Evaluation of succinate-based plasticizers for poly(vinyl chloride)

by

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Abstract

Poly(vinyl chloride) (PVC) is one of the highest volume production polymers, but on its own it is brittle and unstable when exposed to heat and light. As such, the use of additives such as plasticizers are necessary to improve its material properties. Not surprisingly, given the commercial importance of PVC, plasticizers for this particular polymer represent an important segment of the additives market. These are typically small organic molecules that are used to improve the flexibility and processability of PVC. Most commonly, plasticizers are simply blended with PVC rather than chemically bound to the polymer, which is inexpensive and easiest to produce. However, this results in their eventual migration from the polymer matrix, thereby not only rendering the material brittle over time, but also causing health and ecological concerns as the plasticizer is gradually released into the environment. This is the case with the most important commercial plasticizer for PVC, di(2-ethylhexyl) phthalate (DEHP), which is a known endocrine disruptor and a source of toxic metabolites that tend to persist in the environment.

To address the need for alternative plasticizers, a new class of plasticizers based on succinic acid and linear alcohols was studied. This builds upon previous work that showed that succinate diesters are effective plasticizers that can be bio-sourced, produced without organic solvents, and designed to be readily biodegradable. The structure-function relationship of alkyl chain length and performance was investigated by modulating the central and side chain lengths of the plasticizers. The central chain length showed the greatest impact on the plasticizer performance (i.e., glass transition temperature, tensile properties, surface hardness, and leaching). Plasticizers with central chain lengths of three carbon atoms produced blends with greater tensile strength and surface hardness and extending it to five carbon atoms produced softer materials. Further increasing the central chain length led to a noticeable decrease in compatibility with visible plasticizer exudation. In contrast, the side chain lengths showed minimal impact on the blend properties for compounds with similar central groups.

Overall, the succinate-based plasticizers/PVC blends all exhibit equal or improved strain at break (by up to 77%), stress at break (reduced by up to 25%), surface hardness (reduced by up to 43%), and glass transition temperature (reduced by up to 11°C) when compared to blends with commercial plasticizer DEHP at 40 phr. Leaching tests indicate that these plasticizers perform comparably to DEHP, further supporting their suitability as alternative plasticizers for PVC.

The effect of plasticizer loading on the mechanical and thermal performance was also investigated. These results indicate that a lower concentration of these succinate-based plasticizers in PVC is needed to achieve comparable performance to PVC/DEHP blends, making them attractive alternatives to DEHP. Further study is needed to evaluate the biodegradation profiles of these new plasticizers to establish them as a true green alternative.

Résumé

Le poly(chlorure de vinyle) (PVC) est l'un des polymères les plus produits, mais à lui seul est fragile et instable à la chaleur et à la lumière. En tant que tel, l'utilisation d'additifs tels que des plastifiants est nécessaire pour améliorer ses propriétés. Il n'est pas surprenant, étant donné l'importance commerciale du PVC, que les plastifiants pour PVC représentent un segment important du marché des additifs. Les plastifiants sont généralement de petites molécules organiques qui sont utilisées pour améliorer la flexibilité et la facilité de transformation du PVC. Habituellement, les plastifiants sont simplement mélangés au PVC plutôt que liés chimiquement au polymère, car cette méthode est moins chère et permet une production plus facile. Toutefois, cela entraîne leur migration éventuelle de la matrice polymère, ce qui non seulement rend le matériau fragile au fil du temps, mais pose également des problèmes à la santé et écologiques car le plastifiant est libéré dans l'environnement. C'est le cas du plastifiant commercial le plus important pour le PVC, le di(2-éthylhexyle) phtalate (DEHP), qui est un perturbateur endocrinien connu et une source de métabolites toxiques qui persistent dans l'environnement.

Pour répondre au besoin de plastifiants alternatifs, une nouvelle classe de plastifiants basée sur l'acide succinique et des alcools linéaires a été étudiée. Cette étude s'appuie sur des travaux antérieurs qui ont démontré que les diesters de succinate sont des plastifiants efficaces qui peuvent être bio-sourcés, produits sans solvants et conçus pour être facilement biodégradables. Ici, la relation structure-fonction entre la longueur de la chaîne alkyle et de la performance a été étudiée en modulant la longueur de la chaîne centrale et latérale des plastifiants. La longueur de la chaîne centrale a montré le plus grand impact sur la performance du plastifiant (c'est-à-dire la température de transition vitreuse, les propriétés de traction, la dureté de surface et la migration). Les plastifiants avec une longueur de chaîne centrale de trois atomes de carbone ont produit des mélanges avec une plus grande résistance à la traction et une plus grande dureté de surface, et l'extension à cinq atomes de carbone a produit des matériaux plus mous. Une augmentation supplémentaire de la longueur de la chaîne centrale a entraîné une diminution notable de la compatibilité avec l'exsudation visible du plastifiant. En revanche, la longueur des chaînes latérales n'a eu qu'un impact minime sur les propriétés des mélanges pour les composés ayant des groupes centraux similaires.

Dans l'ensemble, les mélanges de plastifiants à base de succinate/PVC présentent tous des propriétés égales ou améliorés d’allongement à la rupture (jusqu'à 77 %), de résistance à la traction (réduite de 25%), de dureté (réduite de 43 %) et de température de transition vitreuse (réduite de 11°C) par rapport aux mélanges contenant le plastifiant commercial DEHP à 40 phr. Les tests de migration indiquent que ces plastifiants sont comparables au DEHP, ce qui confirme qu'ils conviennent comme plastifiants de remplacement pour le PVC.

L'effet de la concentration du plastifiant dans le mélange sur la performance mécanique et thermique a également été étudié. Ces résultats indiquent qu'une concentration plus faible de ces plastifiants à base de succinate est nécessaire pour obtenir une performance comparable à celles des mélanges PVC/DEHP, ce qui en fait des alternatives intéressantes. Des études supplémentaires sont nécessaires pour évaluer les profils de biodégradation de ces nouveaux plastifiants afin de les établir comme une véritable alternative verte.

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Contribution of Authors

The following manuscript-based thesis consists of one article prepared for submission in a peer-reviewed journal, of which I am the primary author:

Godbille-Cardona, G., Nicell, J.A., Maric, M., Leask, R.L. (2022). “Succinate-based plasticizers: Effect of plasticizer structure on mechanical and thermal performance of poly(vinyl chloride) plastic formulations.” (Chapter 3)

I planned and performed the experiments in this article and was responsible for interpreting and analyzing the results. I also prepared and edited the manuscript. My co-authors, Richard Leask, Jim Nicell, and Milan Maric were responsible for funding acquisition, supervision of the research project, and editing of the manuscript.

Chapter 1: Introduction

1.1 Overview

Poly(vinyl chloride) (PVC) is a versatile thermoplastic used in construction, packaging, medical, and domestic applications.[1] It is one the most commonly used plastics, with global production capacity of PVC exceeding 50 million metric tonnes per year.[2,3] On its own, PVC is a brittle material that is unstable to heat and light. Thus, it requires the use of additives for processing, stabilization, and achieving the desired material properties.[4] Plasticizers are an important class of additives that facilitate processing, and provide flexibility to the final product. Some applications of flexible PVC include packaging, wire insulation, toys, medical tubing and more.[4] PVC plasticizers represent one of the largest segments of the additives market as a whole.[5,6]

Plasticizers are materials that are added into plastic formulations to improve the final product properties.[7] These typically consist of small molecules which serve to lower the glass transition temperature of the blend.[8] The glass transition temperature marks the transition of the polymer from a rigid to a more flexible rubbery state.[6] Plasticizers can be classified as either internal or external. Internal plasticization involves chemically modifying the polymer structure by grafting or copolymerization.[7] This strategy is more costly and requires more complex processing than external plasticization.[9] External plasticizers are molecules that are directly blended with the polymer, without the formation of covalent bonds. External plasticization is more commonly used as it is generally less expensive and affords greater control over the end-product properties.[10]

Phthalic acid esters, or phthalates, represent the largest class of plasticizers, accounting for approximately two-thirds of all plasticizer production in 2018.[11,12] The most prominent PVC plasticizer is di(2-ethylhexyl) phthalate (DEHP), representing over half of all phthalate plasticizer production at 3.24 million metric tonnes annually.[12] However, there is increasing societal and regulatory pressure to transition away from phthalate plasticizers.[13–16] Since these compounds are added as external plasticizers, they eventually migrate from the polymer matrix, causing the material to become brittle.[10] It also results in the release of the plasticizer into the environment and in human exposure.[17] This is of particular concern with phthalate plasticizers, which are pervasive in the environment and linked to adverse health effects. For example, DEHP and its metabolites persist in the environment and have been detected in soil, water, and air.[18–21] Studies have linked DEHP to a range of toxic effects,[22–25] and several of its stable metabolites have been shown to be more acutely toxic than the parent compound.[26,27] For these reasons the use of DEHP and structurally similar phthalates is prohibited for use in children's toys in Canada, the United States, and the European Union.[13–16] However, phthalate-based plasticizers remain one of the most developed and important class of plasticizers due to their performance and low cost.[17]

With the concerns surrounding phthalate-based plasticizers, there is a need to develop safer alternatives that can compete with the phthalates in terms of both performance and cost. Such alternatives should also be designed using green chemistry[28] and green engineering principles.[29] Several alternative plasticizers have been proposed; however, few have comparable performance and cost to DEHP and fewer still are of commercial importance.[30,31] The use of alternative, non-petroleum based plasticizers is mostly limited to specialty applications that can support the added expense and diminished performance.[3,30] There remains a need for new, general purpose plasticizers that can meet the growing demand for DEHP alternatives.

1.2 Objectives

The primary objective of this work is to design and evaluate new green plasticizers that can compete with DEHP in terms of mechanical and thermal performance. These plasticizers should also be readily biodegradable, non-toxic, and have reduced migration rates compared to DEHP. For this purpose, a series of succinate-based compounds were synthesized for use as external plasticizers for PVC (Figure 1-).

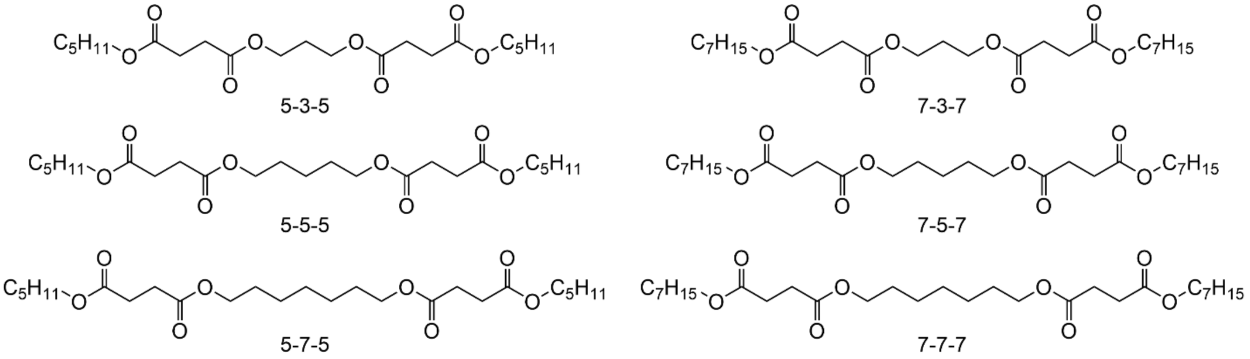


Figure 1-1. Chemical structure of the proposed succinate-based plasticizers. Nomenclature based on the central and side alkyl chain lengths, following the form side-central-side.

This work aims to determine the viability of these new plasticizers as environmentally friendly alternatives to DEHP. The structure-function relationship of the plasticizers was investigated by modulating both the internal alkyl chain length and that of the side chains.

The specific objectives of this study were to:

1. Evaluate the mechanical and thermal properties of the succinate plasticizer/PVC blends;
2. Investigate the permanence of the plasticizer in the PVC blends;
3. Determine the effect of central and side alkyl chain lengths on plasticizer performance; and
4. Compare the performance to previously proposed plasticizers and commercially-available options.

Chapter 2: Background

2.1 Poly(vinyl chloride) and Plasticizers

Poly(vinyl chloride) (PVC) is the second most produced thermoplastic resin, with global production surpassing 40 million metric tonnes worldwide.[3] It is a homopolymer containing one chlorine atom on every second carbon of the polymer backbone (Figure 2-). PVC is largely comprised of amorphous regions, with commercial polymers having 7-20% crystallinity.[32,33] The weak dipole present in the vinyl monomer leads interactions between the polymer chains, restricting molecular motion.[34] As a result, neat PVC has a relatively high glass transition temperature (T_g) of approximately 80°C.[34] Below this temperature, unplasticized PVC is a highly rigid material.

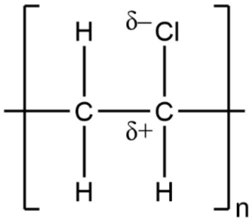


Figure 2-1. Chemical structure of PVC with its weak dipole indicated (δ+ and δ-).

The widespread use of PVC is enabled by its versatility and low cost. Other advantages of PVC are that it is durable, chemically inert, easily sterilized and readily coloured.[35] Compared to other thermoplastics, PVC plastic formulations generally contain a large number of compounding ingredients which can be tailored for different applications, giving it its versatility.[36] Plasticizers are used to lower the glass transition temperature and extend the applicability of PVC.[35] Several other additives are required for stabilizing and processing PVC. Stabilizers are needed to prevent the thermal and UV degradation of the polymer.[36] Processing aids and lubricants are also needed to facilitate manufacturing by lowering the melt viscosity.[36] Overall, additives are an important part of the commercial success of PVC.[37]

Approximately 90% of all plasticizers are manufactured for use in PVC.[5] One of the unique characteristics of PVC is its ability to incorporate high quantities of plasticizer.[5] In fact, plasticizer content can reach up to 50% of a PVC formulation by weight.[30] Often, commercial PVC blends include a primary plasticizer, incorporated in large amounts, and secondary plasticizers, incorporated in smaller quantities. Secondary plasticizers serve to reduce costs or further alter the material properties.[7] As stated, plasticizers reduce the T_g, but they also alter the mechanical properties of the material. Plasticizers are associated with increasing strain at break, reducing tensile strength, and reducing surface hardness.[5,10]

2.2 Plasticization Theories

While several theories seek to explain the mechanism of plasticizer action, none can account for all of the behaviors observed in polymer-plasticizer systems,[10] This poses challenges when developing new plasticizers, as the relationship between structure and performance is not explicitly known. Together, the lubricity, gel, and free volume theories can be used to approximate the fundamental behavior of plasticized materials.[7]

2.2.1 Lubricity Theory

The lubricity theory stipulates that plasticizers facilitate the movement of polymer chains by reducing the intermolecular friction.[7] It assumes that the resin is initially rigid due to the intermolecular forces between polymer chains, which form a rigid network.[38] The addition of plasticizer allows the chains to move freely, sliding over internal gliding planes.[7] It suggests that certain segments of the plasticizer are attracted to the polymer and act as a solvent; while the others shield the polymer chain and act as a lubricant.[38] Based on this theory, an effective plasticizer needs to have functional groups that create points of attraction in both the polymer and plasticizer, and that the location and size of these groups needs to be compatible to facilitate these interactions.[38] However, the applicability of this approach is limited, as it assumes that polymer-polymer and plasticizer-plasticizer interactions are weak.[10]

2.2.2 Gel Theory

The gel theory of plasticization treats the polymer as a network formed by attachments between the polymer molecules. This honeycomb or gel structure of closely attached chains cannot easily deform.[7] External plasticizer molecules improve the flexibility by dynamically solvating and desolvating these sites, allowing the polymer to flex and elongate under external stress.[17] Any unattached plasticizer forms clusters that serves to swell the gel and facilitate polymer motion by reducing the polymer-polymer interactions.[39] Plasticization, under this framework, requires limited swelling as opposed to complete dissolution.[10]

The gel theory can explain some of the behaviors of polymer-plasticizer systems. It can explain the phenomena whereby non-solvents can result in a plasticizing effect, since these molecules still succeed in limiting the polymer-polymer interactions.[40] It also accounts for the fact that internal plasticizers perform poorly at low temperatures compared to external ones, as permanently bound plasticizers do not have as much freedom to dynamically solvate and desolvate sites on the polymer chains.[7]

2.2.3 Free Volume Theory

The free volume theory was later developed to account for the decrease in T_g with plasticization.[40] Experimental observation showed that the specific volume of polymers decreases linearly with temperature until the T_g.[41] Below the T_g the material is glassy and rigid, and the specific volume decreases at a slower rate.[41] This theory attributes the increased specific volume above T_g to an increase in free volume. Free volume is defined as the difference between the specific volume at a temperature of interest and its absolute specific volume (at 0 K).[42] The increase in free volume with temperature is associated with the increase in space between molecules. At temperatures at and below T_g, the structure largely remains the same since the internal mobility is negligible.[7] Above the T_g, the molecules can move more freely.[7] Based on this theory, an increase in free volume is needed to achieve a plasticizing effect.[10]

The main contributors to the free volume are the motion of chain ends, side chains, and the main chain.[10,43] Several approaches for increasing the free volume exist, such as:

1. Lowering the molecular weight to increase the number of end groups;
2. Internal plasticization to increase side chain length and main chain motion;
3. External plasticization to increase the number of end groups; and
4. Raising the temperature to increase overall motion

This theory does explain the reduction in T_g by the addition of plasticizers, but not the changes in other properties, such as viscosity.[7] It also fails to predict antiplasticization at low plasticizer concentrations, where the polymer becomes more rigid compared to its unplasticized analog.[10] Several mathematical models based on the free volume theory have been developed, with limited applicability.[7,40,44] These tend to work well for the more studied dialkyl phthalate plasticizers, but the applicability of the models is limited given that the polymer properties depend on its thermal history, crystallinity, and tacticity, all of which are variable.[44]

While no individual theory can encompass all aspects of plasticization, they are useful as guiding principles when considered together. The gel theory points to the use of external plasticizers over internal ones for better low temperature performance. From the lubricity theory, we can expect that a good external plasticizer should have similar polarity to the polymer with which it will be blended. The free volume theory can be used to inform the design of the plasticizer molecule to lower the T_g by favoring low molecular weight external plasticizers to increase the number of end groups.

2.3 Plasticizer Design

The design of alternative plasticizers needs to be based on the traditional criteria for plasticizer performance and green chemistry. Suitable alternative plasticizers for PVC should meet the following criteria:

1. Have comparable or improved plasticizing performance relative to commercially available products in terms of (a) compatibility; (b) efficiency, and (c) permanence;
2. Be readily biodegradable; and
3. Be a non-toxic compound with non-toxic metabolites.

2.3.1 Conventional Plasticizer Design

Efficiency, compatibility, and permanence are the most important properties for plasticizers. These properties are highly interconnected, and a balance needs to be struck when designing new plasticizers.[45] For example, a purely nonpolar plasticizer for PVC can add lubricity and free volume, resulting in good efficiency, but will suffer from phase separation (poor compatibility) and exudation (lack of permanence). Conversely, a molecule that is too polar may be compatible with PVC and have suitable permanence, but results in poor efficiency. Another feature to consider is arrangement of these polar groups, as internal hydrogen bonding can favor the plasticizer-plasticizer interaction and decrease compatibility.[45] Additionally, the same properties that give good efficiency are related to poor permanence. High efficiency is achieved by using molecules with high mobility within the blend. Compounds with low molecular weights and higher volatility are effective plasticizers but these properties also facilitate leaching.[10] Other structural features such as branching of the plasticizer can limit compatibility but can provide better permanence.[7] Hence, compromises are required to develop suitable alternative plasticizers.

Compatibility

Compatibility of polymers and plasticizers is determined by the chemical structure and polarity of the molecules. This generally follows the empirical rule of “like dissolves like”.[7] It follows from the theories of plasticization that the plasticizer and polymer should have similar polarity to be compatible and to create favorable polymer-plasticizer interactions.[38] If they are too dissimilar, the polymer-polymer and plasticizer-plasticizer interactions dominate and can lead to phase separation.[46]

There are several experimental approaches for determining plasticizer-polymer compatibility. There can be visible signs of poor compatibility such as “perspiration” of the plasticizer and phase separation, though this is not always the case.[45] Plasticizers that are poor solvents for a given polymer have a tendency to form clusters, creating microscopic plasticizer-rich areas within the blend.[45] Experimentally, compatibility can be assessed by dissolving small amounts of polymer in the plasticizer of interest to determine the cloud point and solid-gel transition temperature.[47–49] For crosslinked polymers, swelling tests using a series of solvents can be used to assess compatibility.[50] Spectroscopic methods can also be used to determine the strength of the interactions between the polymer and plasticizer.[51,52]

Indicators such as the Flory-Huggins interaction parameter can be used to estimate compatibility. Based on this model, the interaction parameter for a polymer-plasticizer pair should not exceed a critical value of 0.55 for most polymers.[53,54] Additionally, several empirical correlations for estimating solubility parameters based on cohesive energy density have been proposed for estimating polymer-plasticizer compatibility.[55–57] Solubility parameters may be determined experimentally by measuring the enthalpy of evaporation, though this requires large amounts of highly pure plasticizer.[7] Other indirect experimental methods are based on vapor pressure and boiling points.[58] There are also methods for determining the solubility parameters based on group contribution models. These methods are based on the principle of additivity, one can add up the contributions of chemical groups and bonds to obtain a solubility parameter for a given compound.[59] Overall, solubility parameters are useful for narrowing the plasticizer search as polymer-plasticizer pairs with significantly different solubility parameters will not be compatible.

Even so, similar solubility parameters do not always result in compatibility in practice.[7] While these methods are useful for generally assessing compatibility, it is important to recognize that most commercial formulations involve multiple plasticizing agents. In these cases the effects of cosolvency need to be considered.[60]

Efficiency

Plasticizer or plasticizing efficiency is a broad term that is used to describe the ability of a plasticizer to modify the thermal and mechanical properties of a polymer blend. Efficiency is commonly assessed experimentally, by evaluating the reduction in T_g, increase in elongation at break, reduction in tensile strength, reduction in hardness, or any combination thereof.[5,7] Other measures, relating to toughness, stiffness, ductility and impact strength can also be used.[7] A plasticizer is described as more efficient than another if it can achieve the desired properties at a lower plasticizer concentration.

Several factors can affect the efficiency of a plasticizer. Internal plasticizers often suffer from poor low-temperature performance compared to external plasticizers.[7] The efficiency is related to the polymer-plasticizer interactions, which is influenced by the size, structure, and polarity of the plasticizer.[61–63] The efficiency of a plasticizer also varies depending on the polymer and the presence of other components in the blend such as secondary plasticizers. Secondary plasticizers are other additives that are incorporated in smaller amounts than the primary plasticizer, that also impart flexibility to the blend.[7] The addition of a secondary plasticizer can have a produce a synergistic result.[64–66]

Permanence

Permanence is another important aspect of plasticizer performance. The eventual migration of external plasticizers is inevitable, given the lack of chemical bonds to the polymer matrix. This causes the material to become brittle and unusable. Good permanence is necessary for the product to have a long service life.[67] It is also important to limit human exposure and environmental release of the plasticizer.

Plasticizer migration can occur into a neighboring gas, liquid, or solid. It can also exude from the polymer matrix by compression. The permanence of the plasticizer in the blend can be measured experimentally, by evaluating the plasticizer loss after exposure to a particular media. The plasticizer loss varies depending on the choice of media, temperature, pressure, and plasticizer loading. The nature of the plasticizer is also important, as internal plasticizers are inherently non-migratory. As with compatibility and efficiency, the permanence of the plasticizer is also dependent on the chemical structure, polarity, and size of the plasticizer.

Several strategies to suppress migration have been reported, such as using molecules with long alkyl chains,[68,69] hyper-branched molecules,[70–72] or high molecular weight plasticizers[72–75]. Other approaches include coating and modifying the plasticized PVC surface to prevent plasticizer loss;[76–79] however, these methods often involve additional costs and can impact the performance of the end-product.[11]

2.3.2 Green Plasticizer Design

The design of new plasticizers should be approached holistically, considering the product's entire life cycle. The green chemistry principles of "designing safer chemicals" and "designing for degradation" are particularly important for developing new plasticizers.[80]

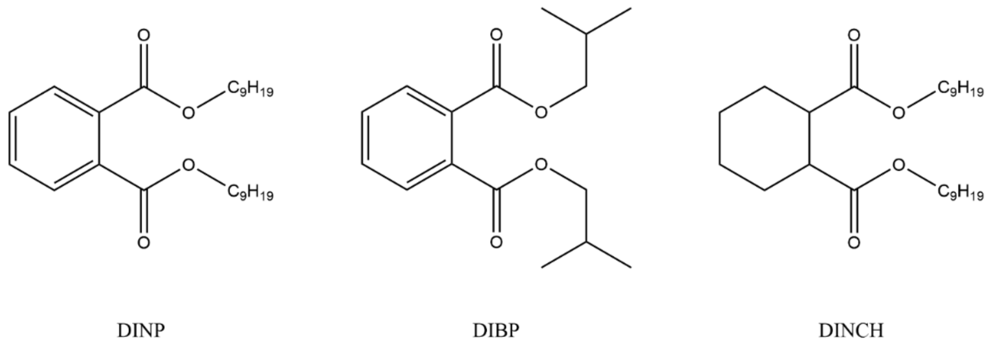
Alternative plasticizers must be non-toxic given their widespread use in toys, food packaging, and medical equipment.[20,35,81–83] Computational strategies, such as quantitative structure-activity relationships (QSAR) can be used to predict the toxicity of a given compound based on its structure.[84] Experimentally, bacterial,[85] yeast,[86,87] and mammalian cell-based assays,[88–91] testing for viability, proliferation, and measures of other toxic effects can be made of the candidate plasticizer and its metabolites. These would then be followed by *in vivo* studies for only the most promising candidates due to cost considerations.[80] At this stage, more specific investigation into reproductive toxicity can be performed to ensure these alternatives are in fact safer options.

Plasticizer candidates can be screened for biodegradability based on their chemical substituents. As a general guide, groups that readily undergo enzymatic hydrolysis such as esters, amides, hydroxyl, aldehyde, carboxylic acids, phenyl rings, and unsubstituted alkyl chains promote aerobic biodegradation.[92] Conversely, groups that are strongly electron withdrawing, such as halogens, can increase the resistance to aerobic biodegradation.[92] Excessive branching can also hinder aerobic biodegradation.[93] The number, position and size of the chemical substituents also affects biodegradability; however, there is no general rule for estimating its impact.[93,94]

Experimental investigation is required since biodegradation depends not only on the compound but also the exposure conditions.[92] Biodegradation requires the presence of suitable organisms that are capable of degrading the molecule and are present in sufficiently high numbers.[92,93] Screening, simulation, and field tests can be used to assess biodegradability.[95,96] The Organization for Economic Cooperation and Development (OECD) outlines a variety of standardized screening and simulation tests for assessing biodegradability.[97] These tests can identify compounds which are readily biodegradable or inherently biodegradable, though test conditions are generally not environmentally realistic.[98–100] Additionally, most standardized tests do not assess the biodegradability of the metabolites.[80] Biodegradation tests should be conducted for the plasticizer candidate and its potential metabolites to avoid regrettable substitution of DEHP.

2.4 Alternative Plasticizers

Many alternative plasticizers have been developed in response to the increased regulation surrounding the use of several phthalate-based plasticizers, though markedly few are of commercial importance. Several petroleum-based alternatives to DEHP are used commercially including diisononyl phthalate (DINP), diisobutyl phthalate (DIBP), and diisononyl cyclohexane 1,2-dicarboxylate (DINCH®) (Figure 2-2). Of these, DINP and DIBP are reported to cause adverse developmental and reproductive effects in rats.[101–103] DINCH® is another important plasticizer that has come under increased scrutiny. The level of urinary metabolites of DINCH® in the general population are increasing.[104,105] Recently, studies have shown the effects of DINCH® and its metabolites on human and animal health, with concerning findings.[106–108] DINP, DIBP, and DINCH may also create an environmental problem as the levels of these plasticizers in waterways and soil are rapidly increasing.[109–112] Other petroleum-based plasticizers such as tris(2-ethylhexyl) trimellitate, 1,4-benzenedicarboxylic acid, bis(2-ethylhexyl) ester (Eastman 168™), are also commercially available. These are predominantly marketed for sensitive applications, such as food contacting materials and toys, where regulations prohibit the use of DEHP. There are also few studies pertaining to the biodegradation and toxicity of these compounds and their metabolites.

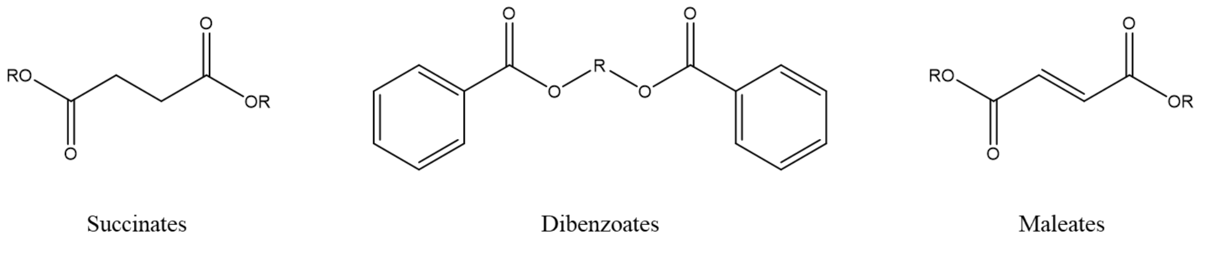


DINP DIBP DINCH

Figure 2-2. Structures of DINP, DIBP, and DINCH.

There is increasing interest in developing bio-based plasticizers as replacements for DEHP. Bio-based plasticizers have been produced largely from plant oils, such as soybean oil and castor oil.[113–116] Other compounds based on citric acid,[117,118] rice fatty acids,[119] lactic acid,[120] and adipic acid[121] have also been proposed. Most of these emerging compounds that are commercially available are used in specialty applications rather than as general-purpose plasticizers due to the complexity and costs associated with their production.[3,30]

Previously, a variety of succinate, maleate, and dibenzoate diesters have been evaluated as replacements for DEHP.[62,113] The general chemical structures for these are shown in Figure 2-3. These studies aimed to determine the effect of branching and length of the alkyl groups, as well as the differences between the central molecules.



Succinates Dibenzoates Maleates

Figure 2-3. Structures of succinates, dibenzoates, and maleates.

It was found that several of these compounds showed comparable or enhanced performance to DEHP and DINCH. The dihexyl maleate and dihexyl succinate compounds were the most effective at plasticization.[62] The alkyl chain length was found to have a significant effect on the plasticizer performance, improving from C2-C6 side chains, and decreasing for C7-C8.[62,113] The leaching of plasticizers from PVC blends into water was also investigated. The leaching of these plasticizers in water was evaluated, and the compounds with long alkyl chains and non-polar branching showed reduced leaching rates.[69] Due to concerns surrounding the toxicity of the maleate diesters and their metabolites, later work has focused on the development of succinate-based plasticizers.[122–124]

Plasticizers based on succinic acid show promise as alternative, bio-based replacements for DEHP. Succinic acid can be renewably produced at an industrial scale by fermentation.[125,126] Stuart *et al* investigated a series of saturated succinic diesters as potential plasticizers. The higher molecular weight di-octyl and di-hexyl succinate produced PVC blends with the lowest T_g.[127] Later studies investigated other succinate-based plasticizers, with different substituents in the middle part of the succinate and as side chains.[63] These compounds showed comparable properties to DEHP. Overall molecule length was positively correlated with plasticizing efficiency, while substituents added to the center of the molecule had negative impacts on performance. Most of these compounds were found to be biodegradable by common soil bacteria without stable metabolites. Branched n-heptyl succinate-based compounds have also been investigated.[70] The degree of branching was associated with reduced plasticizer efficiency, though the migration resistance improved. These studies serve as the foundation for the development of the succinate plasticizers evaluated in this work.

Chapter 3: Succinate-based plasticizers: Effect of plasticizer structure on the mechanical and thermal performance of poly(vinyl chloride) plastic formulations

3.1 Preface

This chapter consists of a manuscript to be submitted for publication. It presents an evaluation of the family of succinate-based plasticizers described in Chapter 2 for use in PVC blends. It includes an assessment of the mechanical and thermal properties of the blends at different concentrations. The objective of this work was to investigate the relationship between plasticizer structure, loading, efficiency, and leaching behavior.

This article establishes that this family of compounds provide high plasticizing efficiency, good thermal stability, and reduced leaching compared to the dominant plasticizer DEHP. These compounds were chosen for evaluation as previous studies showed that succinate diesters can provide good efficiency and are readily biodegradable.[63] The compounds in this study consist of linear alkyl chains capped with monopentyl or monoheptyl succinate at each end. Modulating the central and side chain lengths allowed for the investigation of the structure-function relationship of alkyl chain length and plasticizer performance.

The effect of the central and side alkyl chain length was investigated as previous studies have shown that alkyl chain lengths have a significant impact on the performance of succinate plasticizers for PVC.[63,113] The performance of the plasticizers was evaluated by assessing their tensile properties, surface hardness, and glass transition temperature for blends prepared at 20, 40, and 60 phr. Leaching tests in hexanes were also conducted to compare the migration behavior of these plasticizers to literature data.

3.2 Abstract

A new family of succinate-based plasticizers, consisting of molecules with a linear alkyl chain capped with n-alkyl succinates on both ends, was evaluated as potential bio-based plasticizers for stiff polymers. The influence of the central and side alkyl chain lengths on the mechanical and thermal properties as well as the migration behaviour of poly(vinyl chloride)(PVC)/plasticizer blends was evaluated. The central chain length had the greatest influence on plasticizer performance, with shorter chains leading to blends with higher tensile strength and surface

hardness, whereas long chains produced softer blends. An optimum chain central length of five carbon atoms was observed, with longer chains leading to reduced compatibility and exudation of the plasticizer at higher plasticizer concentrations. The entire family of plasticizers performed comparably or better than the commercial plasticizer di(2-ethylhexyl) phthalate (DEHP) when incorporated into the blend at concentrations of 20-60 parts per hundred resin (phr). Overall, the succinate-based plasticizers/PVC blends all exhibited equal or improved tensile properties (by up to 77%), surface hardness (reduced by up to 43%), glass transition temperature (reduced by up to 11°C), and migration into organic media (reduced by up to 38%) when compared to blends with DEHP at 40 phr.

3.3 Introduction

Plasticizers are materials added to polymers to improve their flexibility, distensibility, and processability.[1–3] Approximately 90% of plasticizers produced are for use in poly(vinyl chloride) (PVC), making it one of the largest segments of the additives market as a whole.[4,5] Most plasticizers for PVC are external plasticizers; that is, discrete materials that are mechanically added to the polymer blend,[5] and which are not chemically bonded to the polymer. External plasticizers are typically low molecular weight organic molecules that lower the glass transition temperature (T_g) and manipulate processing properties of the polymer with which they are blended.[3] The effectiveness of a plasticizer is largely dependent on its chemical structure, which dictates how the plasticizer will interact with the polymer chains and potentially increase molecular mobility.[6,7]

Phthalate-based compounds are the most commonly used plasticizers for PVC, accounting for approximately two-thirds of PVC plasticizers produced in 2018.[8] Of these, di(2-ethylhexyl) phthalate (DEHP) is the most heavily used, with 3.24 million metric tonnes supplied in 2018.[8] While DEHP has dominated the plasticizer industry for decades due to its excellent performance and low cost,[9] it presents significant health and environmental concerns. That is, DEHP inevitably migrates from the PVC blend,[3] resulting not only in product that becomes increasingly brittle over time, but also in the ubiquitous contamination of the environment with DEHP and its metabolites, which have been detected in soil, water, air, and biota.[10–12] There are significant health concerns associated with DEHP and its breakdown products including mono(2-ethylhexyl) phthalate and 2-ethylhexanoic acid.[12–16] While several non-phthalate alternatives have been developed, such as DINCH ® and Eastman 168, and have gained market share, these are petroleum-derived compounds. As such, there remains a need for green plasticizers, that are safe, high-performing, bio-based, and biodegradable.

In order to be practical and satisfy market needs, alternative plasticizers should perform comparably to phthalate plasticizers, while also being non-toxic and biodegradable. They must also balance efficiency, compatibility, and permanence.[17] An efficient plasticizer reduces the glass transition temperature and alters the mechanical properties, though it may suffer from poor compatibility and permanence if the polarity of the plasticizer and polymer are mismatched. For polar polymers like PVC, a molecule that is too polar, while compatible, cannot disrupt the polymer-polymer interaction to provide good plasticizing efficiency. On the other hand, a purely nonpolar molecule would not be compatible and would exude from the material.[9] The interrelationships between these properties make it difficult to develop new plasticizers without compromising other aspects of plasticizer performance.[17]

Alternative plasticizers should also be designed for reduced migration so as to preserve the product's flexibility and minimize leaching into the environment.[1,3] Several approaches to reduce plasticizer leaching have been proposed, ranging from surface modification, internal plasticizers, and the development of new external plasticizers. Surface modification such as surface crosslinking and coating,[18,19] can be effective at limiting leaching, but can negatively impact the polymer properties and increase processing complexity and costs.[6] There are similar problems associated with internal plasticizers, which are chemically bonded to the polymer, as these can be difficult to produce and are expensive compared to DEHP.[20] Polymeric, oligomeric, and branched plasticizers can all reduce leaching rates compared to small-molecule plasticizers, though they often cannot match the plasticizing efficiency and low cost of phthalates.[21]

In recent years, increased focus has been placed on the development of bio-based plasticizers. Many plasticizers derived from renewable feedstocks are described in literature, but few are of commercial importance to-date.[22] However, recent studies have demonstrated that succinate-based plasticizers are promising options for bio-based plasticizers.[23–28] In this work, we propose a new family of succinate-based compounds (Figure 3-1) as alternative green plasticizers. These molecules consist of linear alkyl chains capped with n-alkyl succinates at each end and are synthesized from succinic anhydride and linear alcohols which can be bio-sourced.[28–31] In order to test their viability as alternative plasticizers, in the present study, the PVC plasticization efficiency of these new compounds was assessed by measuring their effect on tensile properties, surface hardness, and glass transition temperature. Moreover, the leaching behaviour of the plasticizers into organic media was also studied. DEHP was used as a control to directly compare plasticizer performance with a commercially important product. Beyond this, the structure-function relationship of the plasticizers was investigated by modulating both the central and side alkyl chain lengths. The effect of these chain lengths on plasticizer performance and the effect of plasticizer loading were evaluated to identify the optimal structural configuration and formulation.

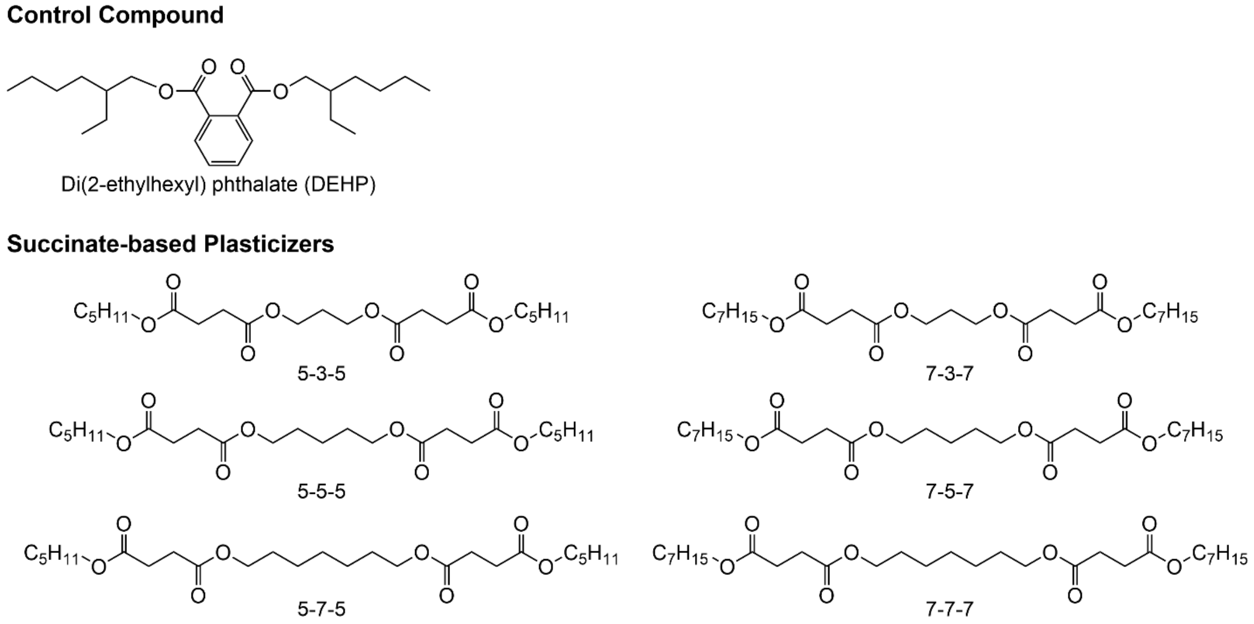


Figure 3-1. Chemical structures of the compounds investigated in this study, including industrial standard DEHP. The nomenclature used for each of the succinate-based plasticizers, Ns-Nc-Ns, is based on the central (Nc) and side alkyl chain (Ns) lengths.

3.4 Materials and Methods

3.4.1 Materials

Unplasticized PVC (UPVC; K50) was supplied by Solvay Benvic (Chevigny, France). Sulfuric acid (98%), stearic acid (97%), 1,7-heptanediol (98%), *n*-pentanol (99%), hexanes, toluene, and benzene were purchased from Fisher Scientific (Montreal, QC). Epoxidized soybean oil was purchased from Galata Chemicals (Southbury, CT). Renewably-sourced *n*-heptanol (99.9%, Oleris) was purchased from Arkema (King of Prussia, PA). DEHP (99%), 1,3,5-trimethoxybenzene (99%), succinic anhydride (99%), 1,5-pentanediol (97%), and 1,3-propanediol (98%) were purchased from Millipore Sigma (Oakville, ON).

3.4.2 Plasticizer Synthesis

The monosuccinates were synthesized according to the previously reported procedure for monoheptyl succinate (Figure 3-2).[25] Briefly, the monosuccinates were synthesized by combining succinic anhydride (100 g, 0.99 mol, 1 eq.) with n-pentanol for monopentyl succinate (108.2 mL, 0.99 mol, 1 eq.) or n-heptanol for monoheptyl succinate (141.3 mL, 0.99 mol., 1 eq), and 250 mL of toluene in a round-bottomed flask. The mixture was refluxed for 6 hours with magnetic stirring. After cooling to room temperature, the solvent was removed under reduced pressure and the products were used without further purification.

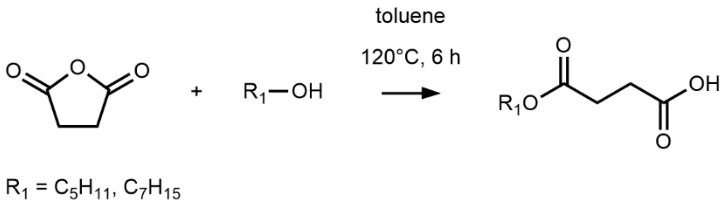


Figure 3-2. Synthesis of monopentyl and monoheptyl succinate refluxed in a round bottom flask.

The plasticizers were synthesized using the previously reported process for the 7-5-7 plasticizer (see Figure 3-1 for nomenclature).[25] The appropriate monosuccinate (2.1 eq. with respect to the diol) and linear diol (1 eq.) were added to a round bottom flask, along with sulfuric acid (0.15 eq.) and 250 mL of benzene (Figure 3-3). The flask was equipped with a Dean-Stark apparatus and condenser. The mixture was refluxed for 4 hours with magnetic stirring. The solvent was removed under reduced pressure and the compounds were used without further purification. Reaction yields and spectral information is given in the Supporting Information, section S1.

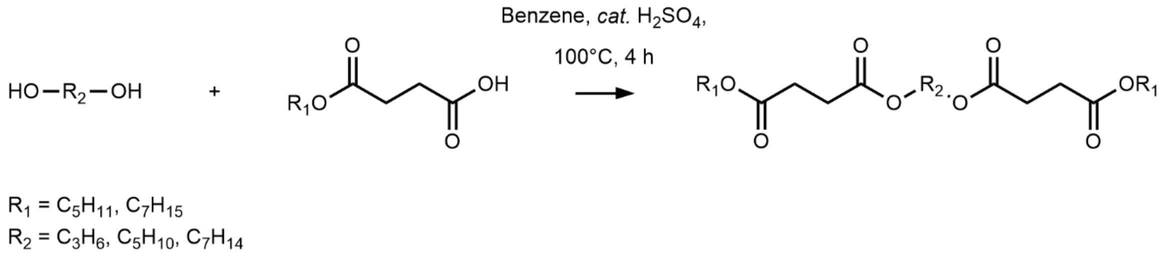


Figure 3-3. Synthesis of plasticizers from linear diols and n-alkyl succinates in a Dean-Stark apparatus.

3.4.3 Extrusion

Blends at 20, 40, 60 parts per hundred resin (phr) of all seven plasticizers were prepared by extrusion using a Haake Minilab conical intermeshing twin screw extruder (Thermo Electron Corporation, Beverly, MA). In accordance with previously described methods,[32] blends at 20 phr plasticizer were first prepared in 3 g batches with the UPVC, 20 phr plasticizer, 5 phr stearic acid (as a lubricant), and 4 phr epoxidized soybean oil (as a heat stabilizer). Each batch was recycled through the extruder to ensure proper mixing. The extrusion was conducted at 130°C with a rotational speed of 30 rpm. Blends with higher plasticizer content were prepared from the 20 phr batch by repeating the extrusion process stepwise, adding 20 phr of the plasticizer each time. No additional heat stabilizer or lubricant was added in these later steps.

3.4.4 Hot press molding

Specimens for tensile testing and circular disks for hardness testing were produced using a heated manual hydraulic press (Carver, Wabash, IN) and steel molds. The molds were filled with the cut PVC from the extrusion process and pressed at 165°C. The pressing was done in three segments, as in previously reported methods,[32] with 5 min at 5 metric tonnes (MT) 10 min at 10 MT, and 30 min at 15 MT. After forming, the specimens were stored in a desiccator (25% relative humidity) until used for testing (Drierite, Fisher Scientific, Montreal, QC). The tensile test bar dimensions were in accordance with ASTM standard method D638. Disks used for hardness testing had a12.5 mm radius and 1.0 mm thickness.

3.4.5 Tensile testing

Tensile testing was conducted using a Shimadzu Easy Test instrument with a load cell of 500 N. The samples were desiccated a minimum 48 hours before analysis and testing was done in accordance with ASTM standard method D638. The dimensions of each specimen were measured with a digital micrometer prior to testing. A strain rate of 5 mm/min was used for all samples. The stress-strain curves were used to obtain the strain (percent elongation) and stress at break.

3.4.6 Hardness testing

Surface hardness of the plasticized PVC blends was determined using a micro-indenter (Nanovea PB1000 with Nano module) equipped with a stainless-steel ball tip of 1-mm diameter. Measurements were conducted at room temperature, indenting the center of each disk. Tests were performed using a trapezoidal loading profile with a loading/unloading rate of 30 mN/min and a maximum load of 20 mN with a 10 s holding time. This holding time was selected to minimize the influence of creep during the unloading phase.

A MATLAB® program was used to calculate the surface hardness according to ASTM standard method E2546 (2007). This method determines the hardness based on the contact stiffness as derived from the slope of the first third of the unloading curve, contact area, and indentation depth.

3.4.7 Differential scanning calorimetry (DSC)

The glass transition temperature of each blend at 20, 40, and 60 phr was determined by temperature-modulated differential scanning calorimetry (mDSC) using a TA Instrument Discovery DSC 2500 (Newcastle, DE). The samples were first quenched at -90°C for 5 min, then heated to 100°C at a rate of 2°C/min with sinusoidal modulation of 1.27°C with a period of 60s. The samples were held at 100°C for 5 min before repeating the cycle. The T_g was determined from reversible heat flow of second heating cycle using the half-height method and TA instruments TRIOS software.

3.4.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a TA Instruments Discovery 5500 (Newcastle, DE) to assess the thermal stability of the plasticized PVC blends. All samples were run under nitrogen flow from 25 to 600°C with a heating rate of 10°C/min. The onset temperature was determined according to ASTM standard method E2550 using TA instruments TRIOS software.

3.4.9 Leaching testing

The leaching tests were performed in accordance with a previously described method.[25] This method was adapted from ASTM standard method D1239-14, “Resistance of Plastic Films to

Extraction by Chemicals.” Quantitative analyses of the leachates were conducted using ^{1}H NMR.[25] Leaching into hexanes was measured at 50°C over the course of 4 hours, since this testing condition allowed for enough plasticizer to be leached for subsequent detection by ^{1}H NMR.

Tensile bars containing 40 phr plasticizer were used in the leaching tests. Prior to testing, the specimens were desiccated at room temperature for at least 48 hours. The bars were weighed before and after the leaching tests. For each sample, a bar of known weight was suspended using an aluminum wire in a 250-mL Erlenmeyer flask with 200 mL hexanes. The flask was plugged with a rubber stopper and wrapped in parafilm before placing in a shaker at 100 rpm for 4 h. After testing, the specimens were removed from the flask, rinsed with 70% ethanol, and dried with a Kim Wipe towel. The bars were placed in a vacuum oven until dried to constant weight. Tensile tests were performed on the dried specimens.

The leachates were concentrated under reduced pressure to remove the hexanes. For ^{1}H NMR analysis, 2 mL of an internal standard solution of 1,3,5-trimethoxybenzene (10 mg/mL) in deuterated chloroform ($CDCl_3$) was used. The plasticizer concentration in the leachates was determined as in the previously reported method,[25] by comparing the integral values of the internal standard with that of each plasticizer (Eq. 1):

$$C_x = \frac{I_x}{I_{cal}}\left(\frac{N_{cal}}{N_x}\right) \cdot C_{cal} \tag{1}$$

where C_x is the concentration of the plasticizer in the leachate, I_x is the integral value of the plasticizer peak, I_{cal} is the integral value of the internal standard peak, N_{cal} is the number of protons represented by internal standard peak, N_x is the number of protons represented by the plasticizer peak, and C_{cal} is the concentration of the internal standard.

3.4.10 NMR spectroscopy

^{1}H NMR spectra were collected using a Bruker AVIIIHD 500 MHz spectrometer (MA, USA) with an average of 16 scans using deuterated chloroform as the solvent. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet (range of multiplet is given in Supporting Information, section S1. Plasticizer Synthesis and Characterization).

3.4.11 Statistics

The data was assumed to be normally distributed and are presented as the mean and standard deviation. Statistical analysis was performed with GraphPad Prism 9 using one-way and two-way ANOVA with Bonferroni post-tests. A *p*-value less than 0.05 was interpreted as significant.

3.5 Results

3.5.1 Plasticizer Loading

The strain and stress at break for plasticizer concentrations from 20-60 phr are shown in Figure 3-4(a) and (b). Both the plasticizer and concentration had a significant impact on the strain at break ($p < 0.0001$, two-way ANOVA). All blends showed a large increase in strain at break from 20 to 40 phr. However, from 40 to 60 phr the strain at break only increased for plasticizers 7-5-7 and 7-7-7. Overall, the strain at break was comparable or superior to DEHP at every concentration tested. Comparing the strain at break of the succinate-based plasticizers, the best performance was achieved with the smallest plasticizer, 5-3-5, which surpasses the elongation of DEHP across the concentration range. While concentration had a significant effect on the stress at break ($p < 0.001$, two-way ANOVA), there was no significant difference between plasticizers. The stress at break for the PVC/plasticizer blends, showed that increasing the plasticizer concentration decreased the stress at break. Each of the succinate-based plasticizers displayed comparable or lower stress at break than DEHP.

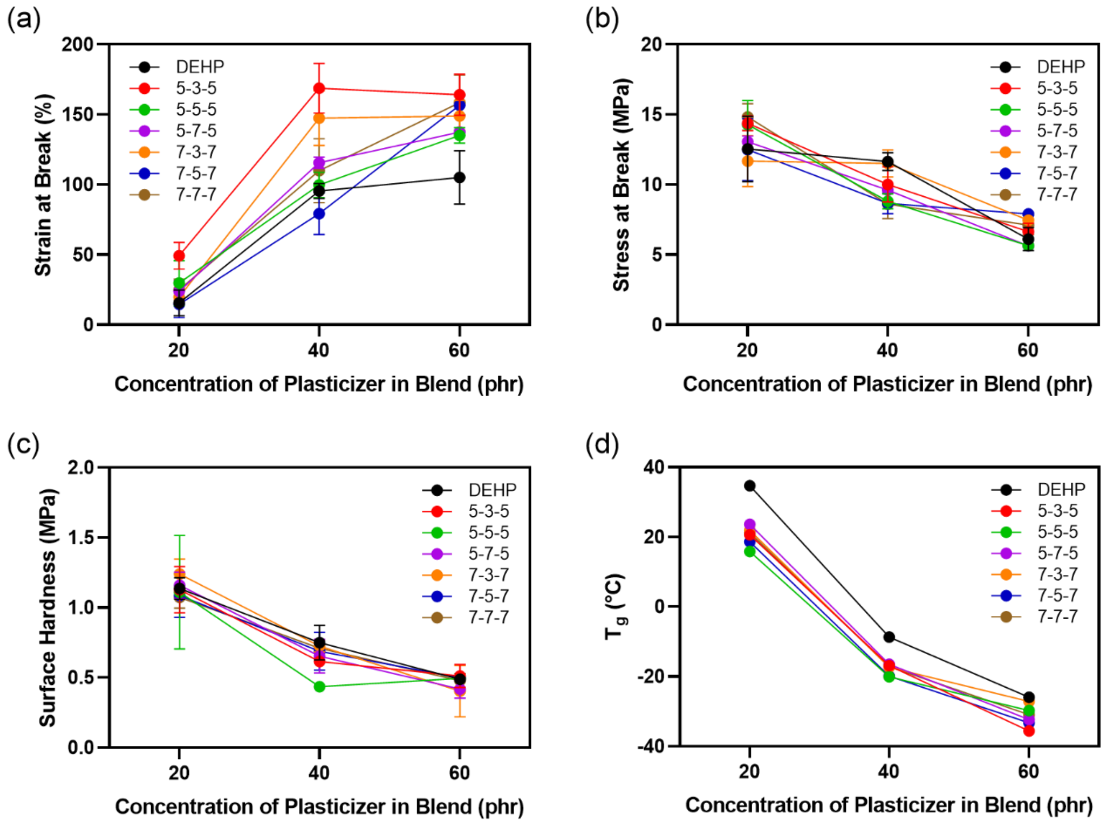


Figure 3-4. Mechanical and thermal properties of PVC/plasticizer blends from 20-60 phr: (a) Strain at break and (b) stress at break (*n* = 5 replicates); (c) Surface hardness by nanoindentation for PVC/plasticizer blends (*n* = 3); and (d) Glass transition temperatures (*n* = 1). Error bars represent one standard deviation with mean shown.

The surface hardness of each PVC/plasticizer blend was also determined through nanoindentation at 20, 40, and 60 phr, as shown in Figure 3-4(c). There was no effect of plasticizer on the surface hardness; however, the concentration of the plasticizer in the blend was significant ($p < 0.0001$, two-way ANOVA). Overall, the hardness decreased as the plasticizer content was increased. As with the tensile properties, the largest difference was seen between 20 and 40 phr. Increasing above 40 phr resulted in lower reductions in hardness for all plasticizers except 5-5-5. All plasticizers investigated performed comparably or better than DEHP across the concentration range.

The T_g of the PVC/plasticizer blends is presented in Figure 3-4(d) and summarized in Table 3-1. The T_g of the PVC/plasticizer blends decreased with higher plasticizer loading for all compounds investigated. As with the mechanical properties, the greatest improvement in the blend T_g was seen between 20 to 40 phr of plasticizer. As plasticizer loading was increased from 40 to 60 phr, the T_g continued to decrease, though less significantly. The T_g of the succinate-based plasticizers blends were comparable to DEHP across the range of concentrations, which suggests that these are effective plasticizers. The plasticizers with central chain lengths of 5 carbon atoms produced blends which exhibited the lowest T_g. Indeed, the 5-5-5 plasticizer showed the largest improvement compared to DEHP at 20 and 40 phr.

The onset of degradation temperature for each plasticizer was determined from TGA and is shown in Table 3-1. Overall, the new PVC/plasticizer blends had comparable thermal stability to DEHP at 20, 40, and 60 phr.

Table 3-1. Thermal properties of PVC/plasticizer blends at various plasticizer concentrations.

	T_g (°C)			**Onset temperature (°C)**		
Plasticizer	**Plasticizer concentration (phr)**			**Plasticizer concentration (phr)**		
	20	**40**	**60**	**20**	**40**	**60**
DEHP	36.9	-8.7	-26.0	251.3	246.2	237.3
5-3-5	20.6	-16.9	-35.6	255.3	251.8	235.3
5-5-5	15.8	-20.1	-29.8	249.2	237.5	239.8
5-7-5	23.6	-16.9	-32.4	253.8	245.5	242.2
7-3-7	21.9	-17.4	-22.3	255.4	252.0	239.8
7-5-7	18.6	-17.4	-33.3	250.0	242.3	241.7
7-7-7	30.1	-17.2	-31.0	253.3	249.0	246.4

3.5.2 Plasticizer properties at 40 phr

It is worth considering the properties of the plasticizers at 40 phr to assess the plasticizer performance. At 20 phr, the plasticizers all performed similarly, with no significant difference in the mechanical or thermal properties. By 40 phr, there was a noticeable difference in plasticizer performance. This concentration is within the typical range for commercial PVC blends, and allows for comparison to previous studies on succinate plasticizers.[25–28]

The tensile properties of the PVC/plasticizer blends at 40 phr are presented in Figure 3-5(a) and (b), and Table 3-S1. There was a significant difference amongst the blends at 40 phr ($p < 0.0001$, one-way ANOVA). The plasticizers with the shortest central groups (5-3-5 and 7-3-7) showed improved strain at break compared to DEHP at 40 phr ($p < 0.001$, Bonferroni post-test). The compounds with the longer central groups demonstrated comparable strain at break to DEHP ($p > 0.05$, Bonferroni post-test). The side chain length did not appear to influence the strain at break as significantly. The compounds with side chain lengths of 5 carbon atoms (plasticizers 5-Nc-5) exhibited comparable strain at break to their 7 carbon atom counterparts (7-Nc-7) for identical central groups. Overall, these results suggest that within this family of plasticizers, higher elongation is observed in compounds with shorter central alkyl chain lengths.

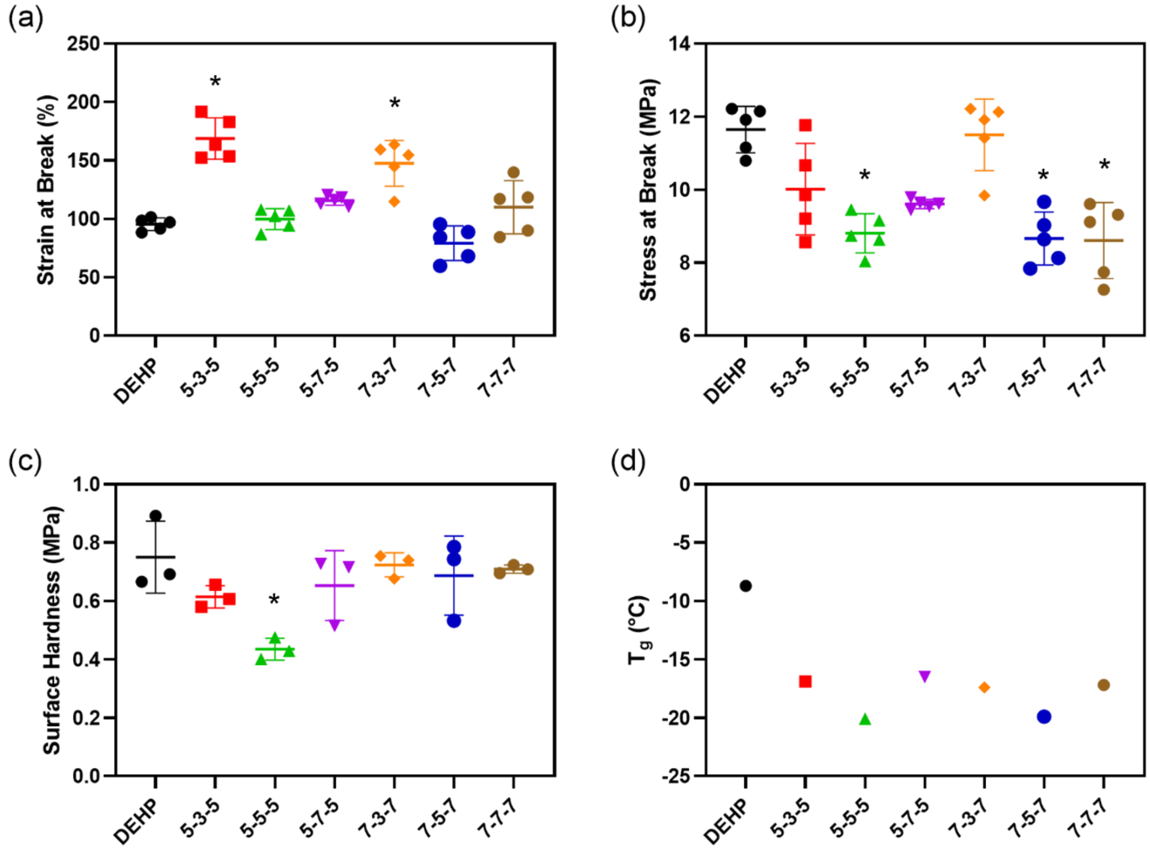


Figure 3-5. Mechanical and thermal properties of PVC/plasticizer blends at 40 phr: (a) Strain at break and (b) stress at break ($n = 5$ replicates); (c) Surface hardness by nanoindentation for PVC/plasticizer blends ($n = 3$); and (d) Glass transition temperatures ($n = 1$). Error bars represent one standard deviation with mean shown. Symbols (*) above error bars indicate statistically significant differences compared to DEHP ($p < 0.05$).

A significant difference ($p < 0.0001$, one-way ANOVA) was seen in the stress at break for all the PVC/plasticizer blends at 40 phr (Figure 3-5(b), Table 3-S1). For the plasticizers with central chain lengths of three carbons, there was no significant difference in stress at break compared to DEHP. In contrast, plasticizers with longer central chains exhibited lower stress at break than DEHP ($p < 0.05$, Bonferroni post-test).

The surface hardness was measured for the PVC/plasticizer blends at 40 phr (Figure 3-5(c),Table 3-S1). A significant difference was found for the surface hardness of all compounds tested ($p <$

0.01, one-way ANOVA). Of these, only compound 5-5-5 was significantly different than DEHP ($p < 0.05$, Bonferroni post-test).

In addition to the mechanical properties, the glass transition temperature, T_g, of the PVC/plasticizer blends was evaluated at 40 phr (Table 3-1, Figure 3-5(d)). The T_g of all the blends were well below that of neat PVC (~80°C),[3] and the succinate-based plasticizers also had reduced T_g compared to DEHP. The plasticizers with central chain lengths of 5 carbons had the lowest T_g, indicating high plasticizer efficiency.

3.5.3 Leaching behavior

The accelerated leaching tests in hexanes at 50°C for 4 hours were used to evaluate the migration performance of the succinate-based plasticizers. The PVC/plasticizer bars used in the leaching tests all showed weight gain following the leaching (Supporting Information, section S3). This increase can be attributed to swelling of the test specimens. The specimens were dried in a vacuum oven to constant mass, with the final mass being lower than the mass of the specimens before leaching. The weight loss computed using the weight after drying can be found in the Supporting Information, Table 3-S2. The plasticizer loss is herein reported as based on the ^{1}H NMR analysis of the leachates.[25] The results of the leaching tests are shown in Figure 3-6 and Table 3-S3. There was a significant difference in plasticizer loss for all compounds tested ($p < 0.01$, one-way ANOVA). Of the succinate-based plasticizers, only compound 5-5-5 showed statistically different plasticizer loss than DEHP ($p < 0.01$, Bonferroni post-test). Plasticizer 5-5-5 showed the lowest leaching, at only 9.8% compared to DEHP with 15.9%. For the compounds tested, the molecular weight of the plasticizer did not have a significant effect on the plasticizer loss; however, the range of molecular weights considered was narrow.

After the leaching tests, the bars were dried to constant weight and their tensile properties were evaluated (Figure 3-6(b)). It was expected that the strain at break would decrease following the loss of plasticizer during leaching. This is the case for DEHP, 5-3-5, 5-7-5, 7-3-7, and 7-7-7. For the plasticizers with the central alkyl chain lengths of 5 carbons, no difference in strain at break was observed before and after leaching ($p > 0.05$, t-test with Welch correction). These species, 5-5-5 and 7-5-7, also exhibited the lowest leaching rates of the plasticizers studied. In terms of the stress at break, there was no statistically significant difference after the leaching test for any of the compounds tested.

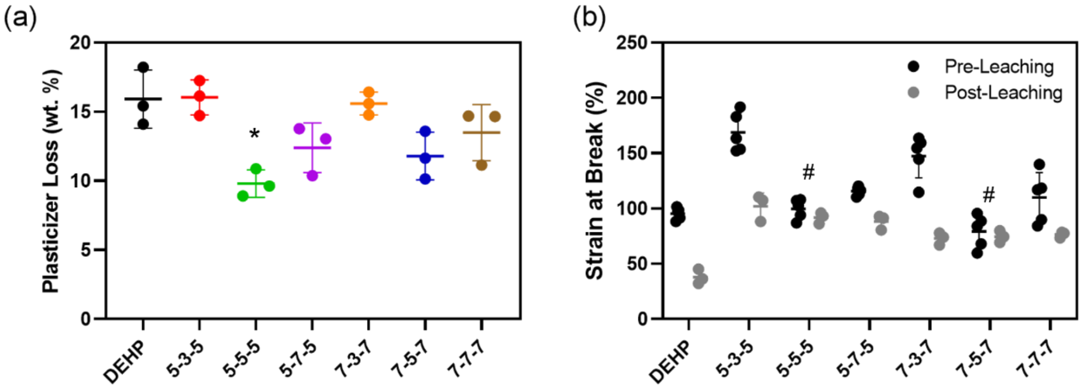


Figure 3-6. (a) Plasticizer leaching into hexanes for four hours at 50°C determined by ^{1}H NMR. (b) Strain at break of PVC/plasticizer blends with and without leaching. Error bars represent one standard deviation with mean shown. Symbols indicate statistically significant ($p < 0.05$) difference compared to DEHP (*) and statistically equivalent ($p > 0.05$) means pre- and post-leaching (#).

3.6 Discussion

While the environmental and health concerns associated with phthalate plasticizers have been well documented, they remain the most frequently used plasticizers. Although replacements have been proposed, these often suffer from poor performance or excessive costs of production.[6,21,22] Thus, there remains a need for commercially-viable alternatives to DEHP that are environmentally benign and that can perform as effectively or better in PVC blends. With the increasing societal pressure to transition from petroleum-derived products, there is special interest in the development of bio-based alternative plasticizers.

In this work we presented a series of succinate-based plasticizers as alternatives to DEHP. The compounds were synthesized from succinic acid and linear alcohols which can be bio-sourced.[28–31] These plasticizers were extruded with PVC at 20, 40, and 60 phr and showed comparable permanence and plasticization efficiency to blends prepared with commercial plasticizer DEHP.

3.6.1 Effect of plasticizer loading

The Hansen solubility parameters and interaction radii for the succinate-based plasticizers were determined using the Hoftyzer-Van Krevelen method (Table 3-S4). Generally, plasticizers for

PVC have interaction radii ≤ 14.644 $(MJ/m^3)^{1/2}$.[33] All the compounds studied are below this threshold, further supporting the use of these succinate-based compounds as plasticizers for PVC. However, their interaction radii were all greater than that of DEHP, which may indicate reduced solubility. This is supported by the experimental findings, where plasticizer exudation was observed for blends containing 60 phr of the 7-5-7 and 7-7-7 plasticizers, suggesting miscibility of PVC and the succinate-based plasticizers occurs over a limited range (< 60 phr).

The mechanical properties of the PVC/plasticizer blends at 20, 40, and 60 phr indicated that the succinate-based plasticizers were largely comparable in performance to DEHP (Figure 3-4). At 20 phr, the mechanical and thermal properties of the blends were all similar to DEHP, aside from the glass transition temperature which was reduced for the succinate-based plasticizers (15.8-30.1°C) compared to DEHP (36.9°C). The material properties improved with greater plasticizer content. For all plasticizers, the strain at break increased with plasticizer loading, while the stress at break and surface hardness was reduced. However, the overall trend showed smaller improvements from 40 to 60 phr than those from 20 to 40 phr. In fact, for many of the plasticizers, the properties reached a plateau after 40 phr, whereby further plasticizer addition did not alter the mechanical and thermal properties. This effect of diminishing returns has been previously reported for PVC plasticizers.[34,35] This plateau effect may be attributed to a saturation effect, whereby further addition of plasticizer does not impart better material properties. This is further supported by the tensile tests conducted post-leaching, in which the 5-5-5 and 7-5-7 plasticizers showed unchanged elongation at break, even after the loss of more than 10% of the plasticizer from leaching (Figure 3-6). For the 5-5-5 plasticizer, which showed this plateau from 40 to 60 phr, it may be possible to achieve the same material properties at a concentration between 20 to40 phr, reducing the amount of plasticizer needed to achieve a flexible product. Overall, these findings suggest that a lower concentration of these succinate-based plasticizers in PVC is needed to achieve comparable performance to PVC/DEHP blends.

3.6.2 Effect of plasticizer structure

An effective plasticizer needs to have good compatibility and plasticizing efficiency, requiring a balance of polar and non-polar components. In this series of plasticizers, the polar groups contributed by the succinic acid interact with the polar groups on the PVC chain that improve the compatibility of the plasticizer and PVC. In contrast, the side and central alkyl chains promote non-polar intermolecular interactions between the plasticizer and PVC chains. These interactions serve to increase the free volume of the polymer blend and impart greater flexibility. However, an excess of non-polar moieties can lead to poor compatibility and exudation of the plasticizer from the polymer blend, and an excess of polar moieties to poor plasticizing efficiency.

With this family of succinate-based plasticizers, the variation in central and side chain length provides further insight into the optimal balance of these polar and non-polar moieties. The central and side alkyl chain lengths showed a significant effect on the performance of the blends at 40 phr. The plasticizers with central chain lengths of three carbons showed improved strain at break compared to the other compounds, however resulted in smaller reductions in stress at break, surface hardness, and T_g. The compounds with central chain lengths of five carbons (i.e., 5-5-5 and 7-5-7) showed the lowest surface hardness, glass transition temperature, and tensile strength at 40 phr compared to analogous plasticizers with different central groups. The plasticizers with the longest central chains (seven carbons) did not differ from DEHP in any of the measured properties. For this series of plasticizers, there is an optimum structure of five carbons in the central chain that provides the best compromise between compatibility and plasticizing efficiency, as demonstrated by their lower plasticizer loss during leaching tests and their mechanical and thermal properties.

The side chain length did not have as significant an effect on the plasticizer performance. At 40 phr, some of the plasticizer with side chains of five carbons perform better than their seven carbon analogs, notably 5-5-5 has a greater strain at break and lower surface hardness than the 7-5-7 plasticizer. The 7-5-7 plasticizer also suffers from poor compatibility with PVC at higher concentrations. At 60 phr, there is visible exudation of the plasticizer from test specimens. This negative effect was also observed with the largest plasticizer of the group, 7-7-7 at 60 phr.

The 5-5-5 plasticizer has the best overall performance of the compounds investigated. At 20 phr, it displayed comparable mechanical properties to DEHP and a lower T_g. At 40 phr it had improved surface hardness, and glass transition temperature. This compound also exhibited the lowest plasticizer leaching, at only 9.8% compared to DEHP with 15.9%. Increasing the plasticizer concentration to 60 phr, the strain at break was improved compared to DEHP, though the other material properties largely plateau.

3.6.3 Leaching

Plasticizer leaching is also an important metric for evaluating plasticizer performance. The succinate-based plasticizers performed comparably to DEHP, aside from 5-5-5 which showed improved migration resistance in hexanes. There was no observable effect of plasticizer structure on leaching performance within the family of succinate-based plasticizers studied. Generally, reduced leaching is observed for higher molecular weight compounds and branched ones.[20] In this family, all the plasticizers have linear structures and represent a narrow range of molecular weights, which may explain their similar leaching behavior. This family of plasticizers also compares favorably to diheptyl succinate, a previously explored succinate plasticizer, which showed 20.8% plasticizer loss under similar conditions.[25] Overall, the leaching of the plasticizers into hexanes was comparable or improved relative to DEHP and diheptyl succinate, though further investigation of the leaching behavior into other media is necessary.

3.7 Conclusion

Overall, the family of succinate-based plasticizers presented in this work are effective alternatives to DEHP. Blends produced with these compounds had comparable or superior performance to PVC/DEHP blends across a range of concentrations (20 to 60 phr). Investigation of the structure-function relationship of these plasticizers revealed that the central alkyl chain length had largest impact on the mechanical and thermal properties of the blend, as well as on the leaching behaviour. The shorter central chains resulted in better compatibility at high concentrations; however, the longer chains produced more effective plasticizers. In contrast, the side alkyl chain length had less of an influence on the mechanical and thermal properties. Finally, the 5-5-5 plasticizer showed the best performance of the plasticizers studied, with improved tensile strength, surface hardness, leaching, and glass transition temperature compared to DEHP at 40 phr. Further work is required to investigate its biodegradability and establish it as a viable green plasticizer.

3.8 References

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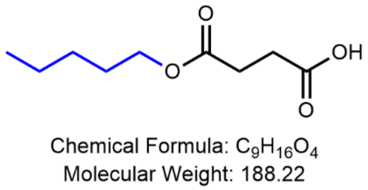
3.9 Supporting Information

The following section is included as Supporting Information to the article.

S1. Plasticizer Synthesis and Characterization

This section includes the reaction yield and spectral data (^{1}H NMR) for the monosuccinate precursors and succinate-based plasticizers synthesized for this study. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet (range of multiplet is given).

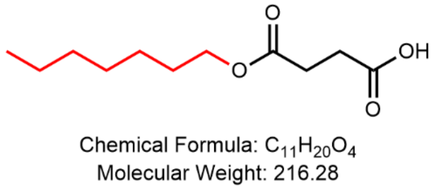
Monopentyl succinate



Reaction yield: 94%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.12 (t, J = 6.8 Hz, 2H), 2.73 – 2.60 (m, 4H), 2.37 (d, J = 0.8 Hz, 1H), 1.65 (p, J = 6.9 Hz, 2H), 1.41 – 1.29 (m, 4H), 0.98 – 0.88 (m, 3H).

Monoheptyl succinate

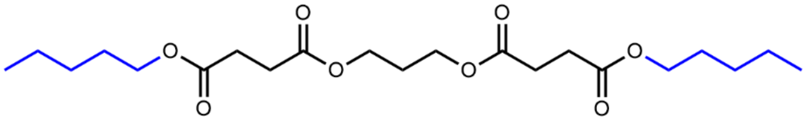


Reaction yield: 95%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.10 (t, J = 6.8 Hz, 2H), 2.69 (ddd, J = 7.2, 5.9, 1.4 Hz, 2H), 2.63 (ddd, J = 7.7, 5.9, 1.5 Hz, 2H), 1.62 (dt, J = 8.1, 6.5 Hz, 2H), 1.40 – 1.25 (m, 8H), 0.93 – 0.86 (m, 3H).

5-3-5

5-3-5



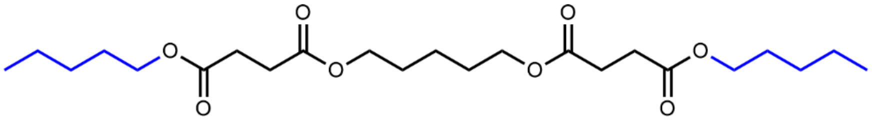
Chemical Formula: $C_{21}H_{36}O_8$
Molecular Weight: 416.51

Reaction yield: 88%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.19 (t, J = 6.3 Hz, 4H), 4.09 (t, J = 6.8 Hz, 4H), 2.64 (q, J = 1.3 Hz, 8H), 1.99 (p, J = 6.3 Hz, 2H), 1.64 (p, J = 6.9 Hz, 4H), 1.34 (dtd, J = 7.9, 4.1, 2.1 Hz, 8H), 0.95 – 0.87 (m, 6H).

5-5-5

5-5-5



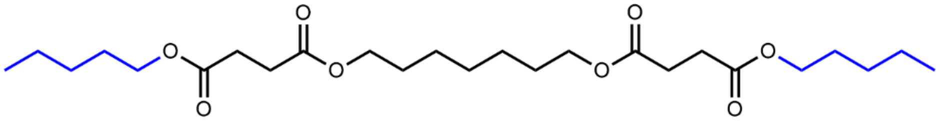
Chemical Formula: $C_{23}H_{40}O_8$
Molecular Weight: 444.57

Reaction yield: 96%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.08 (q, J = 6.7 Hz, 8H), 2.61 (s, 8H), 1.70 – 1.58 (m, 8H), 1.40 – 1.27 (m, 9H), 0.93 – 0.85 (m, 6H).

5-7-5

5-7-5

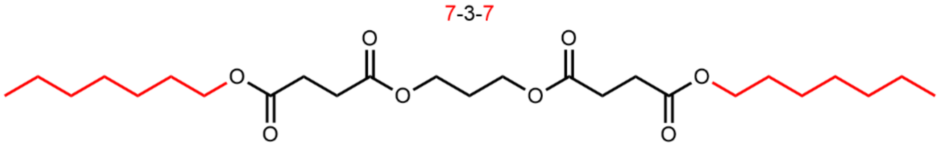


Chemical Formula: $C_{25}H_{44}O_8$
Molecular Weight: 472.62

Reaction yield: 91%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.09 (td, J = 6.8, 1.1 Hz, 8H), 2.63 (s, 8H), 1.68 – 1.59 (m, 9H), 1.40 – 1.28 (m, 15H), 0.96 – 0.87 (m, 6H).

7-3-7

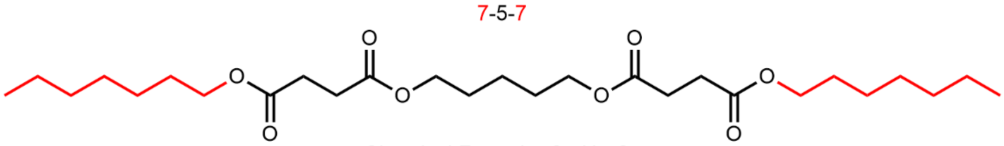


Chemical Formula: $C_{25}H_{44}O_8$
Molecular Weight: 472.62

Reaction yield: 85%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.16 (t, J = 6.3 Hz, 3H), 4.06 (t, J = 6.8 Hz, 4H), 2.67 – 2.56 (m, 8H), 1.96 (p, J = 6.3 Hz, 2H), 1.65 – 1.56 (m, 4H), 1.29 (dddd, J = 18.3, 6.8, 4.8, 3.0 Hz, 17H), 0.90 – 0.83 (m, 6H).

7-5-7



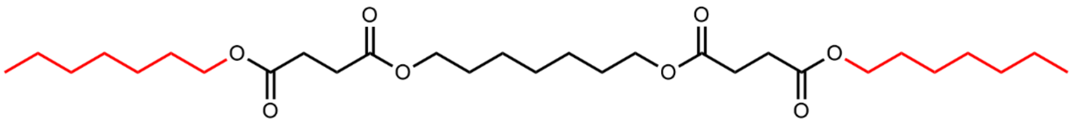
Chemical Formula: $C_{27}H_{48}O_8$
Molecular Weight: 500.67

Reaction yield: 89%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.10 (q, J = 6.8 Hz, 8H), 2.64 (s, 8H), 1.72 – 1.58 (m, 9H), 1.40 – 1.28 (m, 17H), 0.93 – 0.87 (m, 6H).

7-7-7

7-7-7



Chemical Formula: $C_{29}H_{52}O_8$
Molecular Weight: 528.73

Reaction yield:82%

^{1}HNMR (500 MHz, Chloroform-*d*) δ 4.08 (t, J = 6.8 Hz, 8H), 2.62 (s, 8H), 1.61 (ddt, J = 12.9, 6.6, 2.7 Hz, 9H), 1.40 – 1.23 (m, 24H), 0.91 – 0.85 (m, 6H).

S2. Differential Scanning Calorimetry

The DSC results for each of the PVC/plasticizer blends are presented in Figures 3-S1 to 3-S7.

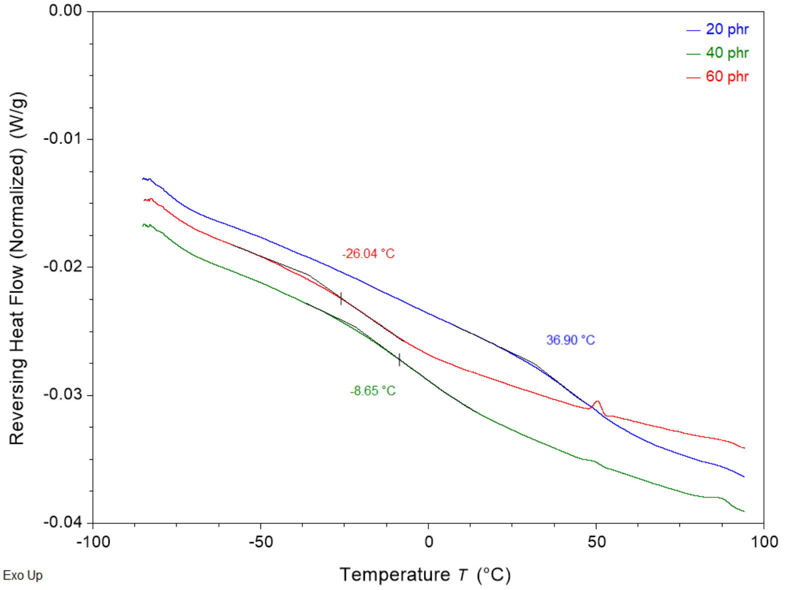


Figure 3-S1. DSC thermograms and glass transition temperatures for PVC/DEHP blends at 20, 40, and 60 phr.

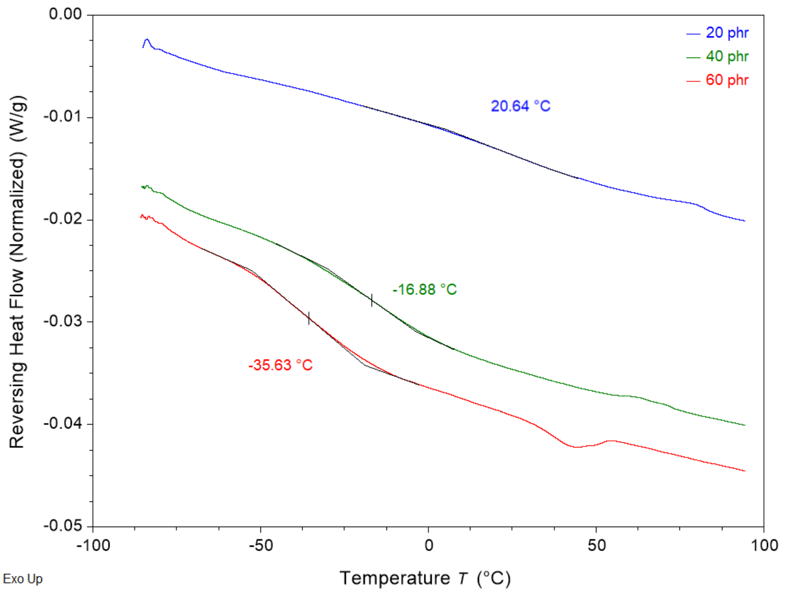


Figure 3-S2. DSC thermograms and glass transition temperatures for PVC/5-3-5 plasticizer blends at 20, 40, and 60 phr.

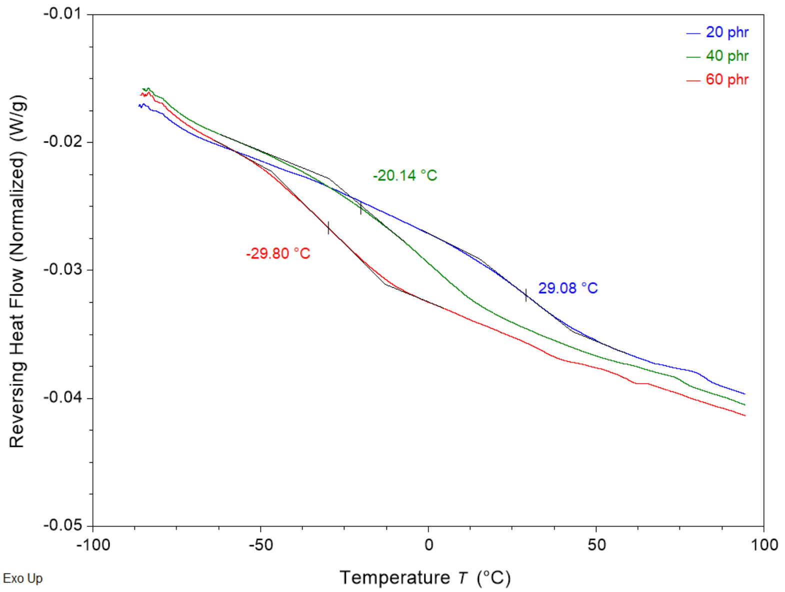


Figure 3-S3. DSC thermograms and glass transition temperatures for PVC/5-5-5 plasticizers blends at 20, 40, and 60 phr.

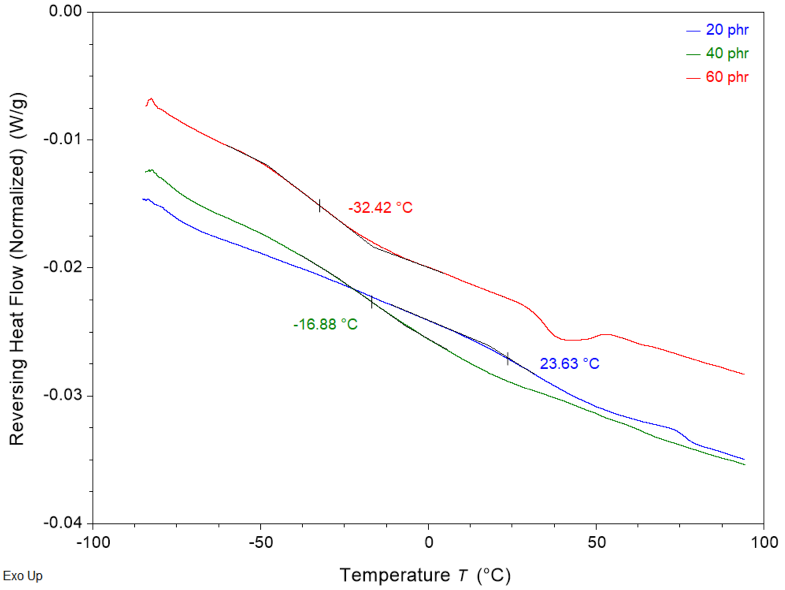


Figure 3-S4. DSC thermograms and glass transition temperatures for PVC/5-7-5 plasticizers blends at 20, 40, and 60 phr.

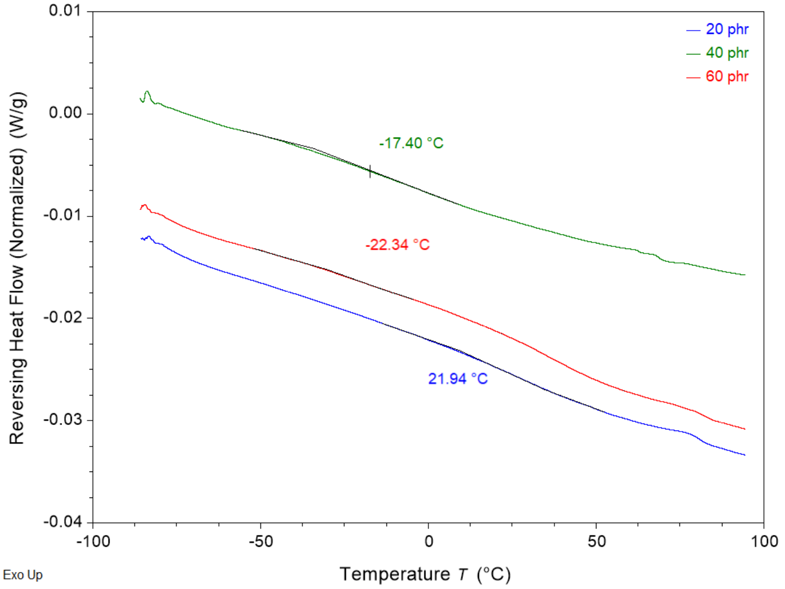


Figure 3-S5. DSC thermograms and glass transition temperatures for PVC/7-3-7 plasticizers blends at 20, 40, and 60 phr.

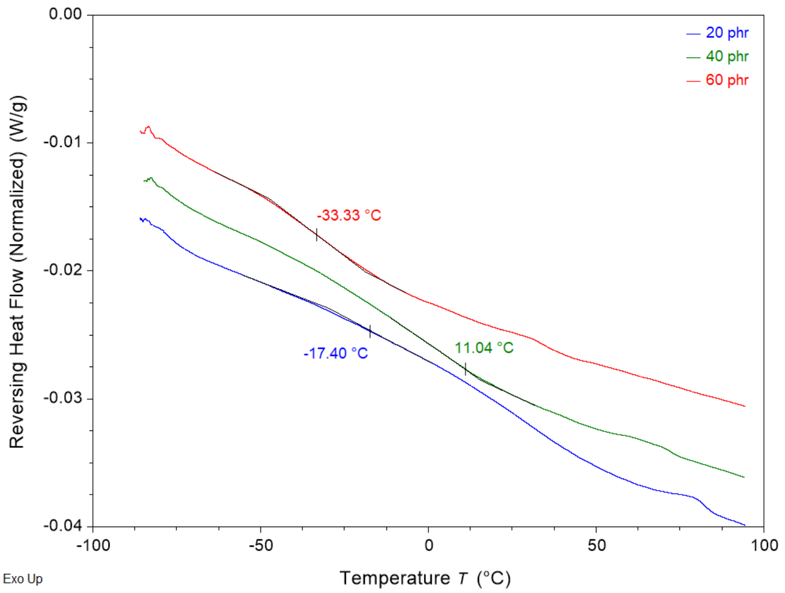


Figure 3-S6. DSC thermograms and glass transition temperatures for PVC/7-5-7 plasticizers blends at 20, 40, and 60 phr.

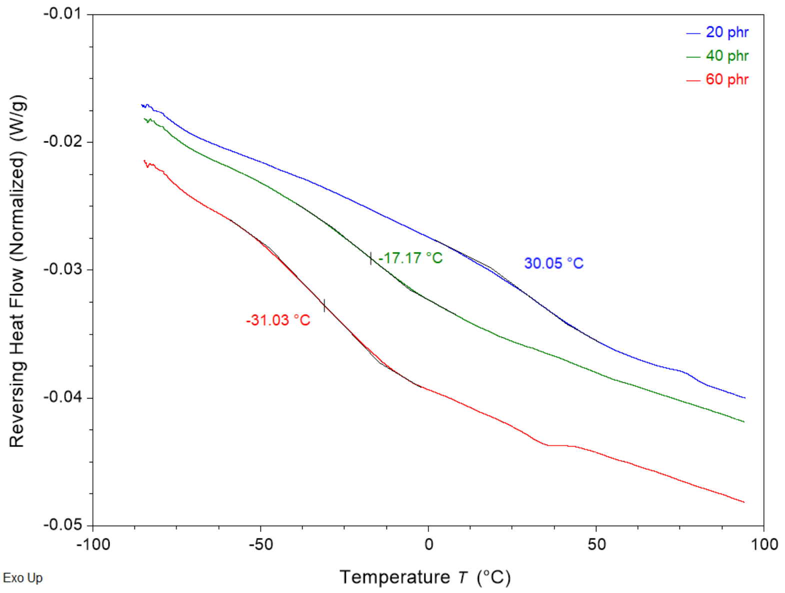


Figure 3-S7. DSC thermograms and glass transition temperatures for PVC/7-7-7 plasticizers blends at 20, 40, and 60 phr.

S3. Mechanical Testing

The results of the tensile and nanoindentation tests for the PVC/plasticizer blends at 40 phr are summarized in Table 3-S1.

Table 3-S1. Mechanical properties of PVC/plasticizer blends at 40 phr. Means and standard deviations are reported.

Plasticizer	**Strain at Break (%)**[a]	**Stress at Break (MPa)**[a]	**Surface Hardness (MPa)**[b]
DEHP	95 ± 5	11.6 ± 0.6	0.75 ± 0.12
5-3-5	168 ± 17	10.0 ± 1.3	0.61 ± 0.03
5-5-5	99.7 ± 9	8.8 ± 0.5	0.43 ± 0.04
5-7-5	115 ± 4	9.6 ± 0.1	0.65 ± 0.12
7-3-7	147 ± 20	11.5 ± 1.0	0.72 ± 0.04
7-5-7	79 ± 14	8.7 ± 0.7	0.69 ± 0.14
7-7-7	109 ± 22	8.6 ± 1.0	0.71 ± 0.01

[a] *n* = 5 specimens,

[b] *n* = 3 specimens

S4. Leaching into Hexanes: Gravimetric Analysis

The gravimetric results of the leaching test are summarized in Table 3-S2. The plasticizer loss based on 1H NMR analysis and the post-leaching tensile test results are shown in Table 3-S3.

Table 3-S2. Masses of tensile bars with 40 phr plasticizer before leaching, immediately after leaching, and after drying in a vacuum oven to constant mass. Replicate experiments denoted by a, b, and c.

Plasticizer	**Initial Mass (g)**	**Post-Testing Mass (g)**	**Post-Drying Mass (g)**	**Final Weight Change (g)**
DEHP	a. 0.7958	a. 0.8612	a. 0.7790	a. -0.0168
	b. 0.8237	b. 0.8646	b. 0.7848	b. -0.0389
	c. 0.8263	c. 0.8654	c. 0.7897	c. -0.0366

Plasticizer	Initial Mass (g)	Post-Testing Mass (g)	Post-Drying Mass (g)	Final Weight Change (g)
5-3-5	a. 0.8353	a. 0.8319	a. 0.7858	a. -0.0495
	b. 0.8267	b. 0.8252	b. 0.7791	b. -0.0476
	c. 0.8312	c. 0.8275	c. 0.7824	c. -0.0488
5-5-5	a. 0.8343	a. 0.8378	a. 0.7954	a. -0.0389
	b. 0.7989	b. 0.8463	b. 0.8059	b. +0.007
	c. 0.8441	c. 0.8479	c. 0.8037	c. -0.0404
5-7-5	a. 0.8284	a. 0.8466	a. 0.7817	a. -0.0467
	b. 0.8230	b. 0.8418	b. 0.7750	b. -0.0480
	c. 0.7893	c. 0.8549	c. 0.7867	c. -0.0026
7-3-7	a. 0.8452	a. 0.8476	a. 0.7875	a. -0.0577
	b. 0.8383	b. 0.8452	b. 0.7868	b. -0.0515
	c. 0.8336	c. 0.8458	c. 0.7867	c. -0.0469
7-5-7	a. 0.8380	a. 0.8496	a. 0.8027	a. -0.0353
	b. 0.8372	b. 0.8528	b. 0.8018	b. -0.0354
	c. 0.8364	c. 0.8478	c. 0.7989	c. -0.0375
7-7-7	a. 0.8845	a. 0.8461	a. 0.7783	a. -0.1062
	b. 0.8155	b. 0.8445	b. 0.7739	b. -0.0416
	c. 0.8146	c. 0.8440	c. 0.7747	c. -0.0399

Table 3-S3. Leaching behaviour of PVC/plasticizer blends into hexanes and post-leaching tensile test results.

Plasticizer	Molecular Weight (g/mol)	Plasticizer Leached (wt. %)	Strain at Break Post-Leaching (%)	Stress at Break Post-Leaching (MPa)
DEHP	390.5	15.9 ± 2.1	38 ± 7	12.8 ± 1.0
5-3-5	416.5	16.0 ± 1.3	102 ± 12	9.7 ± 1.9
5-5-5	444.5	9.8 ± 1.0	92 ± 5	10.3 ± 0.3
5-7-5	472.6	12.4 ± 1.7	88 ± 7	10.3 ± 1.3
7-3-7	472.6	15.6 ± 0.8	73 ± 5	9.9 ± 1.7
7-5-7	500.6	11.8 ± 1.7	74 ± 5	10.1 ± 0.9
7-7-7	528.7	13.5 ± 2.0	76 ± 3	8.6 ± 1.3

S5. Hansen Solubility Parameters

The Hansen solubility parameters were calculated by group contribution theory with the Hoftyzer-Van Krevelen method. The density of the succinate-based plasticizers was assumed to be 1.0 g/cm^3.

Table 3-S4. Calculated solubility parameters (δ) and interaction radius (IR) for PVC and each plasticizer.[1]

Compound	**Molar Volume (cm^3/mol)**	**Group**	**Number of Groups**	**F_{di} ((MJ/m^3)$^{1/2}$ mol^{-1})**	**F_{pi} ((MJ/m^3)$^{1/2}$mol^{-1})**	**E_{hi} (J/mol)**	**δ_d (MJ/m^3)$^{1/2}$**	**δ_p (MJ/m^3)$^{1/2}$**	**δ_h (MJ/m^3)$^{1/2}$**	**δ (MJ/m^3)$^{1/2}$**	**IR (MJ/m^3)$^{1/2}$**
U-PVC	44.6	$-CH_2-$	1	270	0	0	17.9	12.3	3.0	22.0	–
		$>CH-$	1	80	0	0					
		$-Cl$	1	450	550	400					
DEHP	390.6	$-CH_3-$	4	420	0	0	16.9	0.9	6.0	17.9	7.5
		$-CH_2-$	10	270	0	0					
		$>CH-$	2	80	0	0					
		$-COO-$	2	390	490	7000					
		-Ring-	1	1270	110	0					
5-3-5	416.5	$-CH_3$	2	420	0	0	15.5	1.2	8.2	17.6	8.3
		$-CH_2-$	15	270	0	0					
		$-COO-$	4	390	490	7000					
5-5-5	444.6	$-CH_3$	2	420	0	0	15.7	1.1	7.9	17.6	8.1
		$-CH_2-$	17	270	0	0					
		$-COO-$	4	390	490	7000					
5-7-5	472.6	$-CH_3$	2	420	0	0	15.9	1.0	7.7	17.7	7.9
		$-CH_2-$	19	270	0	0					
		$-COO-$	4	390	490	7000					
7-3-7	472.6	$-CH_3$	2	420	0	0	15.9	1.0	7.7	17.7	7.9
		$-CH_2-$	19	270	0	0					
		$-COO-$	4	390	490	7000					

Compound	**Molar Volume (cm^3/mol)**	**Group**	**Number of Groups**	**F_{di} $(MJ/m^3)^{1/2}$ mol^{-1})**	**F_{pi} $(MJ/m^3)^{1/2}mol^{-1}$)**	**E_{hi} (J/mol)**	**δ_d $(MJ/m^3)^{1/2}$**	**δ_p $(MJ/m^3)^{1/2}$**	**δ_h $(MJ/m^3)^{1/2}$**	**δ $(MJ/m^3)^{1/2}$**	**IR $(MJ/m^3)^{1/2}$**
7-5-7	500.7	$-CH_3$	2	420	0	0	16.1	1.0	7.5	17.8	7.8
		$-CH_2-$	21	270	0	0					
		-COO-	4	390	490	7000					
7-7-7	528.7	$-CH_3$	2	420	0	0	16.3	0.9	7.3	17.9	7.7
		$-CH_2-$	23	270	0	0					
		-COO-	4	390	490	7000					

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Chapter 4: General Discussion

The need for bio-based plasticizers for use in polymer products continues to grow. While many bio-based plasticizers have been proposed, few are of commercial importance and their use is mainly for specialty applications. This thesis sought to evaluate a family of succinate-based plasticizers as green alternatives to the existing phthalate plasticizers. This family of compounds shows comparable or improved mechanical, thermal, and leaching performance to the commonly used plasticizer DEHP when incorporated into PVC blends at concentrations up to 60 phr.

The succinate-based plasticizers investigated in this work can be added to PVC in varying amounts to easily tailor the material properties. These PVC/plasticizer blends were produced by extrusion, under realistic processing conditions, further demonstrating their suitability for industrial production. Their mechanical and thermal performance was assessed at 20, 40, and 60 phr. The blends at each concentration exhibit similar or better plasticizing efficiency than DEHP. However, some exudation of the longer chain plasticizers was observed at 60 phr. Further work is needed to comprehensively assess the plasticizer performance in blends produced by different industrially relevant methods, such as calendaring, film blowing, and injection molding. The study of the leaching behavior from 40 phr specimens showed comparable or reduced plasticizer loss in hexanes. By and large, this family of succinate-based plasticizers meet the conventional plasticizer requirements of efficiency, compatibility, and permanence, without compromising on sustainability.

This family of compounds was designed to evaluate effect of central and side alkyl chain lengths and plasticizer performance, to aid in the development of future green plasticizers. The distance between the succinate groups was found to be critical for plasticizer performance. This confirms that not only is the overall polarity of the plasticizer molecule important, but the location of the polar groups also influences its interactions with the polymer. As described by the lubricity theory of plasticization, the plasticizer must contain functional groups that are attractive to the polymer (the polar succinate groups) and these must be compatible with the polymer in terms of size and location.[38] For this family of compounds, a central chain length of five carbon atoms proved optimal for plasticizer performance. In contrast, no significant effect was observed for the side chain length. From the gel theory of plasticization, it may have been expected that the longer non-polar side chains might provide better performance, by limiting polymer-polymer interactions.[10]

From the free volume theory, the reverse may have been expected, that the lower molecular weight plasticizers would have increased plasticization efficiency, as the number of end groups would be increased compared to the compounds with longer side chains and higher molecular weights.[10] Neither effect was not observed in this study; however, only linear side chains of five and seven carbon atoms were investigated. The study of these molecules can be easily expanded to include a wider range of compounds which may prove to be more effective plasticizers. Potential areas of investigation include a wider range of side chain lengths, and branched structures.

Low leachability is an important requirement for green plasticizers. This family of plasticizers show reduced leaching into hexanes; however, leaching into other media remains to be investigated. To verify whether this family of plasticizers is suitable for sensitive applications such as medical equipment and food-contacting applications, the requisite leaching studies, particularly into aqueous media, need to be conducted. Previous investigation of succinate diesters suggests that longer chained species with more non-polar groups show better resistance to leaching inn aqueous media.[69] While the 5-5-5 plasticizer showed lower leaching into hexanes, the longer chained plasticizers may perform better in aqueous solutions. It is possible that several of the plasticizers considered in this work will be useful depending on the target application and desired end-product properties. Different test parameters for the leaching studies can be used to assess the permanence of the plasticizer in the blend under more realistic conditions. To be considered for sensitive applications these leaching tests must be coupled with toxicity studies of the plasticizers and their metabolites, as the leaching tests alone are not sufficient.

The molecular design of these plasticizers was informed by previous biodegradation and toxicity studies, [92,113,122,128] though work remains to experimentally establish these plasticizers as biodegradable and non-toxic. In terms of biodegradability, the compounds consist of saturated linear alkyl chains, connected with ester groups, both of which are known to facilitate aerobic biodegradation.[92] Previous studies of succinate diesters indicate that the predicted metabolites of these compounds should be readily biodegradable.[63,113] Toxicity and biodegradation studies of these new plasticizers are needed to fully assess their viability as green alternatives. These results can then be used to complete a life cycle analysis, which should be performed before industrial production of any new plasticizers to avoid regrettable substitution.

For these plasticizers to be considered green alternatives, their production should also be green, and consistent with the principles of green chemistry[28] and green engineering.[29] One of these principles includes using renewable feedstocks for plasticizer production.[129] This family of plasticizers is synthesized from succinic anhydride, linear diols, and primary alcohols that can be renewably sourced. Succinic anhydride can be obtained by the dehydration of succinic acid. Succinic acid is an important platform chemical that is already being produced industrially by microbial fermentation of biomass.[130] In fact, the fermentative process is even competitive with petrochemical synthesis routes.[131] The diols used in this study, 1,3-propanediol, 1,5-pentanediol, and 1,7-heptanediol can also be produced from biomass-based routes. Of the diols, 1,3-propanediol is the only one produced industrially, at a scale of kilotonnes per year by fermentation of glucose.[132] Similar processes have recently been developed for synthesis of 1.5-pentanediol and 1,7-heptanediol.[133–137] Production of the primary alcohols (n-pentanol, and n-heptanol) using renewable feedstocks is not currently economically competitive with petrochemical routes.[138] Green production methods have garnered renewed interest, as these primary alcohols can be used for biofuels and bio-based polymers.[138,139] The synthesis described in Chapter 4 also involves the use of solvents for the synthesis of the succinate-based plasticizers. Following the principles of green chemistry,[129] the synthesis has been adapted to be conducted without the use of solvents (see Appendix). Other principles of green chemistry including atom economy, designing for energy efficiency, and real-time analysis for pollution prevention should be considered when scaling-up the production plasticizers.[140]

For the next generation of sustainable materials, the focus should be on developing entirely green systems. Here, these plasticizers are evaluated for use in PVC; however, PVC is a petroleum-based product that, because it is challenging to recycle, primarily ends up in landfills after its useful life.[141–143] It is also important to note that manufacturing of the vinyl monomer is hazardous.[144,145] Transitioning to bio-based and biodegradable polymers is necessary to reduce the impact of plastics manufacturing on human health and the environment. It follows that additives used with these polymers should also be sustainable and safe. Hence, the future of plasticizer development should center on the design of green plasticizers for biopolymers such as poly(lactic acid) (PLA) and poly(butylene succinate). In fact, several glycerol-succinate compounds have proven to be effective plasticizers for PLA, significantly reducing the glass transition temperature and producing highly flexible blends.[146] Given these promising results, the series of succinate-based plasticizers explored in this work should also be tested in PLA and other bioplastic formulations.

Chapter 5: Conclusions and Future Work

The purpose of this work was to evaluate a new family of succinate-based plasticizers as green alternatives to phthalate plasticizers for PVC. The plasticizers can be synthesized from renewable succinic acid and linear alcohols. PVC blends prepared with these compounds at 20, 40, and 60 phr show comparable or improved mechanical and thermal properties to DEHP. These plasticizers also exhibit comparable or better leaching properties, though this study only considered leaching into hexanes. Overall, these molecules show comparable efficiency, compatibility, and permanence to DEHP.

The influence of the central and side alkyl chain lengths on plasticizer performance was investigated. The central chain length had the largest impact on plasticizer efficiency, with shorter chains exhibiting better compatibility with PVC, though reduced efficiency. The side chain length did not have a significant impact when comparing molecules with the same central groups. An optimum central chain length of five carbon atoms was observed. In particular, blends with the 5-5-5 plasticizer showed a reduction in tensile strength, decrease in surface hardness, lower T_g, and similar thermal stability when compared to DEHP.

Further work remains to definitively establish these plasticizers as truly green alternatives. Firstly, it is necessary that these compounds can be produced using inherently safe chemicals. Recent work has demonstrated that these compounds can be synthesized without the use of organic solvents, though this has yet to be done for all the compounds in this series. As these succinate compounds are used as external plasticizers, their migration from the PVC matrix is unavoidable. In this work, only leaching into hexanes was evaluated. While these results were encouraging, additional leaching tests into other media, wear testing, and accelerated environmental testing are required to fully assess the permanence of these plasticizers in PVC blends. This is particularly important for plasticizers that can be used for sensitive applications such as food contacting materials and medical equipment. If the leaching studies show unacceptable migration behavior, structural variations such as plasticizers with increased branching may be considered.

The study of the biodegradation profiles of the plasticizers and their metabolites is needed to ensure that these compounds can be considered environmentally benign. With the migration of the plasticizers also comes the question of human exposure. General and specific toxicity studies are needed to ensure these compounds and their metabolites do not lead to adverse effects While previous work suggests that the succinate-based plasticizers should be readily biodegradable and non-toxic,[122,128] experimental investigation is still required. If these compounds are established as being biodegradable and non-toxic, a life cycle assessment should be conducted alongside an economic analysis to investigate the commercial viability of these plasticizers.

Ultimately, plasticizer research should move away from the development of plasticizers for petroleum-based polymers. This is particularly true for PVC where the production of the vinyl monomer is also a hazardous process. There are already several green plasticizers for PVC in various stages of development, including those proposed in this work. Future plasticizer research should be focused on the design of green plasticizers for bio-based and biodegradable polymers, to facilitate the replacement of conventional plastics with sustainable materials.

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Appendix: Solvent-Free Synthesis

Following the principles of green chemistry, it is of interest to develop solvent-free methods of synthesizing the alternative plasticizers presented in this work. A method for producing the 7-3-7 plasticizer (see Figure 1- for chemical structure) was developed based on the solvent-free synthesis of diheptyl succinate previously reported.[113] This protocol can be applied to any of the succinate-based plasticizer considered in this work by simply using the appropriate mono succinate and diol.

Briefly, the monoheptyl succinate (3.512 g, 2.1 eq.), 1,3-propanediol (0.730 g, 1 eq.), and sulfuric acid (148.9 μL, 0.15 eq.) were combined in a round bottomed flask. The flask was equipped with a Dean-Stark apparatus. The contents were stirred at 110°C for 4 hours. Once at temperature, nitrogen gas was bubbled throughout to strip any water generated from the reaction. The product was used without further purification, with a yield of 97%. The product was confirmed by ^{1}H NMR:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.18 (t, J = 6.3 Hz, 3H), 4.08 (t, J = 6.8 Hz, 4H), 2.68 – 2.60 (m, 8H), 1.98 (p, J = 6.3 Hz, 2H), 1.62 (dt, J = 8.2, 6.5 Hz, 4H), 1.38 – 1.22 (m, 16H), 0.92 – 0.85 (m, 6H).