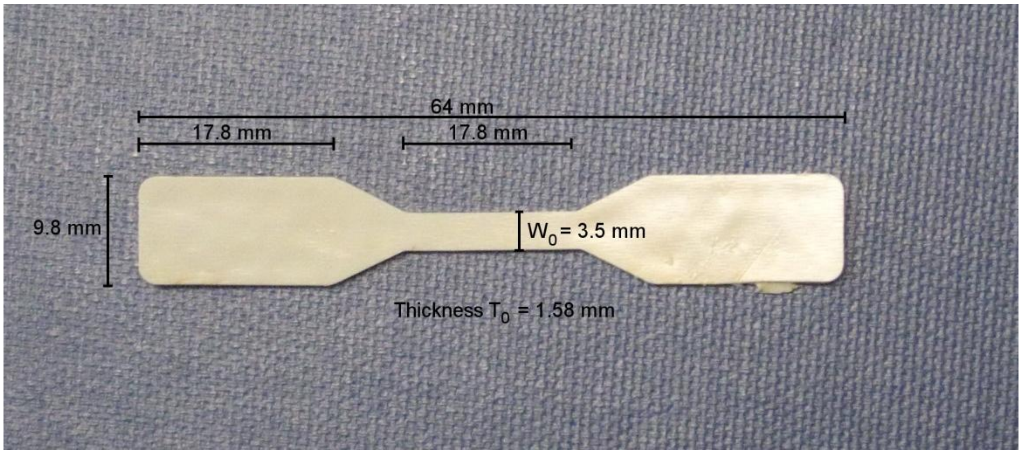


Figure 9 - Dimensions of tensile strength test bars

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 for the calculation of the secant modulus as explained above. The only blends exhibiting Hookean behaviour were all 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)

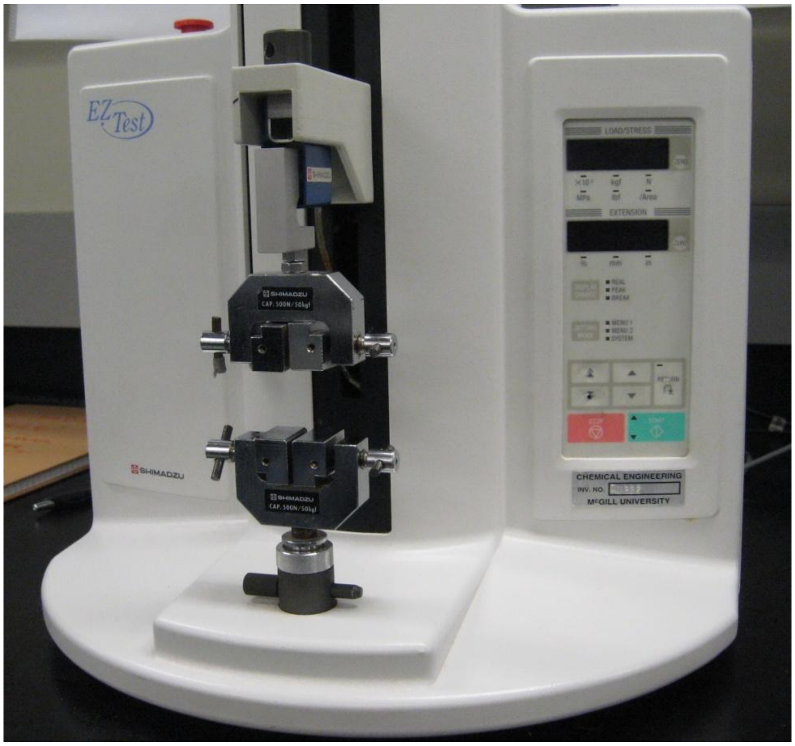


Figure 10 - Yamazu Easy Test for tensile strength testing

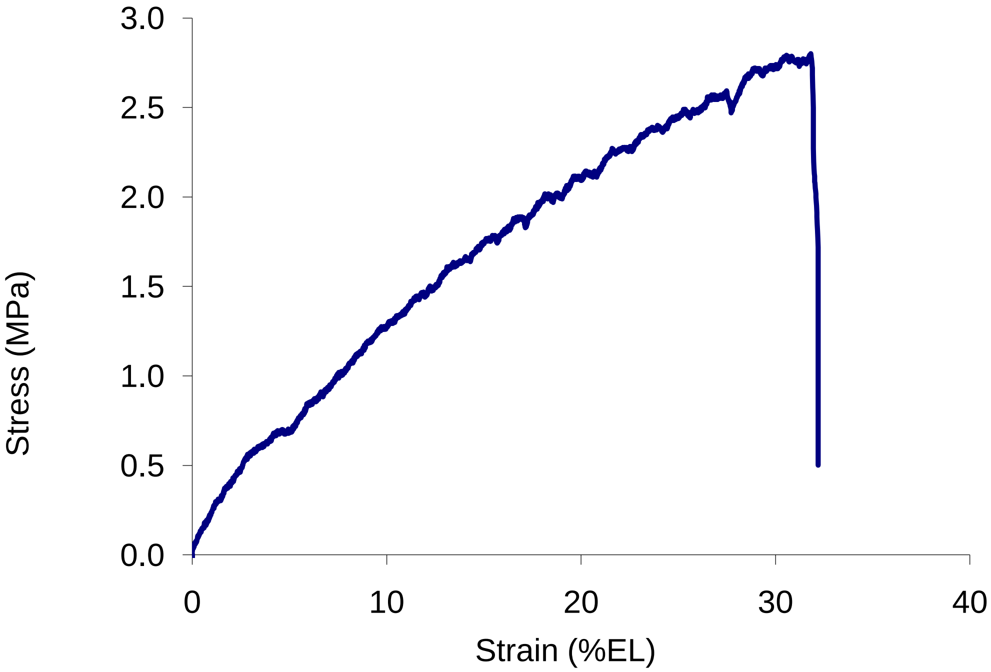


Figure 11 - Sample stress-strain curve for a blend of 40 phr dioctyl maleate and PVC

2.5 Biodegradation

2.5.1 Microorganism, Growth and Sample preparation

The microorganism used was *Rhodococcus rhodocrous*, American Type Culture Collection (ATCC) 13808. All biodegradation experiments were performed using 500 ml Erlenmeyer flasks with foam caps. Each flask contained 100 ml Minimum Mineral Salt Medium (MMSM – see Table 8 for composition), 10 mmol/L plasticizer, 2 g/L hexadecane and 0.1 g/L yeast extract. The flasks were autoclaved at 121 °C and 15 psi for 15 minutes (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, NJ, USA or Multitron II, Infors AG, Switzerland) at 30 °C and 140 RPM for the duration of the experiment.

Table 8 - Composition of Minimum Mineral Salt Medium (MMSM)

Salt	Concentration (g/L)	Supplier
NH_4NO_3	4.0	Sigma Aldrich, Oakville, ON
Na2HPO4	6.0	Fisher Scientific, Montréal, QC
KH2PO4	4.0	
$MgSO_4 \bullet 7\ H_2O$	0.2	
$CaCl_2 \bullet 2\ H_2O$	0.01	
$FeSO_4 \bullet 7\ H_2O$	0.01	
Na_2EDTA	0.014	

Because it was impossible to take representative samples from the mixture, whole-flask extractions were used 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 of pentadecane, which served as an internal standard for gas chromatography analysis. The contents of each flask were added to a separatory funnel and the organic phase was recovered and stored at 4 °C in the fridge until analysis.

2.5.2 Gas Chromatography

Gas Chromatography (GC) was performed for analysis of plasticizer concentrations as well as for the detection and quantification of metabolites. The samples were diluted to an appropriate concentration for the gas chromatograph (Varian CP-3800, Agilent Technologies, Mississauga, ON or Trace GC Ultra with AI3000 Autosampler, Thermo Scientific, Waltham, MA, USA) and then 1.0 μL was injected using a syringe. The column used in both cases was a Restek RTX®-5 (length 30 m, 0.32 mm internal diameter, 0.25 μm film), and a flame ionization detector (FID). The method for the Varian CP-3800 GC is summarized in Table 9, while that for Trace GC Ultra is in Table 10.

Table 9 - Operating conditions for gas chromatography using Varian CP-3800

Operating Condition	**Value**
Injection Temperature	250 °C
Initial column temperature	40 °C
Hold time at initial temperature	2 minutes
Temperature ramp #1	10 °C / min
Temperature for change of ramp	150 °C
Temperature ramp #2	20 °C / min
Final column temperature	250 °C
Hold time at final temperature	17 minutes
Detector Temperature	300 °C

Table 10 - Operating conditions for gas chromatography using Trace GC Ultra with autosampler

Operating Condition	**Value**
Sample Volume	1.0 μL
Injection Temperature	250 °C (Split flow)
Initial column temperature	40 °C
Hold time at initial temperature	2 minutes
Temperature ramp	20 °C / min
Final column temperature	300 °C
Hold time at final temperature	5 minutes
Detector Temperature	300 °C

Calibration curves were prepared in order to calculate concentrations from the ratios of peak areas of the compounds and the internal standard pentadecane.

3 Results

3.1 Plasticizer Properties

The glass transition temperatures at varying concentrations for blends of the three potential green plasticizers with PVC, as well as for the commercial plasticizers DEHP and DEHA as reference are shown in Figure 12. Both the succinate and the maleate are more efficient in lowering the Tg compared to the commercial DEHP, and as efficient as the commercial DEHA. The fumarate seems less capable of lowering the Tg in plasticizer concentrations below 25 weight percent, while above that concentration it seems to be more efficient than DEHP, but not quite as good as the two other potential green plasticizers.

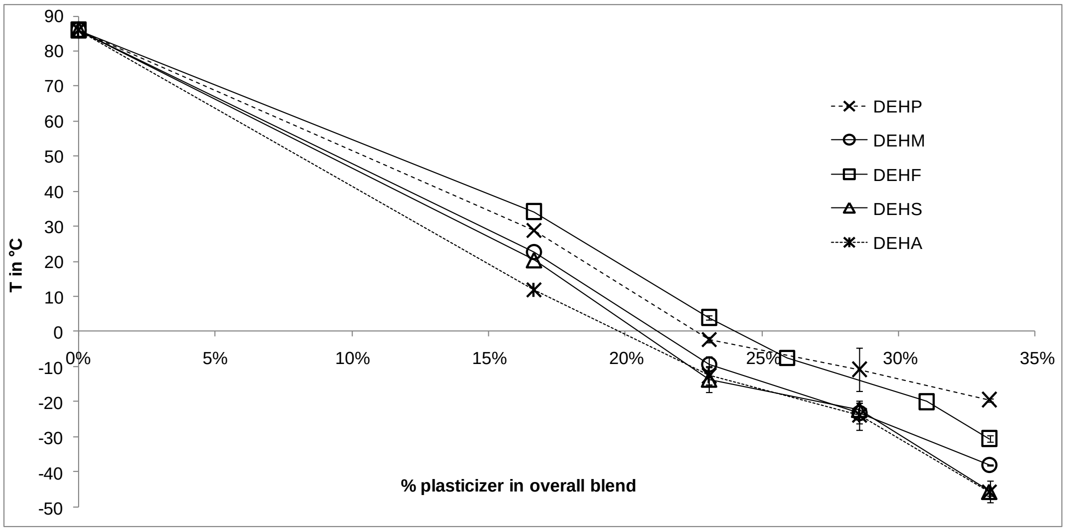


Figure 12 – Glass transition temperatures against plasticizer content for various di 2-ethylhexyl plasticizers (error bars representing standard deviation)

Further analysis done by tensile testing measurements shows the succinate to be performing as well as the commercial plasticizers in terms of elongation at break once a threshold of about 30 weight percent is reached, while also being more malleable then DEHP and as malleable as DEHA, using Young's modulus, or if not applicable the secant modulus at 2 MPa. (see Figure 13 for graphs of strain at break ordered by central molecule and within these by concentration of plasticizer; and Figure 14 for graphs of Young's modulus / secant modulus ordered in the same manner).

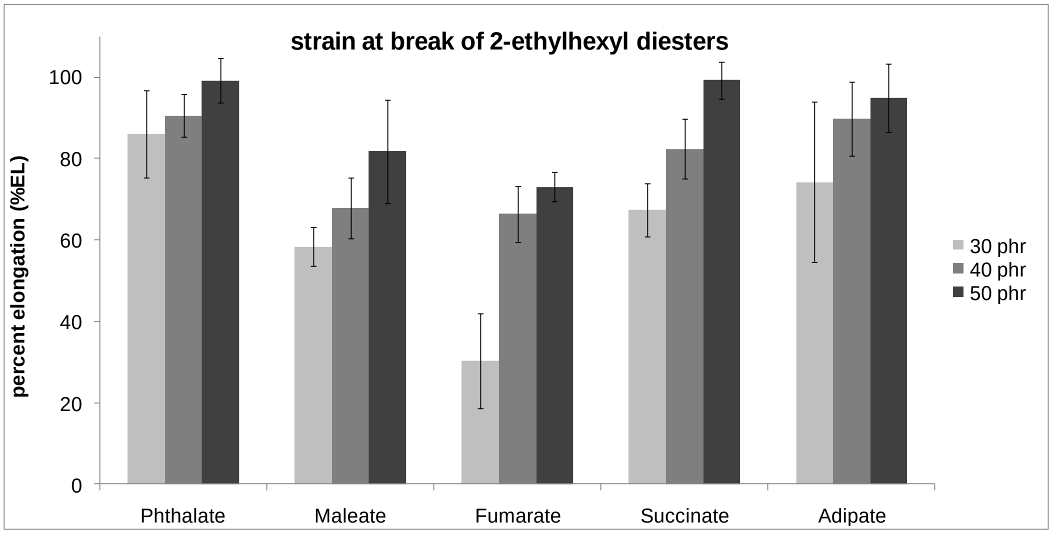


Figure 13 – Strain at break for several blends containing different concentrations of various di 2-ethylhexyl-terminated plasticizers (error bars representing standard deviation)

The secant modulus is reported for all blends except for the blends containing a fumaric acid based plasticizer, because no Hookean behaviour is observed in the stress-strain curves. In that case, the ASTM standard requires the secant modulus to be reported, which is simply a secant to the curve at a set stress value. (ASTM D-638, 2003)

Both the maleate and fumarate blends don't reach values as high as the commercial plasticizers in terms of elongation at break; especially the fumarate, which seems to fracture at much lower strains. Meanwhile for secant modulus at 2 MPa, the fumarate is even less malleable than the phthalate, and the maleate on the contrary is as malleable as the succinate and adipate.

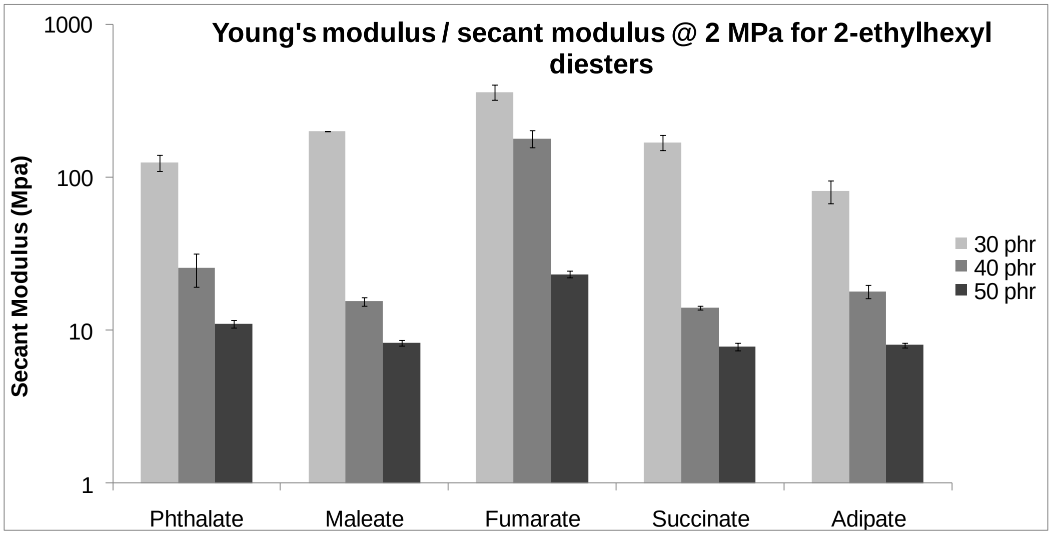


Figure 14 – Young's modulus for the fumarate series and secant modulus for several blends containing different concentrations of various di 2-ethylhexyl plasticizers (error bars representing standard deviation)

Figure 15 and Figure 16 show the glass transition temperature at two different concentrations for blends of PVC with potential green plasticizers with varying side chain length, ordered by the different middle molecules. Within each group the plasticizers are ordered by the length of the longest chain containing carbon and oxygen, for example for the succinates beginning with diethyl succinate (longest chain containing 10 atoms) and ending with dioctyl succinate (longest chain containing 22 atoms). Also included are the results for the Tg of the branched diesters as shown above, and data for commercial DEHP for reference.

At the first concentration (16.6 weight percent; see Figure 15), no clear trend can be seen, as the concentration of plasticizer in the blend is so low that it does not have a big effect on the Tg. It is important to note that this concentration is unrealistic. Usually, in commercial applications no primary plasticizer is used at such a low concentrations because the effects are too small.

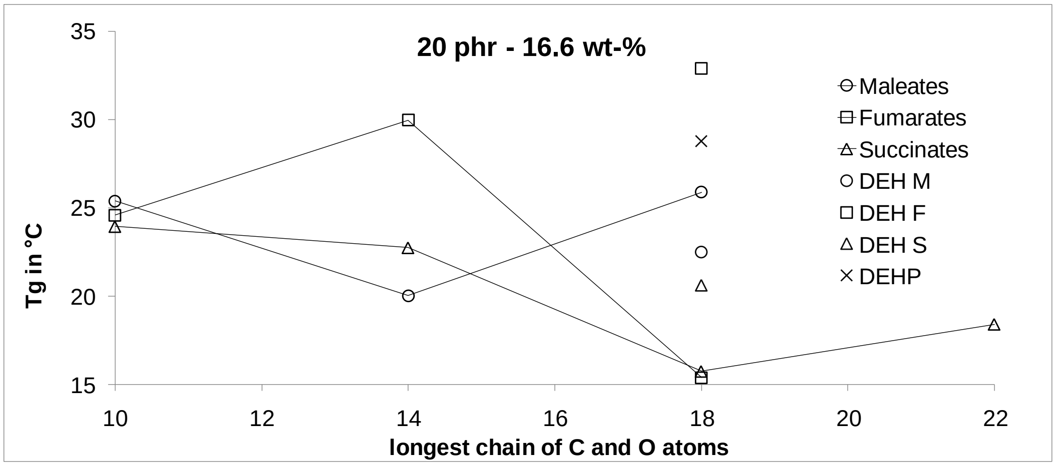


Figure 15 – Glass transition temperatures against molecule length at 16.6 weight-% for various di 2-ethylhexyl plasticizers

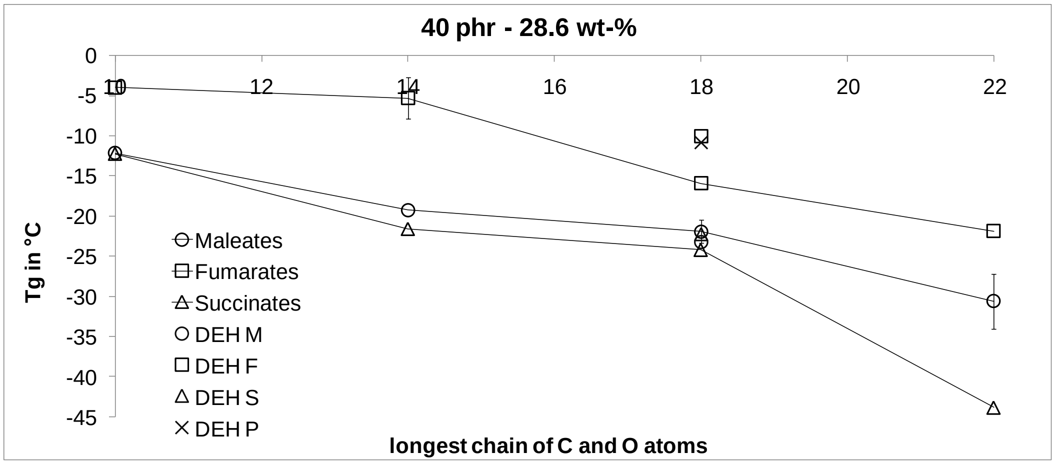


Figure 16 - Glass transition temperatures against molecule length at 28.6 weight-% for various di 2-ethylhexyl plasticizers (error bard representing standard deviation)

The data for 28.6 weight percent (see Figure 16) is of more relevance. A trend can be seen in all series: there is a decreasing glass transition point with increasing length of the overall molecule, and thus the total length of the molecule. As shown before, both succinates and maleates reach lower glass transition temperatures as the fumarates. The only aberration from that trend is the dioctyl succinate which seems to be even more effective in lowering the Tg of PVC than the dioctyl maleate. Comparing the data for the 2-ethly-branched and the unbranched diesters there seems to be no significant difference in Tg reduction for both maleate and succinate, yet for the fumarate there is larger a difference of about 5 °C.

3.2 Biodegradation Properties

Figure 17 and Figure 18 demonstrate the solubilities of two of the plasticizers and their metabolites in chloroform. Figure 17 contains data for one sample taken during the biodegradation of dibutyl succinate. Several extractions with chloroform were performed on the aqueous sample. By the fourth extraction, all of the plasticizer had been removed but a trace amount of the monoester metabolite was still observed. Consequently for the experiments with this plasticizer, five extractions with 20 ml aliquots of solvent were performed and these were then combined for analysis. Figure 18 contains similar data for the system with dihexyl succinate. In this case, one extraction removed most of the compounds of interest from the aqueous sample. Only the metabolite hexanol appeared in significant quantities (only about 7 % of the total hexanol) in the second extract. Hexanol was not of major concern because any produced during the biodegradation was quickly degraded. Consequently, for this system, a single extraction step was considered sufficient to adequately monitor the trends. Similar analyses were done for all of the diesters tested in this study so that the data present represent well the actual amounts of the chemicals being monitored.

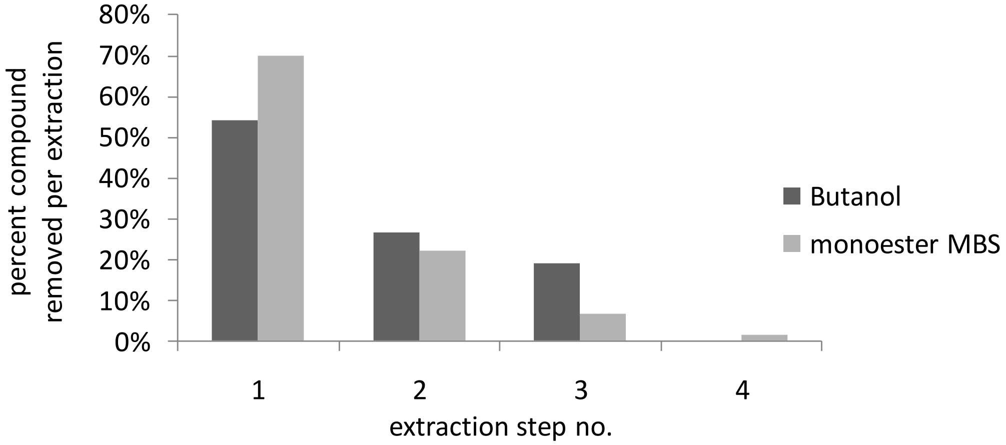


Figure 17 - Solubility of butanol and mono butyl succinate during 4 consecutive extractions with chlorofrom containing internal standard

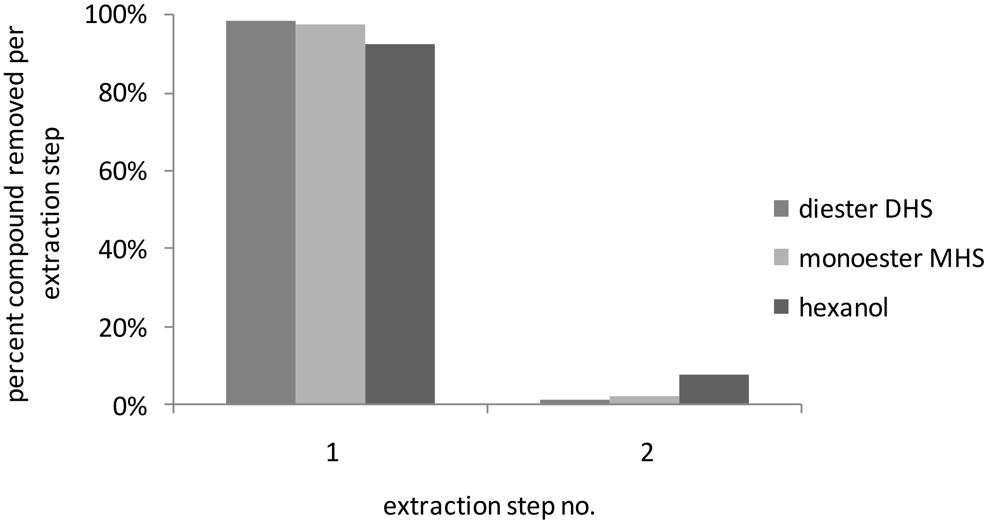


Figure 18 - Solubility of hexanol, mono hexyl succinate and dihexyl succinate during 4 consecutive extractions with chlorofrom containing internal standard

Figure 19 and Figure 20 show data for the biodegradation of dioctyl succinate either with or without hexadecane as a co-substrate. Figure 19 demonstrates that the metabolite, monooctyl succinate, appears as the diester is degraded but it does not reach significant concentrations and is itself degraded. Figure 20 contains the data for the other metabolites, octanol and octanoic acid. In all of these data, there was no significant difference between the experiments with hexadecane added and those without this hydrocarbon. When hexadecane was present, there was no evidence of a decrease in concentration until after most of the diester and its metabolites had been removed.

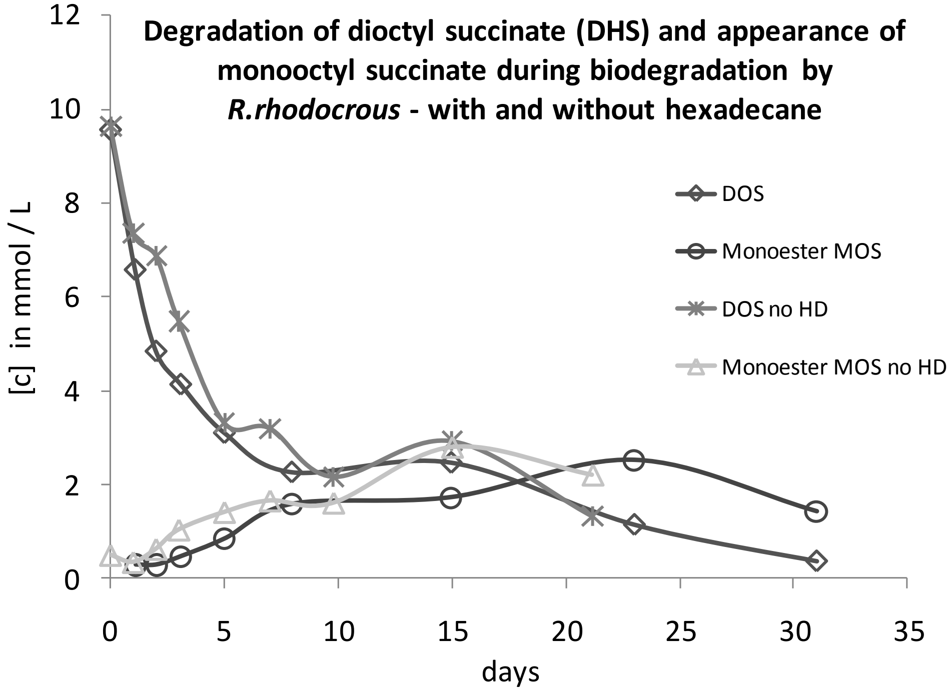


Figure 19 - Biodegradation of dioctyl succinnate and appearance of metabolite mono hexyl succinate in experiments with and without hexadecane present

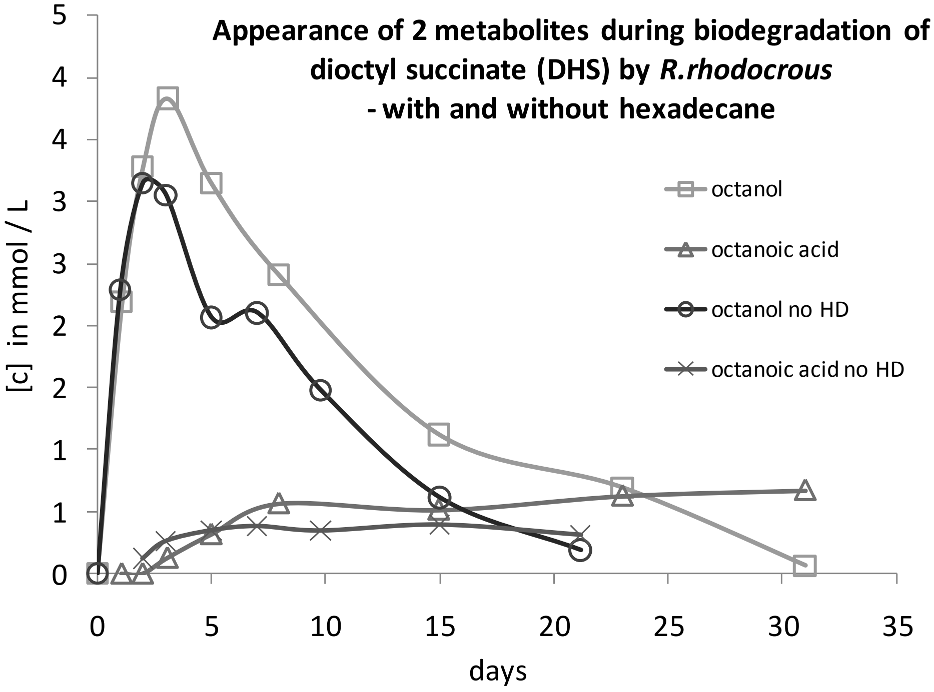


Figure 20 – Appearance of metabolites octanol and octanoic acid during biodegradation experiment of dioctyl succinate hexyl succinate with and without hexadecane present

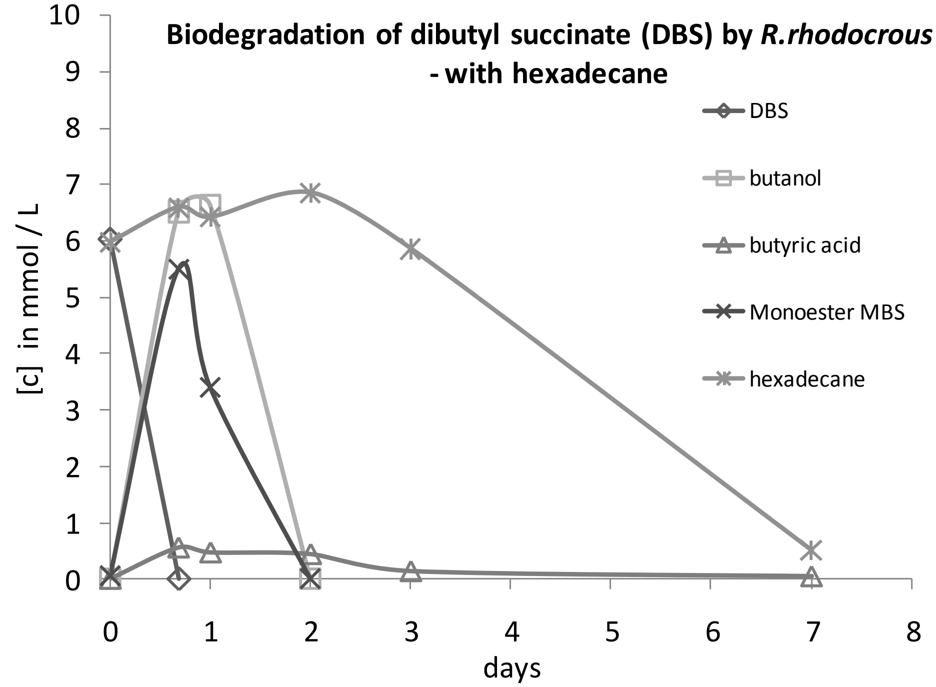


Figure 21 - Degradation of dibutyl succinate, appearance of metabolites and concentration of hexadecane in solution

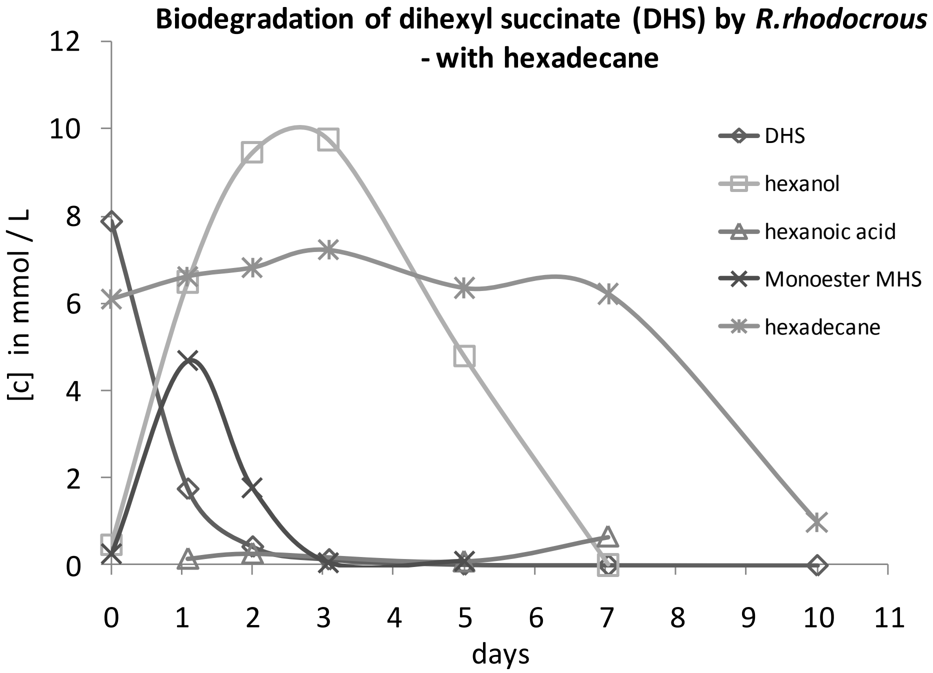


Figure 22 - Degradation of dihexyl succinate, appearance of metabolites and concentration of hexadecane in solution

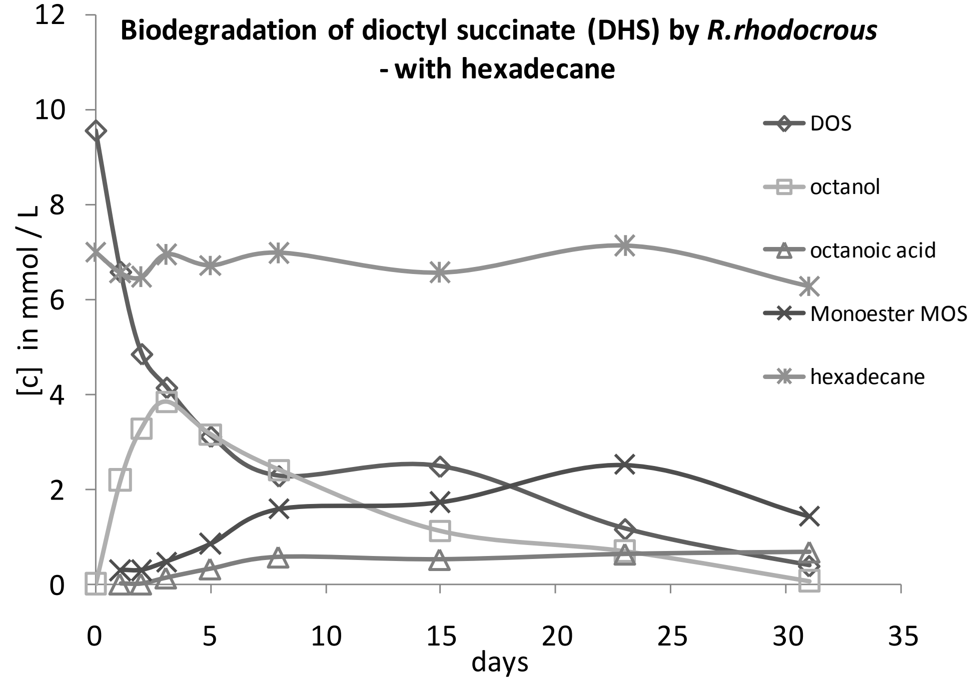


Figure 23 - Degradation of dioctyl succinate, appearance of metabolites and concentration of hexadecane in solution

Figure 21 and Figure 22 show the biodegradation pattern for dibutyl - and dihexyl succinate in the presence of hexadecane. These are similar to the results for dioctyl succinate but significantly faster and only very small amounts of the monoester and the simple carboxylic acid are observed. These figures also show the concentration of hexadecane in the solution and it is clearly visible that its concentration only starts decreasing once all of the other compounds have disappeared. Figure 23 shows the degradation of dioctyl succinate again, also including the concentration of hexadecane in solution, and in that case the hexadecane concentration never decreases, as the metabolites do not disappear over the course of the experiment.

Table 11 - Rate constants and half life of 2-ethylhexyl diesters, assuming first order kinetics

	phthalate	maleate	fumarate	succinate	adipate
R	**-C=C-**	**-CH=CH-**	**-CH=CH-**	**$-(CH_2)_2-$**	**$-(CH_2)_4-$**
Position of ester group	“cis”	cis	trans	saturated	
Rate constant	very small	very small	0.05	0.30	0.12
Half-life	very large	very large	13.1d	2.3d	5.8d
Stable metabolites	Not enough degradation to comment on stable metabolites		2-ethyl hexanol		
Onset of hexadecane-use	Day 0-1	Day 1-2	Day 2-3	Day 1-3	Day 3-4

Table 12 - Rate constants and half life of succinate plasticizers, assuming first order kinetics

	R'-COO-CH2-CH2-COO-R'							
R'	**CH_2C**	**$(CH_2)_3CH_3$**		**$(CH_2)_5CH_3$**		**$(CH_2)_7CH_3$**		**$CH_2CH(C_2H_5)(C_4$**
Carbon	$C_{16}H_{34}$	$C_{16}H_3$	non	$C_{16}H_3$	non	$C_{16}H_3$	non	$C_{16}H_{34}$
Rate	>> 1.45	>> 1.45		1.45	1.45	0.25	0.22	0.30
Half-life	< 0.5d	< 0.5d		0.5d		2.8d	3.2d	2.3d
At least 95% removal of plasticizer	Day 2	Day 2		Day 7		Not observed within 30 days		Stable metabolite 2-ethyl hexanoic acid
Approximate Onset of hexadecane	Day 2	Day 2		Day 7		Not observed		Day 1

Table 11 shows the results for similar experiments conducted with the di-2-ethylhexyl esters of maleic, fumaric, adipic and phthalic acids. The table contains values for the half life each of these estimated using a first order, initial rate approximation. See the Appendix for a sample calculation of rate constant and half-life for a set of the data presented in Table 11 and Table 12. As visible in Table 11 , there was almost no biodegradation observed for either di(2-ethylhexyl) phthalate or di(2-ethylhexyl) maleate. These were the only two compounds in which the two ester functions were in a cis position on the double bond. Dihexyl fumarate, which has a trans orientation, did degrade although the rate was slow. The compound made from the saturated diacids both degraded much more quickly. The length of the internal carbon chain was important and the longer adipate containing compound was the slowest to be biodegraded.

Table 12 on the other hand shows the degradation rates and half-life for compounds that all consist of the saturated succinate central group, but with a varying length of the side chain. Some of the data was collected from experiments done with or without hexadecane. There was no evidence of a difference. It can be seen in Table 12 that as the length of the alcohol chain became longer the rate of biodegradation decreased. The compound made with the branched alcohol 2-ethylhexanol degraded much more slowly than the diester with simple hexanol. However, this compound degraded at a slightly slower rate than the analogue made with octanol, which has the same number of carbon atoms as 2-ethylhexanol.

Table 12 also shows the strong correlation between the mineralization of the plasticizer compounds and the use of hexadecane as carbon source. For those compounds that were made with the straight-chained alcohols, the concentration of hexadecane in the medium only started decreasing when all of the metabolites had disappeared – the extreme case being the dioctyl succinate, where metabolism was so slow that over the course of the whole experiment the hexadecane concentration never declined as there were always metabolites present.

4 Discussion

4.1 Plasticizer Properties

4.1.1 Influence of central group

Plasticizers are used in formulations to make many inexpensive plastic products – especially those of poly (vinyl chloride) (PVC), a rather cheap polymer. Thus, they cannot be too expensive to produce. The general structure of diesters is ideal for this goal as they could be easily synthesized using a Dean-Stark esterification that allows the reaction to go to completion simply by collecting the water from the esterification in a trap attached to a reflux condenser. This was followed by a simple washing step with a solution of sodium bicarbonate, which was shown to remove all unreacted reagents as well as any monoester produced from incomplete esterification. This eliminated the necessity of a more expensive distillation step. For both maleate and succinate the starting material was the 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, inexpensive and would be easy to scale up. However, it is also essential that these compounds could be shown to have the appropriate properties.

First, the compounds were tested that were esterified with the same alcohol as the commercial plasticizers DEHP and DEHA. All of these di 2-ethylhexyl esters tested were found to be as good as or better at plasticizing PVC than the commercial plasticizers. This can be seen in the trends for glass transition temperature, strain at break, Young's modulus and secant modulus.

All of these measurements were done at at least three different concentrations and as expected, the properties became more pronounced as the concentration of added plasticizer increased. In general, the largest changes were observed going from no plasticizer to 30 phr and from 30 to 40 phr. Adding more plasticizer after this did improve the properties but the size of the effect was usually smaller. (Figure 12)

Collectively, these data were analyzed to determine which the best plasticizers were. At the highest concentrations, both the succinate and adipate had the lowest Tg values and the phthalate caused the least effect. Of particular interest was a comparison of the three very similar compounds – the cis and trans structures and the unsaturated analogue. Of these, the trans fumarate consistently had the highest Tg values and the poorest data for the tensile testing, meaning the highest strain and the lowest elongation at break. Overall, the unsaturated succinate was slightly better than the cis maleate isomer.

The experiments done by varying the alcohol used to esterify the anhydride, or the di-ol in case of the fumarates, were consistent. All samples at the same loading of 26.6 wt-% plasticizer, regardless of the alcohol, followed the same trend (see Figure 16). The succinates are the most efficient at lowering the Tg while the fumarates are much poorer at this. This is consistent with the importance of the central structure and the flexibility of the plasticizer to properly mix into the matrix and disrupt crystallinity. This is not surprising as changing the length of the alcohol being used would not be expected to change this order.

One explanation for the superior properties of the succinate could be its relative flexibility due to the freedom of the two ester groups to rotate relative to each other in the saturated molecule. This would allow it to be oriented in the most favourable way for intercalating in the polymer matrix. With this in mind, it then seems that the cis orientation of the unsaturated diesters is more favourable that the trans orientation.

Overall, the succinate also showed comparable or better results relative to the two commercial plasticizers, di-2-ethylhexyl phthalate and di-2-ethylhexyl adipate.

Another possible factor to consider is the polarity of the three new plasticizers. The maleate diester was almost as effective as the succinate. The maleate would be significantly more polar than the fumarate and the succinate, which is free to rotate around the central bond, could also have a configuration that is polar. This can be roughly estimated by looking at the water-solubility of the corresponding acids which is closely related to the polarity of a compound. Maleic acid shows a solubility in water of 788 g / L (Maleic Acid, 2010) due to its strong polarity, while succinic acid has a solubility of an order of magnitude lower at 80 g / L (Succinic Acid, 2009), and the solubility of fumaric acid lies yet another order of magnitude lower at 6 g / L water (Fumaric Acid, 2009), which in fact is not very soluble at all anymore. Possibly the polarity of the plasticizer is important when considering how it is positioned among the large polymer chains.

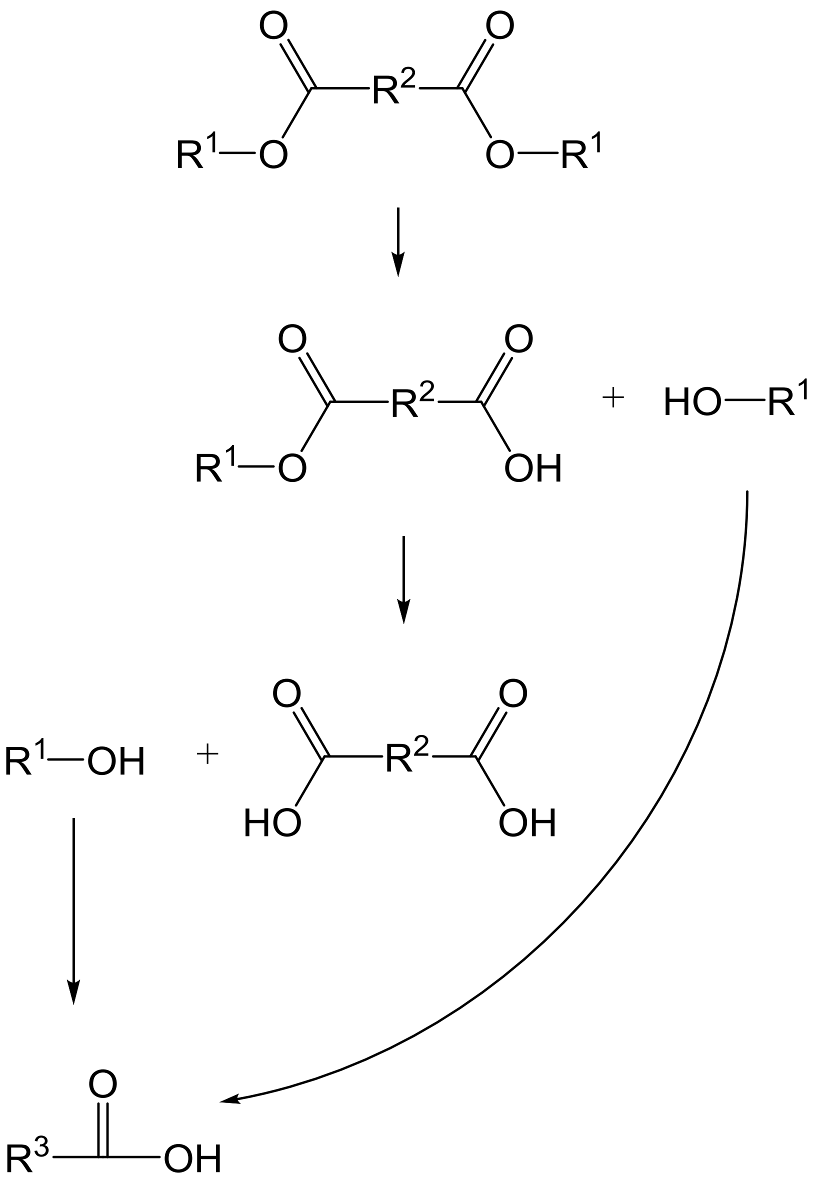
4.1.2 Influence of side chains / overall molecule length

Series of compounds that were esterified using straight-chained alcohols (as opposed to the branched 2-ethyl hexanol used) were also tested for their plasticizer properties.

Glass transition temperature measurements were collected for blends containing 20 phr (16.6 wt-%) and 40 phr blends (28.6 wt-%). There were obvious trends in the data for series of compounds at 40 phr but these were not apparent in the data for 20 phr. The data at 20 phr have Tg values between 15 °C and 35 °C and these temperatures indicate a small effect – the blends would still be hard and glassy, or just on the brink of being flexible. So, at these lower additive concentrations, the effect is small and, consequently, it is not surprising that there are no obvious trends among the data. Usually blends used commercially contain more than 16.6 wt-% plasticizer because of the poor enhancement of properties. Thus, 40 phr were the blends of interest.

Within any one series of the different types of diesters, it is clear that the length of the alcohol does affect the plasticizing properties. It should be noted that increasing the length of the alcohol used to esterify by one carbon atom must increase the overall length of the diesters by two carbon atoms. For the range of alcohols considered here, the longer the alcohol used to make the diester plasticizer, the more effective it was at lowering the Tg. Presumably, as the plasticizer molecule becomes longer, within the range of lengths considered here, the interaction with the polymer chains becomes more effective at disorganizing crystallinity and thus order.

It is interesting that the data for the branched 2-ethylhexyl esters for the two better series of plasticizers, succinates and maleates, are almost identical to those for the esters with hexanol, which have the same overall length. This supports the argument that the length of the plasticizer is important. If the important parameter was the total mass, then the data should have instead been similar to the values for the diesters made with octanol. In contrast to this, the value for the diester of 2-ethylhexanol with fumaric acid does not match the data for fumarate with either hexanol or octanol. However, fumarate data are always poor relative to the other diesters and it is possible that the structure of the fumarate makes this compound more sensitive to the steric effects of adding an ethyl branch to the alcohol.



$R^1 = CH_2CH_3, CH_2CH_2CH_2CH_3, CH_2CH_2CH_2CH_2CH_2CH_3,$
$CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3, CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

$R^2 = CH_2CH_2$, cis-CHCH, trans-CHCH

$R^3 = CH_3, CH_2CH_2CH_3, CH_2CH_2CH_2CH_2CH_3,$
$CH(C_2H_5)CH_2CH_2CH_2CH_3, CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Figure 24 - Observed pattern of degradation for all diester compounds tested

4.2 Biodegradation

4.2.1 Influence of the central group

All of the data are consistent with the biodegradation pattern presented in Figure 24 and this is the same overall pattern that has been reported before for other diesters. (Nalli et al. 2002; Horn et al. 2004; Nalli et al. 2006) The first step was the hydrolysis of one of the ester groups yielding one equivalent each of the alcohol and monoester, which was eventually hydrolyzed at the second ester bond site. This ultimately yielded the free diacid as well as two equivalents of an alcohol. Each alcohol was then quickly oxidized by the microbes to its corresponding acid. In all cases where a linear alcohol was involved, there was no significant build-up in concentration of the corresponding carboxylic acid. This is consistent with earlier biodegradation studies showing that β-oxidation is a rapid pathway for the breakdown of plasticizer metabolites. (Kermanshahi et al. 2009) The only exception was seen in the results for the biodegradation of di-2-ethylhexyl succinate. This leads to the branched 2-ethylhexanol and, eventually, 2-ethyl hexanoic acid. As observed before, (Nalli et al. 2006; Nalli et al. 2006; Kermanshahi et al. 2009) this acid is slow to degrade because the pathway of β-oxidation is blocked in this molecule due to the 2-ethyl branch in the β-position to the acid function.

In the experiments that liberated straight-chain alcohols, these compounds as well as potentially the central diacids could be used as a carbon source by the microbe because they were easily metabolized by β-oxidation. This is proven by the experiments for the succinate diesters, which were done both with and without the presence of hexadecane as a carbon source. There was no significant difference between any of these pairs of experiments. In fact, in every case, there was a pattern of diauxic growth and there was no significant decrease in hexadecane concentration until the last of the plasticizer remnants had been removed (see Table 12). This is probably related to the differences in bioavailability and ease of metabolism. Hexadecane is much less soluble in water than the small alcohols, acids and diacids being liberated. The small acids would be quickly metabolized and both succinic acid and fumaric acid are part of the citric acid cycle.

The longest of the alcohols in this study occurred in dioctyl succinate and this would be expected to lead to the most hydrophobic metabolites. As expected from the above arguments, these exhibited the slowest growth rates for all of the succinate compounds tested. These fragments would be the least soluble and therefore, the least bioavailable. As well, the parent compound should be the least water soluble and this would explain the relative slow rate of the first step, hydrolysis of the ester bond. Despite the slower growth, the plasticizer and its fragments were still used by the microbe before any of the hexadecane was consumed and, even after 31 days, there was no decrease in hexadecane concentration (Figure 23).

The fact that these potential green plasticizers did not need a co-substrate to biodegrade quickly is an important positive consideration because a suitable alternative carbon source might not be present in the environment when required. The use of the straight-chain alcohols instead of 2-ethyl hexanol is an important factor in designing a green plasticizer.

The very slow degradation of di(2-ethylhexyl) maleate is particularly interesting. The geometry of the double bond with two ester functions in the cis orientation is very similar to the portion of the commercial plasticizer, di-2-ethylhexyl phthalate, which is well known to be difficult to biodegrade and persistent in the environment. (Horn et al. 2004) Possible reasons for this stability are steric hindrance interfering with the enzymatic hydrolysis and / or stability due to the delocalization of the ester functional groups with the aromatic ring. While there would be some delocalization in the maleate ester, this compound is not aromatic. Furthermore, the electronic structure of this compound imparts the same stability as would be present for the analogous fumarate. While the fumarate diester is more difficult to biodegrade than the unsaturated succinate diester, this difference was not large and it was hydrolyzed within a period of time in which the maleate remained unaffected. Therefore, a significant amount of the resistance to biodegradation in both the phthalate and the maleate esters must be due to steric effects.

As discussed above, the branching of 2-ethylhexanoic acid makes it resistant to β-oxidation. It is possible that the steric hindrance of this group could interfere with enzymatic hydrolysis as well. However, the cis orientation of the ester groups in both the maleate and phthalates seems to also provide sufficient steric interference between the esters with the enzyme to impart significant resistance to biodegradation. It is obviously important to avoid this arrangement in the development of a green plasticizer.

The fumarate, with esters in the trans-position, was degraded somewhat more slowly than the unsaturated succinate, but much more quickly that the maleate with the two ester bonds in the cis-position. Neither compound is as flexible as the unsaturated diesters and presumably takes longer to interact with the enzymes.

A number of different esters based on the saturated succinic acid used in this study were all degraded very quickly, even the one made with 2-ethyl hexanol (Table 12). This is attributed to the freedom of rotation around the saturated bond between the two ester groups, allowing these compounds to arrange themselves in the most advantageous manner to make these bonds more available to the appropriate enzyme on the surface of the microbes. This is further supported by the fact that even the presence of the ethyl branch in one case showed little effect on the biodegradation rate compared to those compounds not containing the ethyl-branch. This in fact shows that there is an influence of the ethyl-branching, yet not very pronounced. Again, this influence can be based on steric interference as well as on lower solubility of the branched chain of hydrocarbons.

Another relevant consideration is that of solubility. A compound's solubility in water is closely related to its polarity. Although no data on polarity of the diesters is available, looking at the diacid used to make the diester can be of use. As mentioned in section 4.1.1, there exist large differences in the solubility of the diacids in water. (maleic acid: 788 g / L; succinic acid: 80 g / L; fumaric acid: 6 g / L) (Maleic Acid 2010; Succinic Acid 2009; Fumaric Acid 2009) Although these values for solubility aren't valid for the diesters of these compounds, it would be expected that the maleate diesters are more water-soluble than for example the fumarate diesters. In the lights of these numbers it is surprising following Table 11, the di(2-ethylhexyl) maleate was hardly degraded at all, while both di(2-ethylhexyl) diesters of succinic and fumaric acid were. This suggests that solubility does not play a key role in the degradation rate, but rather the ease of interaction between ester-bond and enzyme on the microbe's outside.

The adipate diester was also degraded fairly quickly, as expected, and this is consistent with the argument that there is free rotation about the bonds but it does degrade a bit slower than the succinate diester. This could be due to it being larger and, thus, less soluble in water. For both of these compounds, a small amount of the expected metabolite, 2-ethylhexanol, as well as trace amounts of the monoesters, was found. The alcohol was then oxidized to 2-ethylhexanoic acid, which degraded very slowly. This pattern of metabolites has been shown to be due to the type of alcohol being used and it was expected that the patterns of the appearance and disappearance for these two compounds would be similar.

It has also to be noted that the temporary build-up of monoester indicates that the hydrolysis step of the monoester must be slower than the hydrolysis of one of the ester bonds in the diester. This is somewhat surprising as the water-solubility of the monoester should be higher than the water-solubility of the diester. It is possible though that the site of the ester bond in the monoester is harder to reach for the esterase enzyme, which is on the surface of the microbe due to the aggressiveness of an organic acid. It is also possible that the monoester molecules aggregate to micelles in the aqueous environment, thereby shielding the ester bond from the bacteria.

Two other stable metabolites were identified by gas chromatography for all three potential green plasticizers as well as the two commercial plasticizers tested: 2-ethyl hexanol and 2-ethyl hexanoic acid. These have been reported in the literature and proven to originate from 2-ethyl hexanol, which was used in all experiments on the influence of the middle molecule as the alcohol for esterification. After hydrolysis, the free 2-ethyl hexanol is rather quickly oxidized to 2-ethyl hexanal and ultimately 2-ethyl hexanoic acid. (Nalli et al. 2006) This compound has been proven to be more toxic than the parent compound. (Nalli et al. 2002; Horn et al. 2004) This means that an alcohol other than the 2-ethyl hexanol needs to be used in order to prevent its biodegradation metabolite to be a stable one. A straight-chained alcohol missing the ethyl side group is likely to be non-problematic, as these compounds are commonly mineralized by β-oxidation.

Another factor to consider is the potential for adverse environmental effects of the compounds being tested. Both succinic acid and fumaric acid are part of the Krebs cycle and maleic acid is a common biological chemical. All three of the new compounds are based on natural products, thus they can be considered as “safe” when entering the environment.

4.2.2 Influence of the side chain length and branching

When looking at the influence of the alcohol used to make the diester on the biodegradation rate in Table 12, it is noticeable that the longer the aliphatic chain of the alcohol – and with that also the overall length of the molecule – the slower the overall degradation rate of the compound. This is attributed to the decreasing water-solubility of the compounds due to longer terminal aliphatic chains which generally increase hydrophobicity of the compound and thus making the plasticizer less available to the microbes in their aqueous environment. This argument is supported by the fact that the 2-ethylhexyl succinate is degraded more slowly than the equally long dihexyl succinate, yet only slightly more quickly than the di-n-octyl succinate (Table 12). This has to be attributed to its 2-ethyl branches that add quite some hydrophobicity to the molecule, and by sterically hindering the microbe's access to the ester-bond, which explains the difference in degradation rate.

It is important to note that all succinate compounds degraded in the timeframe of one week, which is significantly faster than, for example, commercial DEHP. This, along with the fact that those succinates containing straight-chained alcohols do not show a build-up of toxic metabolites, renders these compounds superior to DEHP in terms of biodegradation.

5. Conclusion

Although all three of the different types of diesters were as good as or better than DEHP at lowering the glass transition temperature of PVC, the succinates were especially effective, as they also resulted in both a strain at break and secant modulus that were comparable to the values for mixtures with DEHP. This was not true for the maleates or the fumarates. Considering variations of the side chains for a particular type of diester, it was determined that the ethyl-branch did not have a significant influence on plasticization properties. It was also observed that the plasticizing properties improved with a longer side chain, which meant a longer overall molecule. Thus, considering only plasticization, succinic acid, esterified with a long-chained alcohol, would be the best candidate of all of the compounds tested.

When considering biodegradation properties, it was apparent that factors that resulted in rapid biodegradation were (a) orientation of the two ester groups relative to each other (which serves in explaining the difficulty of phthalate degradation), (b) solubility in water (this was concluded from the fact that the shortest plasticizers were the easiest to degrade) and (c) saturation of the central acid. The most biodegradable compounds were the succinates with short side chains.

Overall, the majority of the compounds tested could be considered as plasticizers but to be a green plasticizer, it is obvious that the succinates are preferable. In terms of side chain length, it would be necessary to make a trade-off between long chains that are needed for plasticization and short side chains, which are beneficial for fast degradation rates. A good compromise would be dihexyl succinoate. It gave very good plasticization results and was completely biodegraded in a few days.

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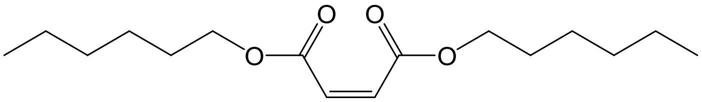
APPENDIX

NMR Results

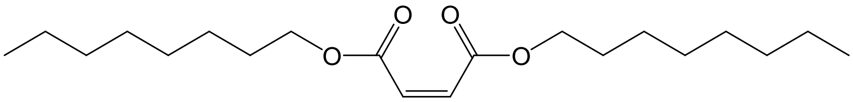
The multiplicity of the signals is abbreviated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet).

Compounds derived from maleic anhydride



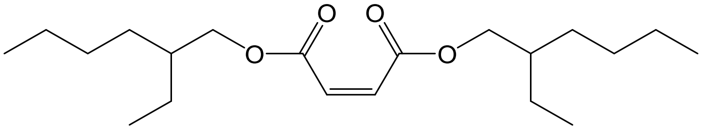
dihexyl maleate
Chemical Formula: $C_{16}H_{28}O_4$
Molecular Weight: 284.39

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 12H, $CH_2(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.63 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 4.08 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.20 [s, 2H, $CO(C\underline{H})_2CO$]



dioctyl maleate
Chemical Formula: $C_{20}H_{36}O_4$
Molecular Weight: 340.50

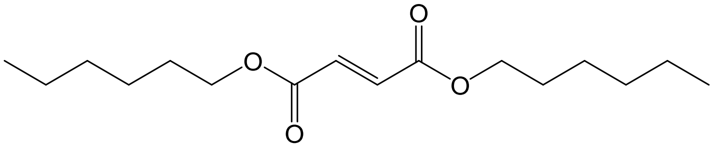
^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 20H, $CH_2(C\underline{H}_2)_5CH_3$], δ (ppm) = 1.63 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 4.08 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.20 [s, 2H, $CO(C\underline{H})_2CO$]



bis(2-ethylhexyl) maleate
Chemical Formula: $C_{20}H_{36}O_4$
Molecular Weight: 340.50

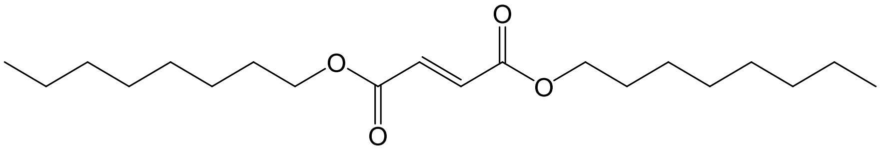
^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [m, 12H, $C\underline{H}_3$], δ (ppm) = 1.20 -1.40 [m, 16H, $CH(C\underline{H}_2CH_3)((C\underline{H}_2)_3CH_3)$], δ (ppm) = 1.60 [m, 2H, $OCH_2C\underline{H}$], δ (ppm) = 4.08 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.20 [s, 2H, $CO(C\underline{H})_2CO$]

Compounds derived from fumaric acid



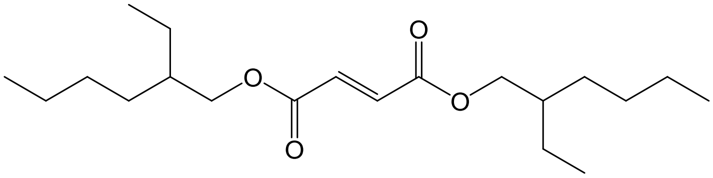
dihexyl fumarate
Chemical Formula: $C_{16}H_{28}O_4$
Molecular Weight: 284.39

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.88 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 – 1.40 [m, 12H, $CH_2(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.65 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 4.19 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.91 [s, 2H, $CO(C\underline{H})_2CO$]



dioctyl fumarate
Chemical Formula: $C_{20}H_{36}O_4$
Molecular Weight: 340.50

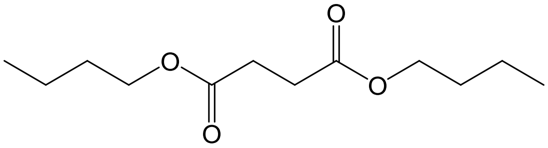
^{1}H-NMR (300.1 MHz in $CDCl_3$): δ (ppm) = 0.88 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.27 [m, 20H, $CH_2(C\underline{H}_2)_5CH_3$], δ (ppm) = 1.60 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 4.19 [t, 4H, $OC\underline{H}_2CH_2$], δ (ppm) = 6.84 [s, 2H, $CO(C\underline{H})_2CO$]



bis(2-ethylhexyl) fumarate
Chemical Formula: $C_{20}H_{36}O_4$
Molecular Weight: 340.50

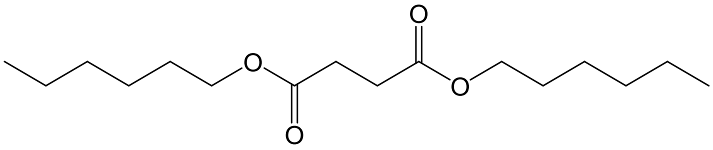
1H-NMR (500.1 MHz in CDCl3): δ (ppm) = 0.92 [t, 12H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 12H, $CH(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.40 [dd, 4H, $CH(C\underline{H}_2CH_3)$], δ (ppm) = 1.60 [m, 2H, $CH_2C\underline{H}$], δ (ppm) = 4.20 [m, 4H, $OC\underline{H}_2CH$], δ (ppm) = 6.81 [s, 2H,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

Compounds derived from succinic anhydride



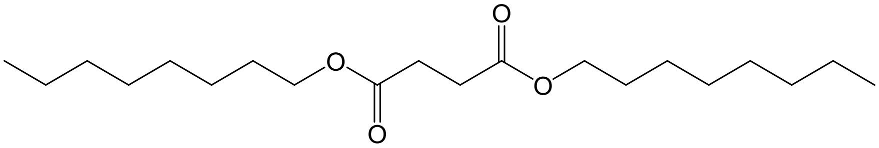
dibutyl succinate
Chemical Formula: $C_{12}H_{22}O_4$
Molecular Weight: 230.30

^{1}H-NMR (300.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 4H, $CH_2C\underline{H}_2CH_3$], δ (ppm) = 1.60 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.62 [s, 4H, $CO(C\underline{H}_2)_2CO$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]



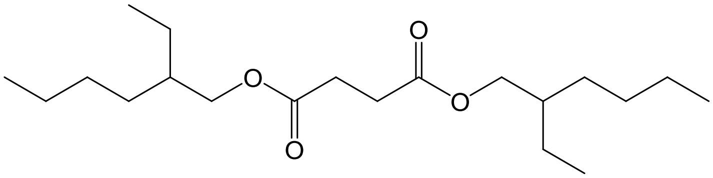
dihexyl succinate
Chemical Formula: $C_{16}H_{30}O_4$
Molecular Weight: 286.41

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 12H, $CH_2(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.60 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.62 [s, 4H, $CO(C\underline{H}_2)_2CO$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]



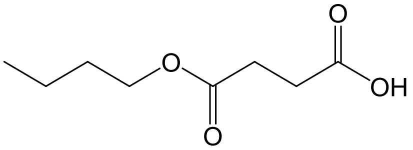
dioctyl succinate
Chemical Formula: $C_{20}H_{38}O_4$
Molecular Weight: 342.51

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 6H, $CH_2C\underline{H}_3$], δ (ppm) = 1.25 [m, 20H, $CH_2(C\underline{H}_2)_5CH_3$], δ (ppm) = 1.60 [m, 4H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.62 [s, 4H, $CO(C\underline{H}_2)_2CO$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]



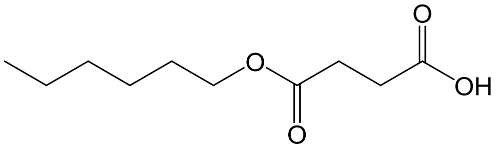
bis(2-ethylhexyl) succinate
Chemical Formula: $C_{20}H_{38}O_4$
Molecular Weight: 342.51

^{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, $OC\underline{H}_2CH$]



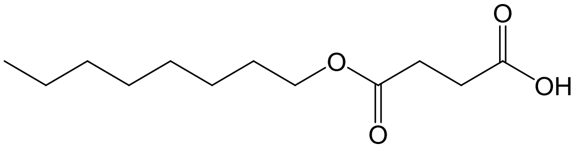
mono butyl succinate
Chemical Formula: $C_8H_{14}O_4$
Molecular Weight: 174.19

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 3H, $CH_2C\underline{H}_3$], δ (ppm) = 1.40 [m, 2H, $CH_2C\underline{H}_2CH_3$], δ (ppm) = 1.60 [m, 2H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.60 [t, 2H, $CH_2OCOC\underline{H}_2CH_2COOH$], δ (ppm) = 2.65 [t, 2H, $CH_2OCOCH_2C\underline{H}_2COOH$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]



mono hexyl succinate
Chemical Formula: $C_{10}H_{18}O_4$
Molecular Weight: 202.25

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 3H, $CH_2C\underline{H}_3$], δ (ppm) = 1.40 [m, 6H, $CH_2(C\underline{H}_2)_3CH_3$], δ (ppm) = 1.60 [m, 2H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.60 [t, 2H, $CH_2OCOC\underline{H}_2CH_2COOH$], δ (ppm) = 2.65 [t, 2H, $CH_2OCOCH_2C\underline{H}_2COOH$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]



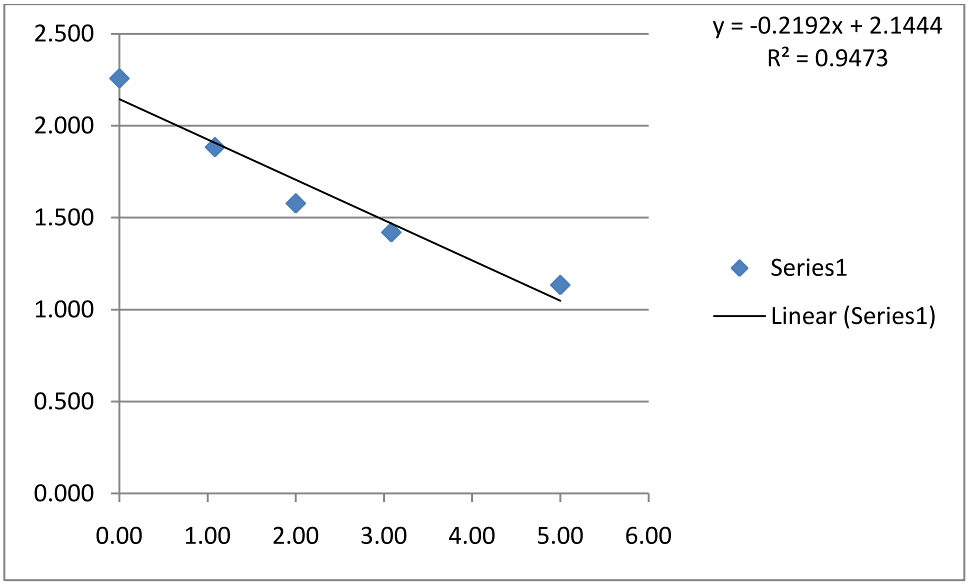
mono octyl succinate
Chemical Formula: $C_{12}H_{22}O_4$
Molecular Weight: 230.30

^{1}H-NMR (500.1 MHz in $CDCl_3$): δ (ppm) = 0.92 [t, 3H, $CH_2C\underline{H}_3$], δ (ppm) = 1.40 [m, 10H, $CH_2(C\underline{H}_2)_5CH_3$], δ (ppm) = 1.60 [m, 2H, $OCH_2C\underline{H}_2CH_2$], δ (ppm) = 2.60 [t, 2H, $CH_2OCOC\underline{H}_2CH_2COOH$], δ (ppm) = 2.65 [t, 2H, $CH_2OCOCH_2C\underline{H}_2COOH$], δ (ppm) = 4.12 [t, 4H, $OC\underline{H}_2CH_2$]

Sample calculations for initial rate approximation

Example: dioctyl maleate degradation

t	log [c]
0.00	2.258
1.08	1.884
2.00	1.578
3.08	1.421
5.00	1.134



<u>Resulting rate constant from slope: 0.22</u>

<u>Half-Life for 1st order kinetics:</u> $t_{1/2} = \frac{\ln(2)}{rate\ constant} = \frac{ln(2)}{0.22} \approx 3.2$ days