Design and evaluation of poly(caprolactone)-based additives for poly(vinyl chloride)

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“Good judgement comes from experience. Experience comes from bad judgement.”

Abstract

Commercial plastic products are made by combining polymers with chemical additives that are used to improve performance and processing characteristics. Most plastic additives are not chemically bound to the polymer and, consequently, have been found to migrate into the environment over time, resulting in long-term exposure of animals, humans and other organisms to these chemicals. The rising rates of plastic production and use, coupled with the migration of common additives, has resulted in widespread recognition that plastic additives are important contributors to global plastic pollution.

Plasticizers are a group of additives that are used to improve polymer flexibility and processability. With growing evidence of the negative health and environmental impacts of additives such as phthalate plasticizers, research has been increasingly directed at developing safer alternative additives. Such research has been largely focused on meeting a particular consumer demand or responding to regulatory prohibitions of certain additives. Unfortunately, research efforts that focus on optimizing plasticizer performance often ignore broader sustainability considerations, or at the other extreme, efforts to design sustainable plasticizers often overlook practical considerations of processability, performance, and cost. This thesis aims to address these deficiencies by simultaneously considering functionality and sustainability when evaluating the performance of alternative additives.

A framework for the design and evaluation of new plasticizers is presented in this thesis. A series of chemical additives was developed using this guiding framework, and, subsequently, their effectiveness as processing aids and as primary plasticizers was investigated. This research demonstrated that newly developed poly(caprolactone) (PCL)-based additives with diester linkers and alkyl chain cappers were effective at preventing the formation of 'gas check' surface defects during calendaring. The incorporation of these additives at concentrations as low as 8 phr was found to completely eliminate 'gas check' defects from calendered films. This research also demonstrated that the PCL-based additives could be used as primary plasticizers for poly(vinyl chloride) (PVC), achieving elongation at break, tensile strength, and glass transition temperature (T_g) values comparable to traditional phthalate plasticizers. Calendered films made with the new

additives demonstrated elongation at break values of between 280-370%, which were within the range of films made with diissononyl phthalate (DINP) and diheptyl succinate (DHPS) which had elongations of 280% and 380%, respectively. The elongation at break of extruded and compression moulded samples (94-113%) made with the new additives were similarly comparable to samples of di-2-ethylhexyl phthalate (DEHP, 96%) and DHPS (93%) prepared in the same way. Furthermore, the incorporation of the new additives was found to decrease the T_g of PVC to between -15 and -30°C. Importantly, the new additives were also shown to reduce leaching into hexanes and were synthesized using renewable feedstock and a solvent-free technique. While DINP and DHPS blends demonstrated 41% and 28% plasticizer loss, respectively, the leaching of PCL-based plasticizers ranged from 2%-14%. Industrial processing techniques, including extrusion and calendering, were used to blend the additives with PVC in order to confirm the feasibility of using these additives with existing processing equipment.

These findings are a significant contribution to the existing plasticizer literature since they establish multiple distinct functionalities for the additives while incorporating elements of sustainable design. The new additives developed through this research can be used as highly effective general-purpose plasticizers, specialty plasticizers to reduce leaching, or processing aids to remove surface defects. The structure-property relationships that were investigated in this work also advance the understanding of plasticizer-polymer interactions for PCL-PVC systems.

Résumé

Les produits en plastique sont fabriqués en combinant des polymères avec des additifs chimiques utilisés pour améliorer la performance et les caractéristiques de transformation des polymères. La plupart des additifs ne sont pas chimiquement liés au polymère et, par conséquent, peuvent subir une migration, entraînant l'exposition des animaux, des humains et d'autres organismes envers ces produits chimiques. Les taux croissants de production et d'utilisation du plastique, jumelé à la migration d'additifs courants, ont conduit à une reconnaissance généralisée du fait que les additifs plastiques sont des contributeurs importants à la pollution plastique mondiale.

Les plastifiants sont un groupe d'additifs qui sont utilisés pour améliorer la flexibilité et la transformabilité des polymères. Avec des preuves de plus en plus nombreuses des impacts négatifs sur la santé et l'environnement des additifs tels que les plastifiants phtalates, les recherches scientifiques se sont concentrées sur le développement d'additifs alternatifs plus sûrs. Ces recherches ont été dictées principalement par les besoins des consommateurs ou les interdictions réglementaires de certains additifs. Les efforts de recherche qui se concentrent sur l'optimisation des performances des plastifiants négligent souvent les considérations de durabilité vis-à-vis l'environnement, ou à l'autre extrême, les efforts pour concevoir des plastifiants durables négligent souvent les considérations pratiques de caractéristiques de transformation, de performance, et de coût. Ce travail de thèse cherche à combiner simultanément la fonctionnalité et la durabilité lors de l'évaluation des performances d'additifs alternatifs.

Pour atteindre cet objectif, un cadre pour la conception et l'évaluation des nouveaux plastifiants est présenté dans cette thèse doctorale. Une nouvelle série d'additifs chimiques a été développée en utilisant cette structure d'évaluation, et, par la suite, leur efficacité comme plastifiants et auxiliaires de traitement a été étudiée. Les résultats présentés dans cette thèse ont démontré que les additifs développés à base de polycaprolactone (PCL) peuvent prévenir la formation de défauts de surface «gas check» pendant le calandrage à chaud ainsi qu'obtenir un allongement à la rupture et une température de transition vitreuse comparables à celles des plastifiants traditionnels phtalates. Essentiellement, les nouveaux additifs réduisent considérablement la lixivation dans les hexanes et ont été synthétisés en utilisant une technique sans solvant avec des matières premières

renouvelables. En outre, des techniques de traitement industriel, tel que l'extrusion et le calandrage, ont été utilisées pour mélanger les additifs à l'état fondu avec du chlorure de polyvinyle (PVC) afin de confirmer la faisabilité d'utiliser ces additifs avec les équipements de traitement des polymères existant.

Ces résultats représentent une contribution importante pour la littérature scientifique sur les plastifiants, car ils établissent de nouvelles fonctionnalités en incorporant la durabilité vis-à-vis l'environnement. Les nouveaux additifs développés grâce à cette recherche peuvent être utilisés comme plastifiants primaires efficaces, comme plastifiants spéciaux avec de faibles potentiels de lixiviation, ou même comme auxiliaires de traitement pour éliminer les défauts de surface. Les relations structure-propriété qui ont été étudiées dans ce travail font également progresser la compréhension des interactions plastifiant-polymère pour les systèmes PCL-PVC.

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Contribution of Authors

This manuscript-based thesis is comprised of three articles, two of which have been published in peer-reviewed journals, and one of which has been accepted for print publication in a peer-reviewed journal and has been published online at this time. The contribution of each author is described for the three manuscripts.

Article 1 (Chapter 3)

Jamarani R., Erythropel H.C., Nicell J.A., Leask R.L., and Maric M. (2018). How green is your plasticizer?, *Polymers*, 10(8), 834.

Roya Jamarani planned the organization of this review article, researched and wrote the article, prepared figures, and contributed to the response to reviewers. Hanno Erythropel contributed to the research and writing of the article. Richard Leask, Jim Nicell, and Milan Maric funded the work and helped plan, write, and edit the manuscript and with revisions in response to reviewers.

Article 2 (Chapter 4)

Jamarani R., Halloran M.W., Panchal K., Garcia-Valdez O., Mafi R., Nicell J.A., Leask R.L., and Maric M. (2021). Additives to prevent the formation of surface defects during poly(vinyl chloride) calendering. *Polymer Engineering & Science*, 61(4), 1209-1219.

Roya Jamarani planned and performed the experiments in this article, interpreted and analyzed the results, wrote and edited the manuscript, and prepared a response to the reviewers. Matthew Halloran, a PhD student trained by Roya Jamarani, helped with the synthesis and ^{1}H NMR characterization of all additives investigated in this study and in the manual counting of film surface defects. Omar Garcia-Valdez, a post-doctoral fellow, contributed to the synthesis of the original additive that formed the basis of this study, triheptylsuccinate-terminated poly(caprolactone) (PCL_{540}-Succ-C7). Kushal Panchal and Roozbeh Mafi were industrial collaborators working at Canadian General Tower Ltd. who helped in the identification of the

defect removal phenomenon, as well as overseeing and helping with the production and testing of calendered PVC films, including the use of their lab-scale roll mill, calender, and tensile tester. Kushal Panchal also contributed to editing the manuscript. Richard Leask, Jim Nicell, and Milan Maric funded the work, guided the planning and direction of the study, contributed to the design of experiments, and contributed to the editing of the manuscript and subsequent revisions in response to reviewers.

Article 3 (Chapter 5)

Jamarani R., Halloran M.W., Panchal K., Nicell J.A., Leask R.L., and Maric M. (2021). Poly(**ε**-caprolactone)-based additive: plasticization efficacy and migration resistance. *Journal of Vinyl & Additive Technology*. Published Online.

Roya Jamarani planned and performed the experiments in this article, interpreted and analyzed the results, wrote and edited the manuscript, and prepared a response to the reviewers. Matthew Halloran helped with the synthesis and ^{1}H NMR characterization of all additives investigated in this study as well as in running a few of the reported DSC tests under the direction of Roya Jamarani. Kushal Panchal, an industrial collaborator working at Canadian General Tower Ltd., helped with the production of calendered PVC films on their lab-scale roll mill and calender as well as with performing tensile tests on the film samples. Richard Leask, Jim Nicell, and Milan Maric funded the work, guided the planning and direction of the study, contributed to the design of experiments, and contributed to the editing of the manuscript.

1

Introduction

1.1 Thesis motivation

Widespread plastic pollution is a global problem which jeopardizes human health and has negative impacts on natural ecosystems [1,2]. Most plastic products contain numerous additives including plasticizers, impact modifiers, lubricants, fillers, flame retardants, and stabilizers [3]. Often, these additives are not covalently bound to the plastic and are therefore extremely susceptible to entering the environment over time [4]. The leaching of hazardous chemical additives from plastics, resulting in human, animal, and marine organism exposure, is one of the ways plastic products pose a threat to humans and the environment [5].

Phthalate plasticizers in particular have attracted a great deal of attention since they have been found to be pervasive in the environment due to their widespread use over the past several decades and because of their associated reproductive toxicity and endocrine disruption characteristics [6,7,8,9]. Thus, several commercial non-phthalate plasticizers have been developed by chemical manufacturers with many more alternatives explored by researchers [10,11]. However, there has been no consistent approach to the development and evaluation of these alternative plasticizers. The need to combine functionality and sustainability formed the cornerstone of this thesis.

Frequently, plasticizers are designed to meet very specific performance requirements such as achieving a particular elongation, hardness, or tear strength, completely ignoring issues of toxicity, biodegradation, and leaching. Similarly, many plasticizers that are touted as ‘green’ are evaluated by a specific criterion such as biodegradability or toxicity with little attention to other sustainability

criteria or practical considerations of processing, performance, and cost. There has been very little consistency amongst various groups in how plasticizers are assessed.

Poly(vinyl chloride) (PVC) is one of the most widely used commodity plastics in the world, with 90% of all globally produced plasticizers used to make flexible PVC [12]. PVC is used in a variety of applications including seepage barriers for reservoirs and pools, medical blood bags, as well as car and furniture trim. Many of these applications require PVC to be processed into films using an industrial process known as calendering. Calendered PVC films can contain a number of surface defects that result in reductions in film mechanical properties as well as undesirable film surface finish. In particular "gas check" defects reduce film quality, requiring the disposal or recycling of film containing these defects, which results in production delays and wasted material.

Therefore, this PhD thesis was motivated by the need to provide and implement a systematic approach for developing and evaluating new plastic additives, with a particular focus on plasticizers that are designed for sustainability and to reduce leaching. This thesis was also driven by the need to develop functional additives that could act as processing aids to eliminate surface defects in PVC films, thereby reducing waste, and also act as primary plasticizers.

1.2 Objectives

The primary research question driving the work in this thesis was "can additive functionality be retained while designing for sustainability?" To answer this question, a series of candidate additives was developed for PVC using the design principles of green chemistry. Studies were performed to evaluate the functionality of new candidate additives as plasticizers and processing aids, as well as to evaluate their permanence in blends with PVC. The specific objectives pursued in order to answer the research question were as follows:

- Objective 1: To develop a framework that combines sustainability and performance for designing and evaluating new plasticizers.

- Objective 2: To (i) synthesize marketable oligomeric additives using the guiding principles of green chemistry (i.e., benign, biodegradable, and permanent); (ii) evaluate the efficacy of these candidate additives in removing surface defects, testing the hypothesis that viscosity is a dominant factor in defect removal; and (iii) identify the role of central group structure, diester group, and chain length in defect removal.

- Objective 3: To (i) demonstrate that the oligomeric additives have competitive performance characteristics as low-leaching primary plasticizers; (ii) compare their mechanical and thermal properties to blends made with commercial plasticizers; and (iii) test the hypothesis that the oligomeric, branched structure of the additives increases their permanence and reduces leaching compared to traditional phthalate plasticizers.

1.3 Organization of the thesis

This manuscript-based thesis consists of six chapters, including three publications. Chapter 2 provides a background of what constitutes an effective plasticizer. This is followed by a review article in Chapter 3 that presents a framework for the design and assessment of green plasticizers. While Chapter 2 focuses on plasticizer performance, Chapter 3 focuses on sustainability criteria, specifically focusing on toxicity, biodegradation, and permanence. Chapters 2 and 3 provide a summary of the literature relevant to this project.

The experimental results in this thesis are presented in Chapters 4 and 5. In the article presented in Chapter 4, a new family of additives was created using the design principles outlined in Chapters 2 and 3. This study included an in-depth analysis of the ability of these additives to remove surface defects, with a focus on understanding which molecular features contribute to this functionality.

The final manuscript is presented in Chapter 5 and reports on the investigation of the plasticizing efficacy of the additives developed in Chapter 4, using two different compounding techniques and blend formulations. The synthesis of the additives was optimized to remove the use of solvent and

include bio-based reagents where possible. This study also included measuring the leaching of the novel additives compared to existing plasticizers.

The conclusions of these works are summarized in Chapter 6, which also includes recommendations for future work and outlines the original contributions to knowledge arising from this research.

2

Background

2.1 Poly(vinyl chloride)

Polyvinyl chloride (PVC) is a homopolymer made of repeated vinyl chloride monomer units (Figure 2-1). PVC is one of the most widely used plastics in the world, with a yearly global consumption of 40 million metric tons in 2016 [13]. PVC is a thermoplastic with a semi-crystalline structure that contains around 90% amorphous regions and 5-10% crystalline regions and has a glass transition temperature (T_g) of approximately 80°C [14].

T_g is the temperature at which a polymer transforms from a soft, rubbery state to a hard, glassy state. A significant change in mechanical and thermal properties, corresponding to a change in the mobility of the amorphous regions of the polymer, occurs at the T_g [15]. Thus, unmodified PVC will be hard and brittle at temperatures below 80°C and soft and flexible at temperatures above 80°C. T_g is one of the most important factors in defining polymer processing conditions as well as end-use applications.

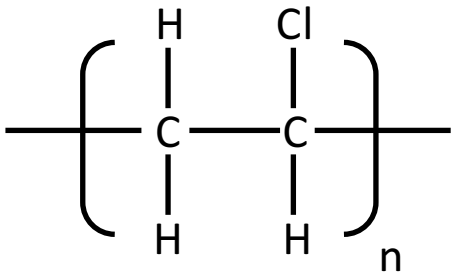

Figure 2-1. Polyvinyl chloride.

Some characteristics that make PVC a popular commodity plastic are its relatively low production cost, high strength to weight ratio, and versatility in end-use applications due to the ease with which material properties can be varied by changing polymer blend formulation [14]. A limitation of PVC is its low thermal stability, which makes it challenging to process at high temperatures. In addition, there are environmental concerns surrounding the use of vinyl chloride monomers and the persistence of PVC over time [14]. A summary of these characteristics is shown in Table 2-1.

Table 2-1. Summary of the main advantages and disadvantages of polyvinyl chloride as a commodity plastic.

Polyvinyl chloride	
Advantages	**Limitations**
• Low cost of production • High strength to weight ratio • High versatility in end-use applications • Durable • Resistant to corrosion and to many different chemicals • Chemically inert • Can be produced in various colors	• Low thermal stability • Brittle at low temperatures unless modified • Environmental concerns relating to vinyl chloride monomer and persistence in the environment

Additives are an essential part of PVC formulations due to the poor thermal stability characteristics of PVC [16]. PVC is unique in its ability to accept a variety of different additives, specifically very high concentrations of plasticizers, while retaining its useful mechanical properties. It has been hypothesized that this ability is due to the presence of the highly polar chlorine atom on the polymer chain (Figure 2-1), which provides compatibility with a variety of additives, in addition to the presence of microcrystalline regions within a predominantly amorphous polymer structure, which allow the polymer to retain its strength while being blended with high concentrations of additives [17]. It should be noted that most additives are mixed with the polymer by melt processing, and are not covalently bound to the polymer matrix, leaving them susceptible to migration over time.

PVC has a wide range of applications including construction products, packaging materials, consumer products, and medical devices. These applications require a range of PVC properties from extremely rigid to very flexible, with service lives of several years to many decades, with 50% of applications having lifetimes of more than 40 years [14]. PVC products come in two forms, either rigid, i.e., unplasticized PVC (uPVC or PVC-U), or flexible, i.e., plasticized PVC (pPVC or PVC-P) [18]. Although they are not plasticized, uPVC formulations still contain several additives such as heat stabilizers, processing aids, and fillers since they would otherwise be virtually impossible to process. uPVC is most commonly used in construction applications including piping, fittings, window casements, and vinyl siding, while pPVC is used in applications ranging from cable insulations to reservoir linings, medical blood bags, clothing, and upholstery [19].

2.2 Plasticizers

Plasticizers are the largest class of polymer additives by volume, with global demand expected to reach 9.75 million tonnes by 2024 [20,21]. Plasticizers are defined based on the properties they confer to the polymer with which they are combined, leading to various definitions of these additives [22]. One of the most common definitions of a plasticizer is a molecule that is incorporated into a polymer matrix to make it more flexible. Other definitions of plasticizers relate to their ability to reduce T_g, improve melt processability (e.g., by lowering fusion and gelation temperatures), and modify melt rheology [22].

Approximately 90% of plasticizers produced globally are used with PVC due to its unique ability to accept and retain high quantities of plasticizer [21]. The composition of PVC products can include up to 100 parts per hundred resin (phr) plasticizer [23]. The designation “phr” is a common term used to express additive concentrations, also known as loadings, during polymer compounding and is defined by the concentration of the additive relative to the concentration of the polymer resin. With the addition of plasticizers, the T_g of a PVC blend can be reduced from 80°C to below 0°C, resulting in a flexible material at room temperature and permitting the use of lower processing temperatures. Some other polymers that are blended with plasticizers include

polyvinyl acetate, acrylic polymers, nylon, polyamides, cellulose compounds, and polyolefins [24].

2.3 Classification of plasticizers

2.3.1 Internal and external

Plasticizers can be classified as either internal or external [21]. Internal plasticizers are added to a monomer before polymerization and are chemically incorporated into the polymer chain in the form of copolymerized or grafted groups. For example, low concentrations of vinyl acetate, vinylidene chloride, acrylonitrile, or vinyl stearate can be reacted with the vinyl chloride monomer to form copolymers with increased flexibility [25]. One of the main advantages of internal plasticizers is the complete suppression of plasticizer migration. However, internal plasticizers are much less versatile than external plasticizers in terms of properties that they can achieve, leading to their less frequent use industrially [26]. External plasticizers are chemical agents that are blended with a polymer during melt processing and are not covalently bound to the polymer matrix. While this makes external plasticizers susceptible to evaporation, migration, and extraction over time, many products formulated with external plasticizers actually appear as homogeneous solids with no significant changes in their physical properties over many years of service [26]. The performance of external plasticizers, combined with their cost-effectiveness, the ability to choose between many different types of plasticizer, and the ease of modifying blend formulations have led to external plasticizers being the most common type of plasticizer used industrially [20]. Therefore, external plasticizers were the main focus of this thesis. The biggest disadvantage of external plasticizers is their tendency to migrate out of the polymer matrix, which has been associated with environmental contamination and human exposure that can be problematic if there are any toxic effects associated with the plasticizers [27].

2.3.2 Primary and secondary plasticizers

Within the category of external plasticizers, plasticizers can further be classified as primary or secondary based on whether or not they can be used as the sole plasticizer in a blend formulation

[22]. This relates to the compatibility of the plasticizer with the polymer matrix. Primary plasticizers will have a high mutual miscibility and compatibility with the polymer, resulting in rapid gelation times and no exuding of the plasticizer from the polymer. This gives primary plasticizers the ability to be used as the sole plasticizer to alter polymer properties [19]. Secondary plasticizers often have a lower compatibility with the polymer and cannot be used alone to achieve the desired change in polymer properties. They are typically incorporated at lower loadings along with a primary plasticizer to enhance a specific property, such as low-temperature flexibility or thermal stability.

2.3.3 Classification by function

Another way of classifying plasticizers is by their intended functions. Some of these categories are listed below [28]:

1) General purpose plasticizers: General purpose plasticizers offer the best balance of performance and cost, and include the most commonly used industrial plasticizers di-2-ethylhexyl phthalate (DEHP), di-isononyl phthalate (DINP), and di-2-propylheptyl phthalate (DPHP).

2) Low volatility or permanent plasticizers: Low volatility plasticizers offer longer service lives compared to general purpose plasticizers and include internal plasticizers, high molecular weight monomeric plasticizers, and polymeric plasticizers. Poly(caprolactone) (PCL) and poly(butylene adipate) (PBA) are examples of two commonly used polymeric plasticizers [29].

3) Low-temperature plasticizers: Low-temperature plasticizers are used in applications such as roofing or outdoor cabling that specifically require improvements in low-temperature flexibility. Some examples of common low-temperature plasticizers are di-2-ethylhexyl adipate (DEHA) and di-isononyl adipate (DINA) [30].

4) Fast-fusing plasticizers: Fast-fusing plasticizers enable the use of lower processing temperatures and shorter processing times. Some examples of fast-fusing plasticizers are butyl benzyl succinate (BBS) and butyl benzyl phthalate (BBP) [20].

5) Specialty plasticizers: Specialty plasticizers are characterized by their limited use and rigorous performance environments as well as their price premiums in comparison to general purpose plasticizers [31].

2.3.4 Classification by structure

Plasticizers can also be categorized based on their chemical structures. With estimates that over 30,000 plasticizers have been developed in the scientific and patent literature [32], the following list is not exhaustive but contains some of the common plasticizer families [21]:

- Phthalate esters
- Dibasic acid esters (i.e., aliphatics)
- Epoxy plasticizers
- Glycol derivatives
- Phosphate esters
- Trimellitates
- Benzoates
- Citrates
- Polymeric plasticizers

2.3.5 Monomeric and polymeric plasticizers

The designation “monomeric” or “polymeric” is used to classify plasticizers based on their molecular size. Monomeric plasticizers are typically small molecules, such as esters, with molecular weights ranging from around 300-600 $g \cdot mol^{-1}$. Polymeric plasticizers have larger molecular weights and can have a variety of structures that contain repeating units, with average molecular weights typically ranging from 1000-10,000 $g \cdot mol^{-1}$ [28]. Plasticizers at the lower end

of this molecular weight range would be more accurately described as “oligomeric”, however they are often referred to as polymeric plasticizers. These plasticizers will be the focus of much of the work presented in this thesis. Polymeric plasticizers have the advantage of lower volatility and higher permanence compared to monomeric plasticizers, but they are generally more expensive to produce, and cause an increase in viscosity which can have negative impacts on processability. Therefore, their use is typically reserved for specialty applications [23].

2.4 Theories of plasticization

While plasticizers have been in commercial use for almost a century, their mechanism of action is still not fully understood. Several useful theories have been proposed to describe the plasticization of polymers [33]. The lubricity and gel theories of plasticization were developed in parallel in the 1940s while the free volume theory was developed a decade later in the 1950s. No relevant theories have been developed since. None of these theories alone is able to describe all of the different observed characteristics of polymer-plasticizer systems, but taken together the three theories can explain most behaviors of plasticized polymers[22].

2.4.1 Lubricity theory

The lubricity theory attributes the performance of plasticizers to their ability to reduce intermolecular friction between polymer chains. As per this theory, some functional groups on the plasticizer form strong attractions with the polymer chains, acting as solvents, while other groups on the plasticizer have weaker attractions and act as molecular lubricants [21]. The incorporation of these lubricating segments is said to decrease the internal resistance polymer chain sliding, increasing mobility and leading to a change in material properties. This theory asserted the importance of the attractive forces between plasticizers and polymers, specifically relating these to their polarities. One of the limitations of the lubricity theory is that it does not consider polymer-polymer attractive forces, and assumes that any resistance to motion stems only from surface irregularities [31].

2.4.2 Gel theory

While the lubricity theory considers the structure of polymer-plasticizer systems as gliding planes, the gel theory considers the polymer structure to be a three-dimensional honeycomb or "gel" network. The gel theory holds that plasticizers work by forming a dynamic equilibrium with the polymer, repeatedly solvating and desolvating different regions within the network, reducing the number of polymer-polymer interactions and thereby reducing the rigidity of the polymer [22]. This theory accounts for the poor low-temperature performance of internal plasticizers compared to external plasticizers since external plasticizers have a greater freedom to solvate and desolvate different sites on the polymer while internal plasticizers do not share this freedom. However, this theory does not consider the contribution of the aliphatic parts of plasticizer molecules that do not interact with the polymer chain and impart flexibility to the polymer, which is explained by the lubricity theory [33]. According to the gel theory, plasticizer effectiveness depends on both the mobility of the plasticizer molecules themselves as well as the strength of the attractive forces between the plasticizer and polymer.

2.4.3 Free volume theory

The free volume theory attributes the action of plasticizers to their ability to increase the "free volume" available to a polymer, allowing polymer chains to move more freely [22]. Free volume is defined as the difference between the specific volume at absolute zero temperature and the specific volume at a given temperature and represents the internal space available within the polymer matrix [34]. All polymers, regardless of structure, are said to have the same free volume at their respective T_g. Free volume is said to occur from chain end motion, side chain motion, and main chain motion [21].

Therefore, free volume, and consequently polymer motion and flexibility, can be increased by increasing the number of chain end groups (i.e., using lower molecular weight plasticizers), increasing the length of side chains (i.e., internal plasticization by grafting, using branched plasticizers) or copolymerizing with flexible segments [21]. The free volume theory is able to explain how low concentrations of plasticizer can cause large reductions in T_g. One of the

limitations of the free volume theory is that it does not explain the phenomenon of "antiplasticization" that is observed in some systems, where the addition of small concentrations of plasticizer can lead to reductions in T_g but increases in elastic modulus that correspond to a higher material stiffness. Another limitation of this theory is that it does not consider plasticizer compatibility, meaning that according to this theory, any molecule that creates free volume should be able to be used as a plasticizer for any polymer [35].

2.5 Plasticizer selection criteria

The most common criteria, besides cost, that have historically been used to evaluate and select plasticizers have been compatibility, efficiency and permanence [21]. In recent years, these selection criteria have grown to include sustainability and green chemistry principles, which are introduced in Chapter 3, including considerations of toxicity, biodegradability, and the use of renewable feedstocks. The specific testing methods and benchmarks used to evaluate plasticizer properties vary greatly within the literature as well as in industrial settings [36]. The selection or development of new plasticizers is a continuous balancing act between different requirements. Structural features that make plasticizers favorable with respect to some selection criteria can decrease performance with respect to other criteria. Some examples of this are [36]:

- Polar groups tend to improve permanence and compatibility, but reduce efficiency.
- Long, aliphatic chains improve efficiency, but tend to decrease permanence and compatibility.
- Linear plasticizers tend to be less compatible than branched molecules but have been shown to have better low temperature performance and thermal stability.
- Branched plasticizers tend to exhibit faster fusion times but lower thermal stability.

2.5.1 Compatibility

One of the important features of a plasticizer, which relates to the strength of its interactions with the polymer matrix, is its compatibility [26]. As with the other selection criteria discussed in this

chapter and the next, there is not a standard approach for measuring compatibility. Rather, in the literature and industrially, a variety of different methods, both theoretical and experimental, have been used to estimate compatibility.

Theoretical procedures include computing Hildebrand or Hansen solubility parameters, with close matches between polymer and plasticizer solubility values indicating compatibility [14]. Polarity parameters have also been used as predictors of compatibility, with low values indicating high compatibility [14]. These theoretical methods have proven useful in comparing compatibility within families of monomeric plasticizers, but less effective at predicting differences between different families. A limitation of both methods is that they are not effective at predicting polymeric plasticizer compatibility [14].

Qualitative assessments of plasticizer compatibility can be made by observing polymer blend characteristics throughout their processing. For example, visual signs of an incompatible plasticizer include phase separation such as blooming, which results in exuding or sweating of the plasticizer from the polymer matrix which form a film or oily droplets on the surface of the plastic [26]. While these observations have proven more practical than some theoretical predictions, they cannot distinguish between underlying sources of compatibility, for example between solvating power and diffusibility [37]. A number of experimental measurements can also be used to estimate plasticizer compatibility including the solid-gel transition temperature, cloud point temperature, and glass-transition temperature [14]. There are also two American Society for Testing and Materials (ASTM) tests for assessing plasticizer compatibility, namely, the loop compatibility test (D3291) and the humid aging test (D2383). Compatibility is known to depend on plasticizer polarity, molecular weight, and structure (e.g., branching and arrangement of polar groups) [22].

2.5.2 Efficiency

Plasticizer efficiency describes the effectiveness of a plasticizer in achieving a desired property. More specifically, it refers to the amount of plasticizer required to produce a functional change, with a plasticizer being deemed “more efficient” than another if it can be used at lower concentrations to achieve a specific change in properties. Since plasticizer efficiency will vary

depending on the polymer with which the plasticizer is blended, and since it is defined in relation to a variety of polymer properties, there is no absolute definition of efficiency. Often, the efficiency of a given plasticizer is compared against that of a well-known plasticizer such as DEHP or DINP [38] .

Some properties that are commonly used as measures of plasticizer efficiency are T_g, elongation at break, hardness, tensile strength, elastic modulus, melt viscosity, and fusion time [19]. While some plasticizers are evaluated based on only a few of these properties, certain industrial applications require efficacy to be measured with respect to dozens of different properties. The experimental methods used to measure efficacy are highly dependent on the property changes that are being measured. Similar to compatibility, efficiency also depends on plasticizer molecular weight, polarity, and size. The nature of the plasticizer-polymer interactions (e.g., internal vs. external plasticizers) and the diffusion rate of the plasticizers also impact their efficiency [21].

2.5.3 Permanence

Another important consideration in plasticizer selection is permanence, which describes the tendency of a plasticizer to remain within a polymer matrix throughout the service life of the material [21]. Poor permanence will result in a deterioration of the material properties throughout the useful life of a polymer product as plasticizer is lost from the blend.

Plasticizer loss can occur through evaporation into air, extraction into a liquid (i.e., leaching), migration to a neighboring solid, or exudation under compressive stress, all of which can be measured experimentally [21]. Methods such as weight loss, spectroscopy, and chromatography are used to measure plasticizer content in different environments, at various temperatures and times [39]. Under given conditions, the permanence of a plasticizer in a flexible polymer product depends on several factors including its structure, chemical composition, molecular weight, and polarity. In addition to affecting performance, plasticizer loss has important implications on environmental contamination and human exposure to plasticizers. Therefore, the topic of permanence is covered in more detail in the review article presented in Chapter 3.

The goal of this thesis was to develop efficient plasticizers for PVC with an emphasis on performance and sustainability. This was done by using the aforementioned criteria in combination with the green principles outlined in Chapter 3.

3

How green is your plasticizer?[1]

3.1 Preface

This chapter was published as a review article in 2018 in the journal *Polymers* on the topic of designing and evaluating safe plasticizers. The objective of this review was to outline a holistic, multi-disciplinary approach with respect to the principles of green chemistry that could act as a guide for anyone seeking to develop a new plasticizer. The emphasis of the review was on those green chemistry principles that were most relevant to creating new plasticizers, specifically: (i) designing non-toxic chemicals, (ii) designing for biodegradation, (iii) designing for permanence, and (iv) green production. Studies that included robust methodologies for evaluating plasticizer performance with respect to each of these concepts were reported in the review to be used as a framework for researchers in planning future experiments.

With respect to the research presented in this thesis, this review provides a background and literature review on criteria that can be used in the development and evaluation of plasticizers in relation to their sustainability. More specifically, this review introduces an approach that was applied in the design of the novel additives presented in Chapters 4 and 5 and provides a framework for the leaching study outlined in Chapter 5. The principles outlined in this review were combined with traditional engineering performance criteria, described in Chapter 2, to evaluate our additives.

[1] Reproduced with permission from Jamarani R, Erythropel HC, Nicell JA, Leask RL, Maric M. How green is your plasticizer? *Polymers.* 2018; 10(8),834.

Chapter 3 outlines the green chemistry considerations that must be included along with traditional performance criteria in order to develop and evaluate plasticizers.

3.2 Abstract

Plasticizers are additives that are used to impart flexibility to polymer blends and improve their processability. Plasticizers are typically not covalently bound to the polymers, allowing them to leach out over time, which results in human exposure and environmental contamination. Phthalates, in particular, have been the subject of increasing concern due to their established ubiquity in the environment and their suspected negative health effects, including endocrine disrupting and anti-androgenic effects. As there is mounting pressure to find safe replacement compounds, this review addresses the design and experimental elements that should be considered in order for a new or existing plasticizer to be considered green. Specifically, a multi-disciplinary and holistic approach should be taken which includes toxicity testing (both in vitro and in vivo), biodegradation testing (with attention to metabolites), as well as leaching studies. Special consideration should also be given to the design stages of producing a new molecule and the synthetic and scale-up processes should also be optimized. Only by taking a multi-faceted approach can a plasticizer be considered truly green.

3.3 Introduction

Plasticizers are additives, typically small organic molecules, that decrease the glass transition temperature (T_g) of the polymer they are blended with, creating flexible or semi-rigid products with improved processing characteristics [1]. Approximately 90% of all globally produced plasticizers are used to make flexible poly(vinyl chloride) (PVC), with di(2-ethylhexyl) phthalate (DEHP) being the most frequently used plasticizer [2]. Plasticizers can be classified as either internal or external. Internal plasticizers achieve flexibility by lowering T_g through grafting or copolymerization of softer monomer units to the polymer chain, while external plasticizers, such as DEHP, are simply blended with the polymer at elevated temperatures and do not form covalent

bonds [3]. Internal plasticizers are less commonly used, and often for specific purposes, because the fixed chemical bonds offer less freedom and limited properties compared to external plasticizers. External plasticizers offer higher flexibility to adjust the final polymer properties, given that the plasticizer is added after polymerization [1,3]. Additionally, the type and amount of plasticizer can be carefully tailored to produce a wide variety of formulations and product properties and impart different levels of flexibility depending on the desired application. Furthermore, because no chemical reaction is involved, external plasticization also tends to be more cost-effective, and are thus used to a greater extent. Therefore, this review will focus exclusively on external plasticizers.

The lack of a chemical bond between external plasticizers and polymers allows the plasticizer to diffuse within and out of the blend over time. Once plasticizer molecules reach the surface of the blend, leaching into their surroundings occurs that results in human exposure and entry of the compounds into the environment [4,5]. For example, DEHP and its metabolites have been found to be ubiquitous environmental contaminants, likely due to their slow degradation rates combined with high rates of entry into the environment [6,7]. Phthalate plasticizers including DEHP have been detected in a wide variety of environmental samples, including house dust [8–10], air [11], soil [12], watersheds [4], and animals [6]. This is especially problematic given that many studies have linked DEHP and its metabolite, mono(2-ethylhexyl) phthalate (MEHP), to endocrine disruption in human and animal models, and negative effects on male reproductive development (anti-androgenic effects) [13–17]. As a result of these findings, the use of DEHP and other phthalates has been regulated in consumer items such as children's toys in many countries, including Canada [18], the United States [19], the European Union [20], and Japan [21]. Therefore, there is a need to develop alternative, safer, plasticizers.

The traditional view of plasticizers has held that in order to develop a well-functioning plasticizer, a balance must be struck between the compatibility, efficiency, and permanence of the plasticizer blended with PVC, as reflected by the three vertices of the triangle pictured in Figure 3-1 [22]. This scheme reflects the fact that achieving desirable effects with respect to one of the properties can negatively impact upon other properties. For example, molecular features such as polar groups on a plasticizer are attracted to polar sites on the PVC molecule and will render the plasticizer

more compatible with PVC; however, if only polar components are present in a plasticizer, its plasticizing effectiveness is not very high. Conversely, the non-polar segments of the molecule generally provide good plasticization, but if they are too large or numerous, the plasticizer might be poorly miscible with PVC and lead to exudation. This careful balancing act of optimizing plasticizer performance has been the primary focus of research and development work for many years. However, given the significant negative impacts of phthalate plasticizers noted above, in this review we endeavor to outline approaches to plasticizer design and evaluation that also incorporate elements of green chemistry thinking, in addition to traditional performance considerations [23,24]. Therefore, the schematic shown in Figure 3-1 reflects the inherent and growing importance of maintaining plasticizer performance while considering green design elements such as toxicity, biodegradation, and leaching in developing safe and effective plasticizers. In order to answer the question 'how green is your plasticizer?', we need to not only ensure that compounds meet the balanced criteria of an effective plasticizer, but we must assess the effects of the plasticizer from non-traditional measures, informed by green chemistry, shown in Figure 3-1.

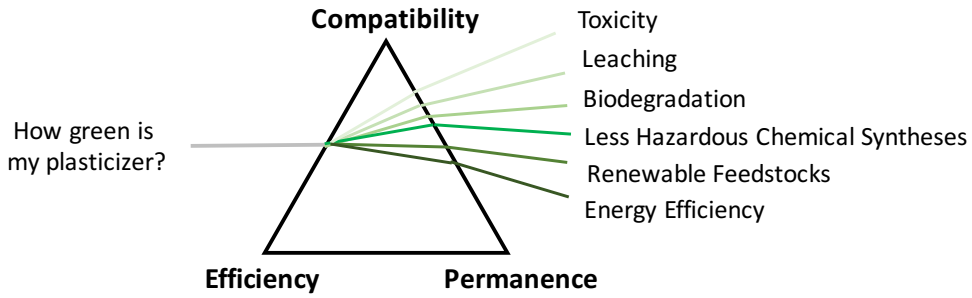

Figure 3-1. Green plasticizer design considerations. Adapted from R.F. Boyer, 1951 [22].

At its core, the growing field of green chemistry aims to reduce or eliminate the use or generation of hazardous substances. This applies not only during the usage stage of a material, but also includes its production and end-of-life stages. A crucial component of green chemistry is thus the design stage, during which much of the future fate of a molecule or substance is already decided. Anastas and Warner first introduced the 12 principles of green chemistry, listed in Figure 3-2, and outlined the concept of green chemistry as a mindset in 1998 [23]. In brief, these principles offer

guidance on how to design or improve materials and processes while adhering to the ideals of green chemistry. These principles include designing for degradation, designing benign or less toxic compounds, and preventing the production of waste, amongst others. A number of the remaining principles apply more specifically to the chemical synthesis itself such as using renewable feedstocks, using benign solvents, and improving atom economy [23]. To develop a truly green plasticizer, we propose to use these principles as a framework for design and testing.

12 Principles of Green chemistry

1. **Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals:** Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency:** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives:** Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Designing for Degradation:** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for Pollution Prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Figure 3-2. The 12 Principles of Green Chemistry. Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, NY, USA, 1998; p. 30. By permission of Oxford University Press [23].

Applying a holistic, multi-disciplinary approach that incorporates many of the green chemistry principles is essential for designing safe plasticizers. In order to do so, collaboration between chemists, toxicologists, biologists, and engineers, amongst others, is required. Unfortunately, however, research and development activities often focus on addressing a limited subset of the 12 principles (e.g., reducing human toxicity or designing for biodegradation), and are often

undertaken with little input from other disciplines, and a compound will questionably be touted as green according to its performance with respect to those few selected criteria. In this paper, we seek to outline the variety of green chemistry considerations that can apply to plasticizer design, highlighting those that are most important, and showing that plasticizer performance should be evaluated with respect to all of these relevant considerations in order to be considered green. That is, in addition to performing well as a functional plasticizer [25–27] a green plasticizer also needs to be (1) non-toxic and harmless to humans, animals, and the environment, (2) biodegrade quickly, without producing stable or toxic metabolites, and (3) leach as little as possible from the PVC blend. This review will focus mainly on these three principles since much of the experimental testing of new plasticizers will center upon them. Beyond these criteria, several other parameters, mostly pertaining to the synthesis of the compounds, such as using renewable feedstocks, maximizing atom economy, using safer solvents and reaction conditions, and using catalysts should also be considered. Additionally, life-cycle assessment (LCA) is another tool that can be used to assess the environmental impact of introducing a new compound to market [28]. In this review, we aim to demonstrate how to avoid toxicity, ensure biodegradability, and impart low leaching to plasticizers, while keeping all the different principles of green chemistry in mind.

3.4 Historical perspective

PVC was first synthesized in the 1800s, but due to its poor processability in the absence of plasticizers and heat stabilizers it was not commercialized at that time [29]. It wasn't until the early 20th century that the German chemist Fritz Klatte at Griesheim-Elektron started blending this hard and brittle polymer with esters and oils as 'softeners' that PVC could be produced commercially [3]. Thus, the idea of using plasticizers as key components of plastic formulations was born, allowing for the easy processing of PVC and its use in many different and diverse applications. By 1943, the demand for PVC products had increased considerably and there were already over 150 commercial plasticizers in use [30].

Esters of phthalic acid quickly became the most important class of plasticizers, and still remain so, due to their all-round plasticizing efficiency and low cost of production [3]. In particular, the

compound DEHP (Figure 3-3) became the most widely used plasticizer [3,31]. Plasticized PVC products were increasingly manufactured due to their low cost, ease of fabrication, suitable mechanical properties, and compatibility with blood and medical solutions [32]. However, it was not until the 1980s that concerns over the deleterious health effects of plasticizers, such as DEHP, started to be more thoroughly investigated and the need for green replacement compounds was established [32–34]. The development of green consumer products is governed by conventional considerations such as cost reduction and performance enhancement that undoubtedly remain relevant to manufacturers but also by factors such as government regulation and spending, pressure from non-profit organizations and industry leaders, and consumer social awareness. These forces have become increasingly important in driving a more proactive and green approach to replacing problematic compounds.

The first step on the road to developing green plasticizers was the research that established the toxicity of DEHP and its metabolites [13,14,16]. This was followed by many studies on exposure that demonstrated the ubiquity of phthalate plasticizers in the environment and led to regulations requiring the labelling or banning of DEHP in various products [4,9–12,18–21]. In response to existing and looming regulations, a number of replacement compounds were introduced to the market [35]. Non-phthalate compounds, such as BASF's Hexamoll DINCH®, Dow ECOLIBRIUM™ and HallStar Hallgreen, were released commercially, amongst others [36,37]. Data from the European PVC industry [38] suggests that DEHP was mainly replaced by other phthalate plasticizers such as di(isononyl phthalate) (DINP), di(2-propylheptyl) phthalate (DPHP), and diisodecyl phthalate (DIDP), or structurally similar compounds such as trioctyl trimellitate (TOTM)–which is essentially DEHP with an added 2-ethylhexyl ester arm, and diisononyl cyclohexane 1,2-dicarboxylate (DINCH), which is hydrogenated DINP (see Figure 3-3) [38].

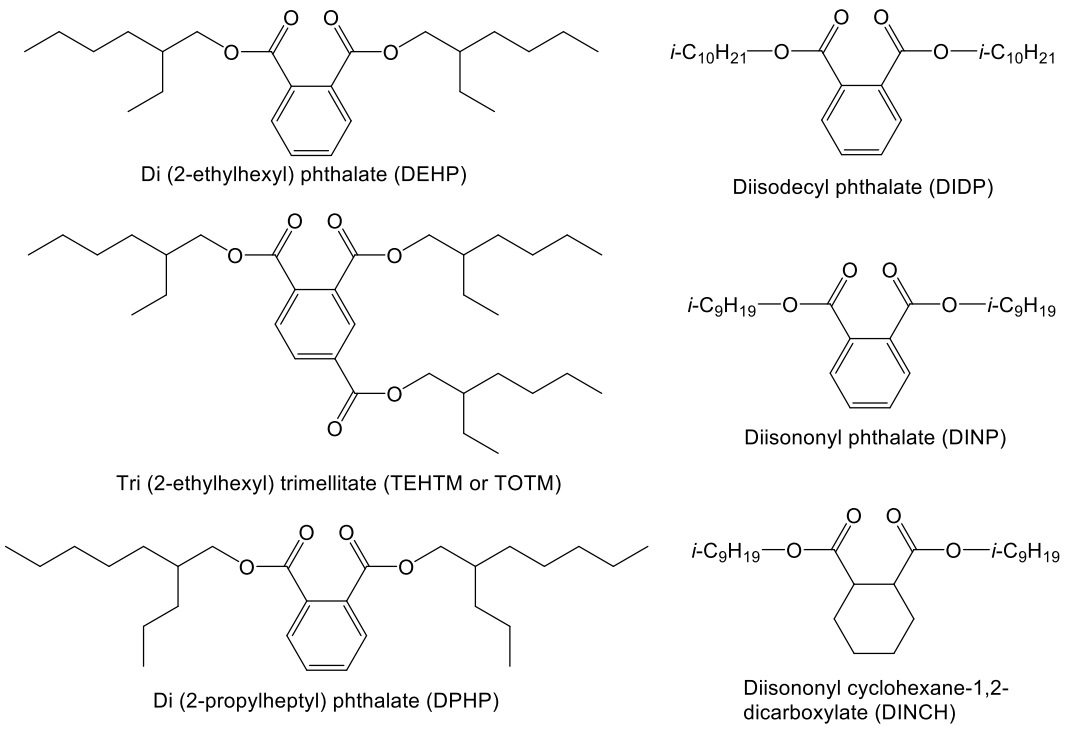

Figure 3-3. Chemical structures of four commercial phthalate plasticizers and two structurally similar compounds [39].

Still, data gaps exist in the evaluation of many of these phthalate and non-phthalate compounds. For example, there is a lack of information regarding the toxicity of and the fate of the metabolites of alternative plasticizers (which is particularly important given that many of the negative health effects associated with DEHP are known to stem from its metabolites rather than the parent compound), including toxicological endpoints such as carcinogenicity and endocrine disruption [40]. As new concerns have been raised about some of these DEHP replacements, such as DINP [11,41–45], it is increasingly important to produce truly green replacement plasticizers, with the factors advancing hazard reduction playing a bigger role in plasticizer development. Furthermore, with hundreds of commercial plasticizers available today for numerous applications, it is important to ensure that these and new plasticizers are evaluated and designed systematically and thoroughly, to avoid the 'regrettable substitution' of one problematic compound with another [35].

3.5 Designing non-toxic chemicals

Given the large variety of plasticized PVC applications, including in sensitive materials such as hospital tubing, blood bags and children's toys, ensuring the non-toxicity of green plasticizers is of utmost importance. Since several currently used phthalate plasticizers, such as DEHP and DINP, are suspected endocrine disruptors, particular attention should be paid to reproductive toxicity. This is, of course, no small task and collaboration between chemists and toxicologist can ensure that the challenge is met.

In the last decade, the availability of computing power to support complex tasks such as modelling the interactions of molecules with biological systems has increased, and, as a result, efforts are underway to use in-silico (i.e., computational) methods to predict toxicity through, for example, quantitative structure-activity relationships (QSAR) [46]. These simulations are used to inform the earliest stage of chemical design, thereby helping to reduce the amount of costly experimental testing required of compound candidates [47–49]. In support of this goal, databases have been established that contain large inventories of chemical compounds and their known toxicological properties [24,47], which can, and should, act as important resources for designers of green plasticizers. While such approaches are very useful in the early stages of molecular design, toxicity tests in living systems will ultimately be required.

In accordance with the principles of green chemistry [24], toxicity considerations should influence plasticizer development as early as in the design phase of the molecule. To ensure that any designed green plasticizers are in fact non-toxic, it is imperative to measure different toxicity end points in a variety of species, which may also be required by regulators for new products entering the market. These tests range from bacterial assays and assays on mammalian cell lines to long-term *in vivo* studies. In the following sections, examples of safer chemical design and toxicity testing of plasticizers are presented. The list of examples is not intended to be exhaustive but is illustrative of such tests.

Bacterial assays have been used to estimate microbial plasticizer toxicity [50], however it is notable that most bacterial studies involving plasticizers have focused on the biodegradability of

plasticizers after leaching from the resin [51–56]. In turn, this means that the acute microbial toxicity of plasticizers should not be overly concerning, since the bacteria are able to grow and feed on plasticizers as substrates in the biodegradation studies. Therefore, to address the question of reproductive toxicity, yeast-based assays have been developed for initial screening for estrogen agonists [57,58], but cell-based assays also exist [59]. In vitro assays using mammalian (or other) cell lines are regularly performed and these are used to asses a wide range of effects ranging from general toxicity (e.g., viability assays [60]), to whether cell growth and division is inhibited (proliferation assays), to gene expression, steroidogenesis, mitochondrial integrity, etc. [13,61–64]. It is particularly important to test the toxicity of plasticizer metabolites [63] since these can sometimes have greater adverse effects than their parent compounds [13,51]. Recent advances have also allowed for automated high-throughput screening (HTS) of chemicals, generating large in vitro databases such as ToxCast and Tox21 [65–67].

As a next step, *in vivo* studies are often performed. However, due to the labor-intensive and costly nature of *in vivo* experiments, only serious green plasticizer contenders should proceed to this testing stage. *In vivo* studies can test not only for general toxicity, but for more specific biological effects such as reproductive toxicity. This is done by conducting multi-generational experiments, examining both the parent animal and their offspring and monitoring various endpoints such as organ weight, steroid levels, sperm quality, and gene expression [45,68–72]. Numerous studies on DEHP and other phthalates demonstrate the reproductive effects of these compounds [45,68–72], yet in vivo studies for proposed alternative plasticizers are much less common. Some examples of such studies, mainly performed in rats, do exist, including the following:

- In a one-generational study, a “hyperbranched polyglycerol” plasticizer was shown not to be acutely toxic [65].
- In a two-generational study, two proposed green plasticizers, dioctyl succinate (DOS) and 1,4-butanediol dibenzoate (BDB), were both shown to exhibit no acute toxicity, and DOS also showed no reproductive toxicity, while BDB could produce “subtle but significant alterations of estrogen signaling in the adult testis” [34,66].
- In a two-generational study, commercially-available di(2-ethylhexyl) adipate (DEHA) was shown to have developmental toxicity at doses above 200 mg/kg/day as evidenced

by increased postnatal deaths, yet no reproductive toxicity (antiandrogenic effects) was found [67].

- In several one- and two-generational studies, the commercially available DINCH (hydrogenated DINP) showed no acute toxic effect [68], yet there were some indications that it might have an effect on the developing reproductive system of male rats as well as a similar effect as observed with BDB (see above) [30,34,66].
- In a one-generational study, a plasticizer candidate closely resembling DINCH ("DL9TH") was shown to be safe for adult rats, with a further claim that the compound also showed no reproductive toxicity. This was based on tests with adult animals, not a two-generational study [69].

3.6 Designing for biodegradation

Toxicological risk is defined as a function of hazard and exposure [73]. The previous discussion on toxicity concerns the first term, hazard, which relates to the intrinsic chemical toxicity of the compound. While reducing or eliminating hazard is at the core of the twelve principles of green chemistry [24], a reduction in exposure would also lead to lower overall risk. Reducing exposure can be achieved by developing biodegradable compounds or by reducing migration and leaching of the plasticizer out of the polymer blend. Therefore, a truly green plasticizer would be a compound that would not be persistent in the environment nor produce stable or pseudo-persistent metabolites during its breakdown [23,74]. Pseudo-persistent compounds enter the environment (e.g., due to continuous plastic disposal) at a greater rate than they are removed. Monitoring the kinetics of degradation and, in particular, the fate of metabolites is a key component of plasticizer biodegradation testing, due to the known effects of plasticizer metabolites such as MEHP [13,14,16]. Thus, biodegradation is a crucial component of any assessment of green plasticizers.

However, assessing the biodegradation potential of a new or existing chemical is not always straightforward, since it can be influenced by many environmental factors including temperature, atmosphere (e.g., aerobic versus anaerobic), and the presence of specific soil and water microorganisms [75]. Furthermore, results can vary depending on the use of different test

protocols. Several heuristics do exist and can be used as a starting point to design for degradability. For instance, ester groups, amides, oxygen in the form of hydroxyl, aldehyde, or carboxylic acid groups, unsubstituted linear alkyl chains, and phenyl rings are generally features that increase aerobic degradability. Conversely, strongly electron-withdrawing groups like chlorine, branched structures with a quaternary carbon, and highly substituted structures are less likely to be biodegradable [76]. As with any heuristic, exceptions to these rules can be found, however they are a useful starting point. A number of computer models also exist to predict the biodegradability of organic chemicals. Some commonly used models are Biowin, a group contribution model, and CATABOL, a knowledge-based system that can be used for predicting pathways [76].

Several varieties of tests exist to assess biodegradation experimentally. These include screening tests, simulation tests, and field tests. Screening tests are the simplest form of tests, where compounds are suspended in an aqueous solution, generally inoculated with a polyvalent inoculum (i.e., a mix of multiple microorganisms collected from local wastewater treatment plants, river water, soil, etc.). The most common screening tests are "ready" biodegradation tests and "inherent" biodegradation tests. Ready biodegradation tests provide a basic determination of whether a compound is "readily biodegradable" (and often result in an underestimation of biodegradation potential) while inherent biodegradation tests provide a fuller assessment of degradation potential by using higher inoculum concentrations, thereby creating a more favorable degradation environment [77]. Simulation tests are more sophisticated than screening tests and measure the rate and extent of biodegradation, usually in a continuous system designed to simulate real-life conditions such as anaerobic degradation occurring in a waste water treatment plant [78]. Field studies are the most complex, but least controlled, type of test which involve monitoring the degradation of the compound in a natural matrix [79]. The Organization for Economic Co-operation and Development (OECD) has defined several biodegradation tests (which fall under the categories of screening and simulation tests) based on measuring parameters such as oxygen consumption or carbon dioxide evolution as indicators of bacterial growth and compound mineralization (i.e., total breakdown of the compound to water and CO_2). The OECD tests include closed bottle tests using sludge, obtained for example from wastewater treatment plants [78,80]. While these tests are rapid and easy to conduct, they possess some drawbacks, and suggestions for their improvement have been made [81]. Importantly, these tests, along with most other screening

and simulation tests, do not call for metabolite analysis, possibly missing the presence of stable breakdown products that might go unnoticed following the standard protocol. As seen, this is particularly important when evaluating plasticizers, since commercial plasticizers, such as DEHP, have been shown to have stable metabolites (e.g., MEHP) that exhibit toxicity [13,14,16]. Since the task of monitoring metabolites can be complicated by the use activated sludge or other complex mixtures, biodegradation experiments using singe-strain cultures of common soil bacteria have also been developed, allowing for improved recovery of the hydrophobic plasticizer and metabolite molecules [51,52]. Of course, these experiments do not fully reflect degradation under natural conditions, however they can be particularly useful for comparisons between plasticizer groups, and for metabolite analyses [51,54].

In order to design plasticizers for biodegradability, a common strategy is to examine the chemical structures of commercially-used plasticizers, seek to understand which functional groups cause slow biodegradation kinetics or toxicological implications, and then use this knowledge to re-design the molecule to circumvent these problematic properties, while ideally retaining plasticizing effectiveness. For example, the biodegradation of succinate, maleate, fumarate, adipate and dibenzoate diesters has previously been investigated [51–54,82–87]. In a first step to developing alternative biodegradable plasticizers, several common soil bacteria and yeasts were tested for their biodegradation potential, and *Rhodococcus rhodocrous* was identified as the most promising micro-organism to use in kinetic testing due to its ability to grow on hydrophobic substrates [51,52]. In the next step, the biodegradation pathway for DEHP was determined (see Figure 3-4). Briefly, DEHP biodegradation yields the following metabolites: MEHP, phthalic acid, and 2-ethyl hexanol, which is subsequently oxidized to 2-ethyl hexanoic acid [86–88]. Both MEHP and 2-ethylhexanoic acid have been shown to be persistent in the environment [89–91].

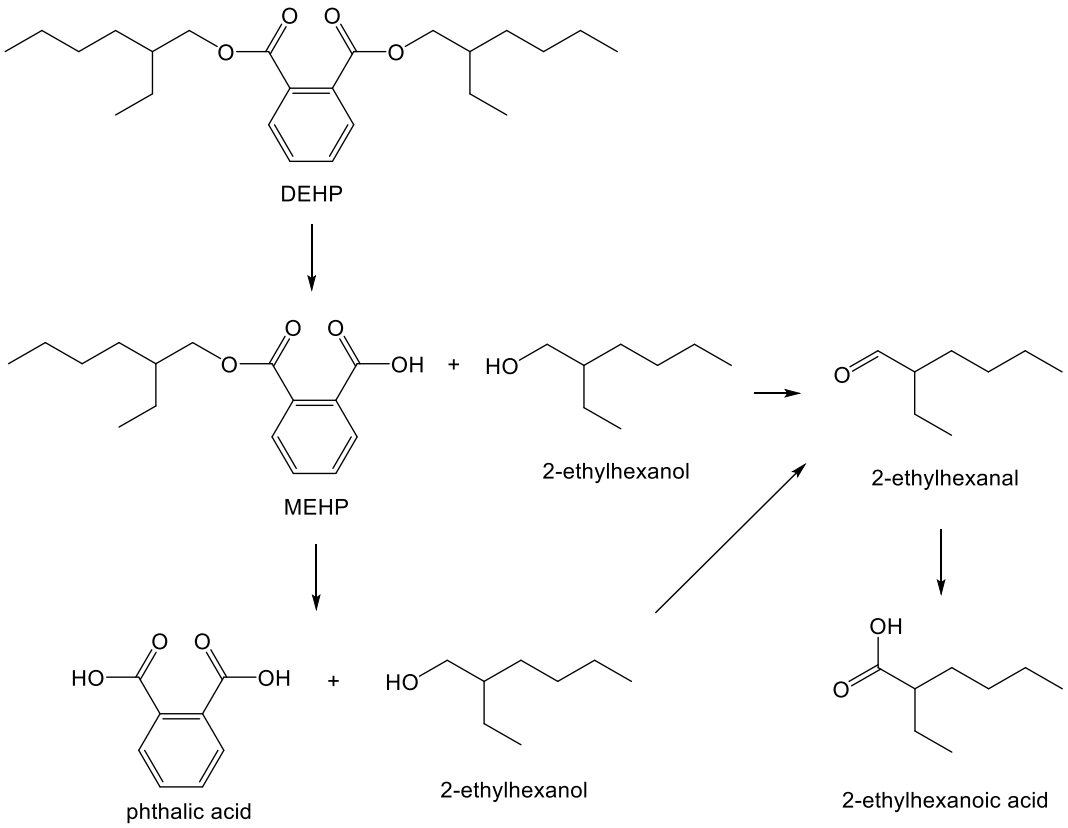

Figure 3-4. Biodegradation of di(2-ethylhexyl) phthalate (DEHP) through the action of esterases in microbes. Reprinted by permission from Springer Nature: Springer. Applied Microbiology and Biotechnology. Leaching of the plasticizer di(2-ethylhexyl)phthalate (DEHP) from plastic containers and the question of human exposure, Erythropel et. al., copyright 2014.

Several candidate green plasticizers were designed based on these biodegradation pathways to avoid producing breakdown structures known to be toxic or persistent (see Figure 3-5). These included diesters based on succinic acid, maleic acid, and fumaric acid, which resemble the phthalate structure, esterified with linear alcohols to avoid the buildup of 2-ethylhexanoic acid following biodegradation of the parent compound [54,84,85,92]. The compounds were found to be effective plasticizers and biodegradation experiments revealed that the geometry of the central structure of the molecules played an important role in how quickly the compounds were degraded. The saturated succinate esters that can rotate around the central bond were more rapidly biodegraded by *R. rhodocrous* than the unsaturated maleates and fumarates (see Figure 3-5). Following similar steps, the dibenzoate plasticizer 1,5-propanediol dibenzoate (1,5-PDB) was designed with the intent that it would biodegrade much more quickly than the commercially-

available diethylene glycol dibenzoate (DEGDB) by the simple replacement of an oxygen atom of the ether function in DEGDB with a carbon atom to form 1,5-PDB (see Figure 3-5). Both compounds also exhibited similar plasticizing effectiveness in PVC [93].

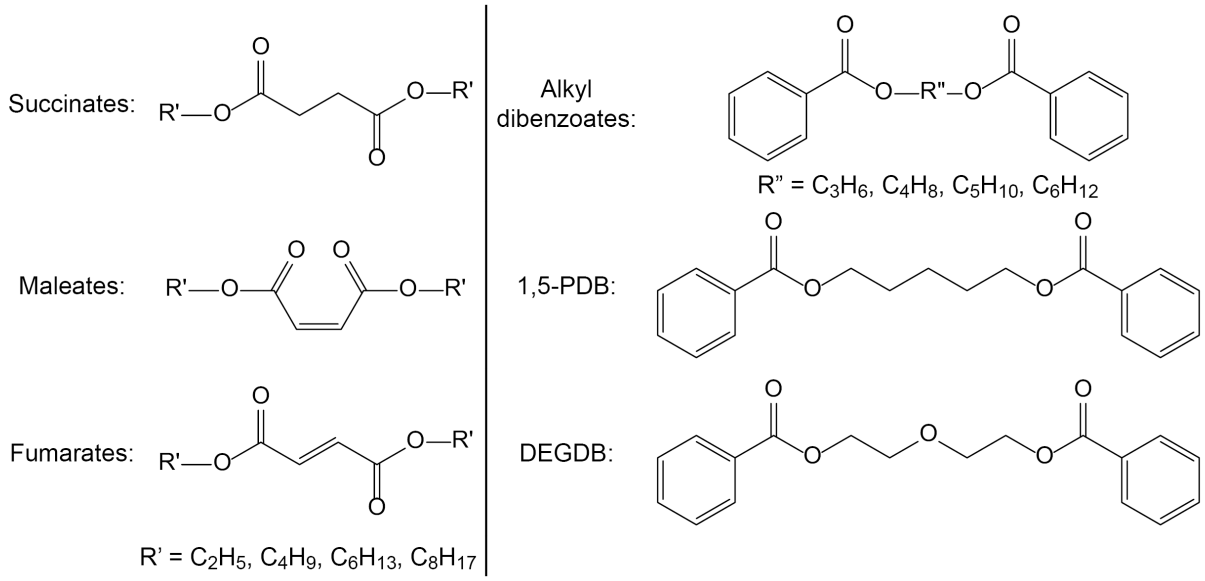

Figure 3-5. Candidate green plasticizer families: succinates, maleates, fumarates (all with unbranched side chains), and linear alkyl dibenzoates. The only difference between the dibenzoate 1,5-PDB and the commercial diethylene glycol dibenzoate (DEGDB) is the molecule in the center of the diol linker: carbon (in the case of 1,5-PDB) or oxygen (in the case of DEGDB). 1,5-PDB is 1,5-pentanediol dibenzoate, DEGDB is diethylene glycol dibenzoate.

The biodegradability of candidate green plasticizers is still not a routine assessment. Consequently, few papers were found in the published literature on the topic. The focus of the limited number of papers that are available is often on the degradation behavior of the polymer blends (for example plasticizers blended with biodegradable polymers such as PHA or PLA) rather than the plasticizer itself. The lack of biodegradation work on plasticizers intended for use in PVC is a significant shortcoming since the development of biodegradable plasticizers could drastically reduce the environmental impact of this class of additives. A few examples of biodegradation studies for candidate plasticizers and their metabolites that can be used as guidelines for future testing include the following:

- Biodegradation testing of poly(caprolactone)-based plasticizers by *R. rhodochrous*, which demonstrated rapid biodegradability and no build-up of stable metabolites [92].
- Biodegradation testing of various dibenzoate plasticizers similar to 1,5-PDB, both in batch conditions and in a continuous bioreactor. While biodegradability was generally found to be good, the degradation of some compounds resulted in a build-up of toxic metabolites [44,80,81,91].
- Biodegradation testing of DEHP and 15 diesters of varying side chain length based on succinic acid, maleic acid, and fumaric acid by *R. rhodocrous*, as discussed above. The experiments revealed the influence of both central structure as well as side chain length and its branching on biodegradation kinetics [45,82,83].

3.7 Designing for permanence

The concept of risk being a function of hazard and of exposure is also important when considering plasticizer leaching. Exposure can be reduced by increasing the permanence of plasticizers within blends, thereby limiting their leaching potential. This addresses the issue of acute exposure, for example from hospital tubing or blood bags, and has less bearing on chronic exposure since the plasticizer will still eventually leach from the blend, due to the fact that no chemical bond exists between the plasticizer and PVC. Even at very low leaching rates, plasticizers can eventually migrate from the blend into the environment, as observed in landfill sites or in natural environments where plastic waste is present over the long term [4,94]. Whether this leaching occurs over the timescale of months, years or decades, plasticizers will ultimately enter the environment and, if they are not readily biodegradable, their persistence and bioaccumulation (as seen for DEHP and other phthalates) will become an environmental problem [4,95]. Additionally, excessive leaching is also detrimental to the durability of the plastic product. The minimization of leaching is important both for the sake of the product performance and its safe use. Therefore, lowered or suppressed leaching rates are favorable to reduce acute human exposure, to minimize the scope of environmental contamination and to improve performance and are, therefore, important considerations in green plasticizer design.

Plasticizer leaching rates are closely tied to the compatibility and miscibility of the plasticizer within the PVC blend. Immiscible plasticizers will blend poorly with PVC and be at higher risk of leaching. Yet plasticizers that demonstrate good permanence often do not provide an adequate plasticization effect (see Figure 3-1). Striking a balance is important when designing a plasticizer with good plasticizer effectiveness, yet low rates of leaching. More detailed examination of the complex relationship between plasticizer compatibility and leaching rates is available [3,25,96]. Additionally, the molecular weight of plasticizers seems also to have an effect on leaching, as evidenced by decreased leaching rates into water with increasing molecular weight for several ester-based plasticizers [5,97]; however, this could also be related to the low water solubilities of these higher molecular weight plasticizers.

Given this complexity, the experimental determination of plasticizer leaching rates is required to ensure both good plasticizing performance and low acute exposure. ASTM D-1239 outlines a standard testing method [98] to test for leaching into a variety of matrices including water, soapy water (1% soap), cottonseed oil, mineral oil, kerosene, and ethanol (50% in water) to accommodate for a variety of environments into which leaching can occur. Leaching rates of plasticizers into aqueous media is of particular importance since this is the most representative of actual plasticizer leaching into the environment, and many studies of proposed alternative plasticizers have focused on this. While not an exhaustive list, examples of leaching studies include the following:

- Leaching of the commercial plasticizers DEHP, DINCH, TOTM/TEHTM and di(2-ehtlyhexyl) terephthalate (DEHT) from hospital tubing into 50% ethanol in water [99].
- Leaching of several commercial plasticizers including phthalates and DEHA found in food packaging into aqueous acetic acid (3%), distilled water and ethanol (15% in water) [100].
- Leaching of alternative dibenzoate, succinate, maleate, and fumarate-based plasticizers from PVC disks at 29 wt % loading into reverse-osmosis water [4].
- Leaching of oligomeric ε-caprolactone in PVC disks at 39 wt % loading in *n*-hexane [92].
- Leaching of oligomeric poly(butylene adipate) in PVC films at 40 wt % loading into water [97].

- Leaching of curcumin-derived plasticizer candidates at 5, 15, 25, and 35 wt % in PVC into water and *n*-hexane [101].
- Leaching of tetra-esters based on pentaerythritol at several concentrations in PVC into distilled water, olive oil, ethanol (10% in water), acetic acid (30% in water), and petroleum ether [102].
- Leaching of DEHP from hemodialysis tubing, with and without polyurethane coating, into newborn calf serum [103].

Several techniques have been explored to avoid leaching, including internal plasticization [99–101], coating of polymer surfaces [102], and plasma surface treatment [103,104] to create a barrier through which plasticizer molecules cannot penetrate. Most of these techniques require further processing of the plasticized material, thereby making the product more expensive, more complicated to produce, and sometimes resulting in a decrease in plasticizer effectiveness [105].

3.8 Green production

While this review has focused largely on the experimental assessment and design of green plasticizers, the chemical synthesis and scale-up of the production of these compounds should also be considered, though there is a lack of literature in this area. In order for a plasticizer to be deemed green, it is not sufficient to examine only the hazards associated with the compound itself, rather one must also consider how the compound is produced, including feedstock sourcing and synthesis methods.

Once a candidate plasticizer has been assessed and deemed suitable in terms of its performance, toxicity, biodegradation and leaching, it is important to scrutinize the synthetic techniques that are employed in its production using green chemistry principles. A number of these principles concern chemical synthesis and can be applied to plasticizers such as the use of safer solvents and auxiliaries, less hazardous chemical synthesis, waste prevention, atom economy, catalysis, and reduced number of derivatives, but also energy efficiency and real-time analysis for pollution prevention [23]. However, there is a lack of published work on the topic of green synthetic

techniques applied specifically to plasticizer production. Nevertheless, the aforementioned principles can be applied as a starting point for new research.

The use of renewable feedstocks for plasticizer production rather than the use of petroleum-based feedstocks should be considered when designing a truly green plasticizer. The most commonly used class of plasticizers are esters, which are made up of organic acids esterified with alcohols, of which there is increasing renewable supply available. For example, a report by the U.S. Department of Energy Biomass program identified a range of "building block" compounds including small organic acids and alcohols, that are accessible from renewable sources [106]. Starting materials include starches, sugars, and wood components such as cellulose, hemicellulose, and lignin, as well as oils and proteins [106]. One compound that has garnered considerable interest as a renewable feedstock is succinic acid, which is already produced by fermentation at an industrial scale and can be used as a good platform chemical as-is, or by its further reduction to 1,4-butanediol [107,108]. Plasticizers based on succinic acid have been explored in several recent studies [85,109].

Special consideration should be given to using renewable materials that do not displace food production in order to avoid important social and economic repercussions [110]. For instance, renewable materials that are derived from agro-industrial residues and from non-edible biomass can be used as chemical feedstock for plasticizer synthesis [111]. An analysis of renewably sourced materials by LCA procedures is generally recommended. It is worth noting that one of the key limitations of this discussion is that it has focused exclusively only on plasticizer hazards, and begs the follow-up question 'how green is your product?'. Since most plasticizers are used with PVC, a non-renewable and petroleum-sourced polymer, there is much work that still needs to be done in the realm of improving vinyl chemistry to make it more sustainable.

3.9 Conclusion

Considerable care should be taken when designing green plasticizers. The "design" stage itself cannot be stressed enough as it will have a huge bearing on the properties of the final product, and

only a well-designed plasticizer can strive to meet the highest standards that are needed for wide-ranging, and often sensitive, PVC applications. The designer of a green plasticizer should be concerned not only with the effectiveness of the compound in plasticizing PVC, although this remains an indisputable prerequisite, but also with its behavior once in contact the human body and the environment, throughout its entire life cycle. While the term 'green' is often used loosely to characterize compounds that have been improved with respect to one, or a few, of the criteria discussed in this review, in order for a compound to be truly green it must be evaluated broadly against many different principles. In the case of green plasticizers for PVC, we suggest endeavoring to create compounds that do not possess negative health consequences, form harmful metabolites, or persist in the environment. Beyond these three key parameters, improving synthetic steps in accordance with the principles of green chemistry and utilizing renewable feedstocks when available is also important. As a guiding framework, the concepts of green chemistry are very suitable for confronting the task at hand. It is particularly important to integrate knowledge and expertise from different disciplines in order to address the complex and varied concerns of green design. In order to not repeat the mistakes of the past, it is crucial for any plasticizer designer to address these issues together and often in parallel, rather than separately, for only in this way can a genuinely safe, and thereby green, plasticizer be designed in an efficient manner.

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4

Additives to prevent the formation of surface defects during poly(vinyl chloride) calendering[2]

4.1 Preface

This chapter was published in 2021 as an article in the journal *Polymer Engineering and Science* and, together with the findings reported in Chapter 5, formed the basis of a provisional patent that was filed in 2020 (United States Provisional Patent 63/126,937). The green chemistry considerations outlined previously in Chapter 3 were applied in the early design stages of producing the additives investigated in this study. Specifically, the combination of poly(caprolactones) (PCLs) with succinic acid and heptanol to make triheptylsuccinate-terminated poly(caprolactone) (PCL_{540}-Succ-C7)[3] was driven by previous work that had established the biodegradability of these building blocks, their miscibility with PVC, and their toxicological safety. The decision to use macromolecular PCLs as the core of the new oligomeric additives was intended to decrease migration.

During the initial screening of PCL_{540}-Succ-C7 for compatibility with PVC, it was observed that the calendered films that were produced had unusually smooth surface finish compared to films produced with commercial blend formulations. This study investigated the phenomenon of defect removal and the role of rheological properties in eliminating these defects. The findings were

[2] Reproduced with permission from John Wiley and Sons and Jamarani R, Halloran MW, Panchal K, Garcia-Valdez O, Mafi R, Nicell JA, Leask RL, Maric M. Additives to prevent the formation of surface defects during poly(vinyl chloride) calendering. *Polym Eng Sci.* 2021; 61(4),1209–1219. © 2021 Society of Plastics Engineers

[3] All molecular weights reported in Chapter 4 have units of g/mol

expanded to develop an entire family of additives that could all remove ‘gas check’ surface defects. This represented the first reported use of chemical additives to eliminate gas check defects. With hundreds of commercial additives and plasticizers on the market for manufacturers to choose from, establishing a new and important niche function for these additives is an important step towards their eventual commercialization and adoption by industry. The findings presented in this chapter complement the work in Chapter 5 that establishes the efficacy of these additives as plasticizers.

4.2 Abstract

Gas checks are visible fleck-shaped defects that occur on the surface of poly(vinyl chloride) (PVC) films during industrial calendering. Films containing these surface defects often do not meet minimum product specifications and therefore must be disposed of or recycled, resulting in increased cost and material waste. Currently, gas checks are controlled by keeping film gauge low and through trial-and-error modifications of processing parameters by calender operators. In this work, our group developed a series of chemical additives that can be blended with PVC to prevent the formation of gas check defects. We found that a series of poly(caprolactone) (PCL)-based compounds with diester linkers and alkyl chain cappers were all effective at preventing the formation of gas checks during calendering, with additive concentrations as low as 8 phr producing films with no gas checks. We found that the blends produced with our additives had higher melt viscosities than those produced with additives that do not remove gas checks, suggesting that viscosity plays an important role in preventing gas check defects.

4.3 Introduction

Calendering is an industrial process in which a polymer melt is passed through a system of heated rolls (i.e., the calender), producing a continuous film with controllable thickness [1]. This technique is commonly used in the production of poly(vinyl chloride) (PVC) films [2], which are used in a wide variety of applications including packaging, construction, and automotive manufacturing [3]. Example products made with PVC films include seepage barriers such as

swimming pool and water reservoir liners, automotive seat coverings, hospital blood and intravenous (I.V.) bags, roofing materials, and meat packaging films among many others [4, 5]. The global demand for PVC continues to grow yearly and the global market is projected to reach USD 72.0 billion by 2025, with almost a quarter of this market share belonging to films and sheets [6].

Calendered PVC films can contain a number of surface defects that reduce overall film quality, resulting in inferior products that are often rejected and discarded during the manufacturing process. Some categories of calendered PVC sheet defects include dimensional faults (e.g., variations in thickness leading to profile irregularity), structural defects (e.g., low tensile strength, excessive uniaxial orientation), and defects or faults manifested in appearance [4]. Within the latter category of faults that are manifested by their physical appearance, a number of known defects include “fish-eyes”, “crow foot marks”, and “sharkskin” [7]. This work focuses on a different visual defect within this category, pictured in Figure 4-1. These defects have been referred to by a variety of different names including specks [8], gas entrapments [9], air bubbles, air inclusions [10], and flecking [4], among others. In this paper we refer to these defects as ‘gas checks’, a name used in the plastics processing industry due to the particular shape of the defect. They are thought to be caused by air entrapped in the calender bank, which is the area of polymer-buildup just upstream of the narrow gap separating consecutive calender rolls, thereby producing blemishes on the surface of the film. Gas checks can occur in different sizes and appear elongated in the direction of calender flow. These visible defects frequently interfere with PVC sheet processing and can cause local reductions in film mechanical properties at the defect site, sometimes even resulting in perforation of the films [10]. In addition, for many PVC film applications, such as furniture covers, automotive trim, and swimming pool liners, the appearance and surface finish of the films are crucial for their marketability. The presence of gas checks renders the films unusable and causes delays and inefficiencies in production as manufacturers must recycle or dispose of films containing these defects. Despite the prevalence of gas checks in calendered film products throughout the plastic manufacturing industry, the mechanisms of gas check evolution during film production is unknown. Therefore, in order to produce high quality films without gas checks and increase overall process efficiency while reducing waste and costs, it is essential to gain a broader understanding of this phenomenon so that measures can be taken to minimize or eliminate them.

Figure 4-1. Gas check defect on a PVC film.

In the very few publications that exist on controlling the formation of gas checks during calendering [9-12], there have been no studies on the use of additives to prevent gas checks. The number of gas checks in a film has previously been related to the pressure in the calender bank, which can be controlled by the nip opening (i.e., the distance between two consecutive rollers, which determines the final gauge of the film) and calender speed. It has been hypothesized that operating under conditions of smaller nip distances and higher calender speeds, and using polymer blends of higher viscosities would reduce or eliminate gas checks in the final film [10, 11]. Therefore, to avoid the formation of gas checks, current industrial practice requires calender operators to manually manipulate processing parameters such as roll speed and nip distance, and yet even the most experienced calender operators still produce films containing gas checks. Additionally, the downside of manipulating processing parameters to obtain films with satisfactory properties is that it requires operators to work within certain limits that will affect the properties of the final product. For example, it is well known that gas check defects are particularly significant when producing higher gauge, i.e., higher thickness, films [10]. Using a smaller calender nip distance is proven to reduce the occurrence of gas checks, however it also results in the production of films with a lower thickness. Therefore, there is currently an upper limit to the thickness of film that can be produced industrially through calendering, with industrial calenders typically only being used to produce films below ~0.01 to 0.02 in (0.25 to 0.5 mm) in thickness [12, 13]. This has led to work-arounds such as ‘plying-up’ multiple layers of low-gauge films when the

production of a thicker film is required. In these cases, two or more smaller gauge films must be calendered separately and then laminated to form a defect-free, high-gauge film. Being able to calender high-gauge film in a single step would increase the efficiency of film production and improve profitability.

Our research group has previously worked extensively on the development of alternative 'green' plasticizers for PVC to replace environmentally-problematic phthalate plasticizers [14-21]. Poly(ε-caprolactone) (PCL) and succinate-based compounds have both shown good compatibility with PVC [22-24]. Over the course of this work, while screening a new PCL-based oligomeric additive for compatibility with PVC film formulations, we observed that the addition of this compound, even in very small concentrations, prevented the formation of gas checks entirely in calendered films produced at the lab-scale. Given the important impact that these surface defects have on the calendering industry, this observation motivated the current study to explore how gas check formation can be avoided in PVC films through the use of additives.

In this work, we report the development of a series of chemical additives that can be used in PVC formulations to prevent the formation of gas checks during the calendering process, without having to alter processing parameters. We investigated the effect of additive concentration and molecular structure (including molecular weight, diacid group type, alkyl chain length, and branching) on the formation of gas checks. We sought to explain the mechanism of gas check removal by investigating the effects of viscosity and surface tension of the individual liquid additives and overall polymer melts. To the best of our knowledge, this is the first reported study on controlling gas check formation through means of a chemical additive, rather than through modifying calendering process parameters.

4.4 Experimental

4.4.1 Materials

Poly(ε-caprolactone) (PCL) triol (M_n = 300, 540) (99%) was purchased from Scientific Polymer Products Inc., NY, USA. PCL triol (M_n = 900) (99%), PCL diol (M_n = 530) (99%), fumaric acid (99%), oxalic acid (98%), adipic acid (99%), 1-butanol (99%), 1-decanol (98%), *n*-heptanol (99%), and succinic acid (99%) were purchased from Sigma Aldrich, Missouri, USA. Sulfuric acid (96%) was purchased from Fisher Scientific, Ottawa, Canada. Diheptyl succinate (DHPS) was synthesized in accordance with the method previously described by our group [24]. Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), antimony oxide Hi-Tint (99.68%), silica (99%), stearic acid (99%), barium/zinc stabilizer (1.046 specific gravity at 20°C), and acrylic processing aid (99.8%) were supplied by Canadian General-Tower Limited (CGT Ltd.). All chemicals and reagents were used as received without further purification.

4.4.2 Synthesis of PCL-based additives

The syntheses of the star-shaped PCL analogs, listed in Table 4-1, were performed via two-step reaction in a single flask. In the first step, PCL triol (1 stoichiometric equivalent) was massed directly into a three-necked round-bottom flask followed by the diacid reagent (3 equiv.). Benzene was then added to the flask, and the mixture was stirred at room temperature for 5 minutes. Catalytic amounts of sulfuric acid (0.15 equiv.) were then added dropwise to the reaction mixture. The reaction flask was fitted with a Dean-Stark apparatus (to collect water) and a condenser, then placed in a pre-heated oil bath at 100 °C. After two hours, the mixture was cooled to room temperature. In the second step, the alcohol reagent (3 equiv.) was added to the same flask equipped with the Dean-Stark apparatus and condenser, and the mixture was re-heated to 100 °C in an oil bath. After two hours, the flask was cooled to room temperature. The mixture was then concentrated using a rotary evaporator to remove the benzene and obtain the star-shaped PCL analogs as viscous oils. The code names for the PCL analogs listed in Table 4-1 will be used for all subsequent discussion.

In the first step of the synthesis of the linear PCL compound, listed in Table 4-1, PCL diol (M_n=530, 1 stoichiometric equivalent) was massed directly into a three-necked round-bottom flask followed by the diacid reagent (2 equiv.) and catalytic amounts of sulfuric acid (0.15 equiv.), and subjected to the same conditions described above. In the second step, heptanol (2 equiv.) was added to the same flask and subjected to the same reaction conditions described above. Linear-PCL_{530}-Succ-C7 was obtained as a viscous oil.

Table 4-1. Poly(caprolactone) (PCL)-based additives.

PCL-based additive name	Code	# of PCL branches	M_n (g mol^{-1})
Poly(caprolactone) triol	PCL_{540}-triol	3	540
Triacetate-terminated poly(caprolactone)	PCL_{540}-Acet	3	666
Triheptylsuccinate-terminated poly(caprolactone)	PCL_{300}-Succ-C7	3	897
	PCL_{540}-Succ-C7	3	1137
	PCL_{900}-Succ-C7	3	1497
Tributylsuccinate-terminated poly(caprolactone)	PCL_{540}-Succ-C4	3	1009
Tridecylsuccinate-terminated poly(caprolactone)	PCL_{540}-Succ-C10	3	1261
Triheptyloxalate-terminated poly(caprolactone)	PCL_{540}-Oxa-C7	3	813
Trihepylfumarate-terminated poly(caprolactone)	PCL_{540}-Fum-C7	3	891
Triheptyladipate-terminated poly(caprolactone)	PCL_{540}-Adi-C7	3	981
Diheptylsuccinate-terminated poly(caprolactone)	Linear-PCL_{530}-Succ-C7	1	928

4.4.3 Film production

All blend components were weighed according to the formulations reported in Table 4-2, to a total mass of 300 g, and manually premixed in a bowl. Every blend contained 100 parts per hundred resin (phr) PVC 70K suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid. ‘phr’ is a way of measuring additive concentration in relation to the total amount of polymer resin (in this case PVC) by expressing the weight of any component relative to 100 parts per weight PVC resin. The pre-mixture was blended using a Hartek two-roll mill HTR-300 (d=120 mm, T=160°C, 45 rpm). The

mill was pre-heated for a minimum of 1 hour after which time the pre-mixture was added to the mill. Mixing was performed for 7 minutes, starting from the time of film formation on the mill rolls. The milled film was cut into four pieces, each of which was fed separately into the lab-scale calender (d=180 mm, T=160-170°C, P=45 psi hps, 50 rpm). The calender nip distance was set to achieve a film gauge of 0.4 mm +/- 0.05 mm. Each of the four pieces was mixed for 1 minute on the calender before being removed. Each blend resulted in 3 or 4 sheets of film.

Table 4-2. Formulations for PVC film blends prepared in this study. 'Gas check additive' represents the compounds that were tested for their ability to prevent the formation of gas checks. DINP was used as the primary plasticizer in all blends other than those in which the gas check additives were added at 55 phr.

Blend Formulations					
DINP 55	**DINP 65**	**4 phr**	**8 phr**	**10 phr**	**55 phr**
55 phr DINP	65 phr DINP	55 phr DINP	55 phr DINP	55 phr DINP	---
---	---	4 phr gas check additive	8 phr gas check additive	10 phr gas check additive	55 phr gas check additive

Note: Every blend contains: 100 phr PVC 70K suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid.

4.4.4 Counting gas checks

A 7 cm × 7 cm grid was used to count gas checks on each film. The gas checks within the grid were manually counted from three regions on each film: the top left corner, the center, and the bottom right corner of the film. The number of gas checks counted in each area was then averaged to calculate the number of gas checks per film. This was repeated for all 4 films. The average number of gas checks was normalized per m^2 of film.

4.4.5 Rheology

Liquid additive viscosities were measured by steady-shear tests using a strain-controlled rheometer (Anton Paar MCR 302, Anton Paar Canada, St-Laurent, Quebec, Canada) with parallel plate

geometry (25 mm plate diameter) with a CTD 450 convection oven and double gap geometry for low-viscosity samples. Shear rate was increased logarithmically from 0.1 to 100 s^{-1} at 25°C (±0.3°C).

Polymer melts were characterized by measuring storage modulus (G′), loss modulus (G″), damping factor (tanδ), and complex viscosity (η*), through dynamic oscillatory tests using the same rheometer described above. Parallel plate geometry (d=25 mm) and a CTD 450 convection oven were used, operated under nitrogen to prevent PVC degradation. A strain amplitude (5%) within the linear viscoelastic range was applied over a frequency range of 0.01 to 100 $rad \cdot s^{-1}$ at 170°C. Anton Paar RheoCompass™ software (version 1.23, 403-Release, Anton Paar Germany, Ostfildern, Germany) was used for the analysis of all rheological results.

The PVC disks used for rheological testing were made using a hot press (Carver Manual Hydraulic Press with Watlow Temperature Controllers, Carver Inc., Wabash, IN, USA) and a corresponding mold. The calendered films were punched into 25 mm diameter circles. A stack of 8 film cut-outs was pressed into circular disks of approximately 1 mm thickness and 25 mm diameter at 165°C (329°F). The samples were pressed at 5 tons of clamping force for 1 minute, then at 20 tons of clamping force for 4 minutes. Samples were cooled using circulating cold water at 20 tons of force, until they reached room temperature. The disks were removed from the mold and placed in a desiccator (filled with Drierite™ obtained from Fisher Scientific, Ottawa, Canada) for a minimum of 48 hours before the evaluation of their rheological properties.

4.4.6 Surface tension

The interfacial tension between the liquid additives and air was measured using the pendant drop method [25]. A typical pendant drop apparatus was developed for this purpose, similar to previously reported apparatuses [26-28], and used to obtain the profile of the pendant drop. The apparatus consists of an illuminated experimental chamber with a syringe insert, a viewing system consisting of a camera and lens, and an attached computer used for data acquisition. The software used to analyze the drop profile was Image J (version 1.52q) with the open source Pendant Drop plug-in [29].

The pendant drop method requires the sample density to be known. A 25 mL specific gravity bottle pycnometer was used to measure unknown liquid densities. Three measurements were taken for each liquid, and an average value was used.

4.4.7 Statistics

To establish whether the additives had a significant effect on gas check removal, GraphPad Prism version 8.0 was used to perform a one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison post hoc test (α=0.05) to evaluate whether there were any significant differences in gas check removal between DINP, DHPS, PCL_{540}-Acet, and PCL_{540}-Succ-C7. Similarly, to investigate the effect of additive concentration on gas check removal, a one-way ANOVA was used followed by Tukey's multiple comparison test (α=0.05).

4.5 Results and discussion

4.5.1 Preventing gas check formation using additives

During the screening of our PCL-based additives for their compatibility with PVC, it was observed that blends containing PCL_{540}-Succ-C7 resulted in the production of calendered films with remarkably few surface defects, as shown in Figure 4-2.

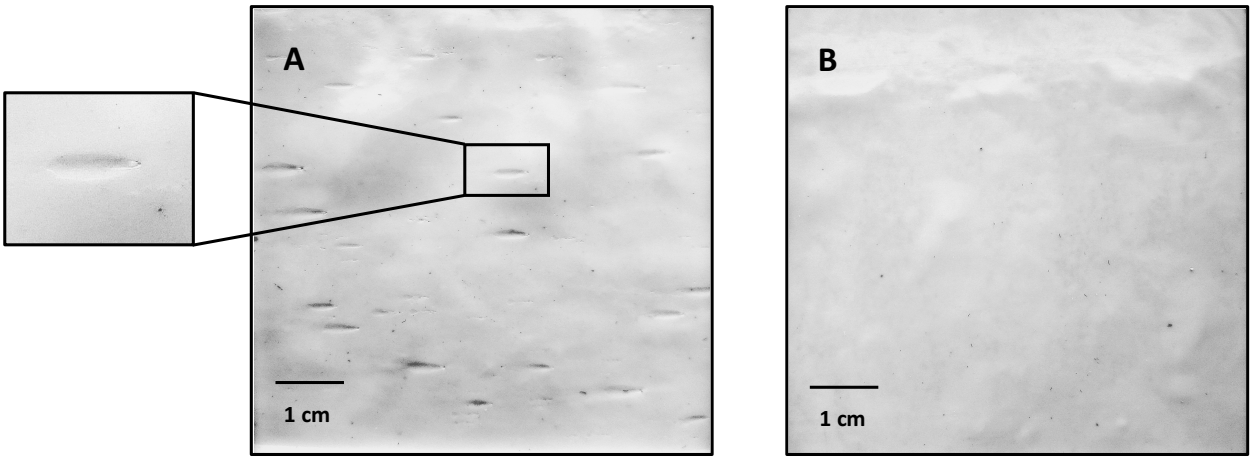
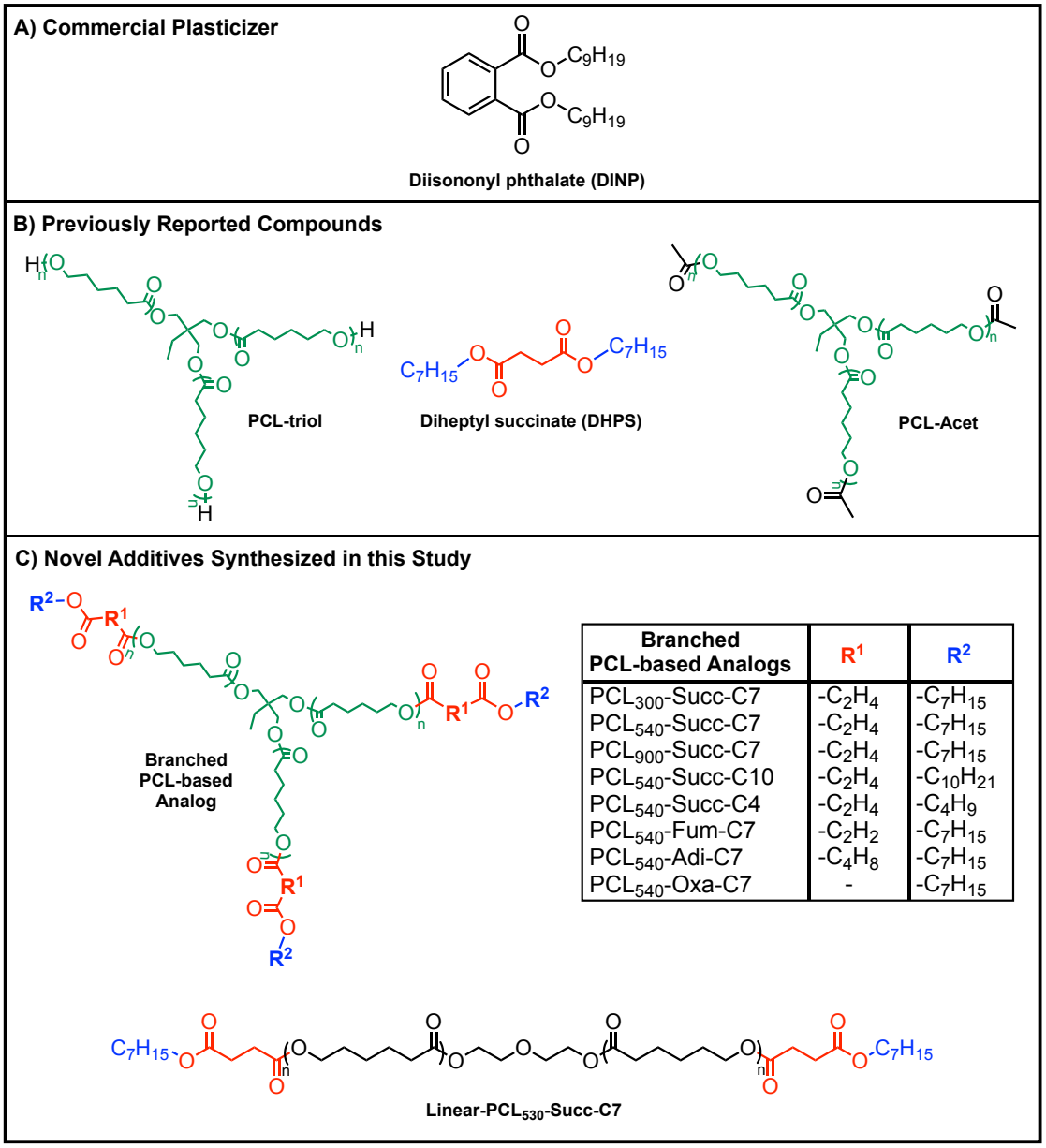


Figure 4-2. Calendered PVC film (A) with gas check defects (no additive used, 55 phr DINP plasticizer) and (B) without gas check defects through use of PCL_{540}-Succ-C7 as an additive at 10 phr (55 phr DINP plasticizer).

In fact, it was found that using PCL_{540}-Succ-C7 in PVC blends at 55 phr (32.5wt%) resulted in the production of calendered films with no gas checks (n=3). In contrast, the use of DINP, which is the current industrial plasticizing standard, in PVC blends at 55 phr resulted in films with an average of 5115 gas checks per m^2 of film (n=6). The chemical structures of PCL_{540}-Succ-C7 and DINP are shown in Figure 4-3.



Branched PCL-based Analogs	R^1	R^2
PCL_{300}-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL_{540}-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL_{900}-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL_{540}-Succ-C10	$-C_2H_4$	$-C_{10}H_{21}$
PCL_{540}-Succ-C4	$-C_2H_4$	$-C_4H_9$
PCL_{540}-Fum-C7	$-C_2H_2$	$-C_7H_{15}$
PCL_{540}-Adi-C7	$-C_4H_8$	$-C_7H_{15}$
PCL_{540}-Oxa-C7	-	$-C_7H_{15}$

Figure 4-3. Chemical structures of compounds investigated for their ability to remove gas checks: (A) current industrial standard for film plasticization (DINP), (B) previously reported compounds used as 'building blocks' for our novel additives, (C) novel PCL-based analogs synthesized in this study.

After the initial observations that our parent molecule eliminated gas check surface defects, we sought to investigate which of the molecular components or 'building blocks' that make up PCL_{540}-Succ-C7 were responsible for this effect. Thus, two separate PVC blends were prepared: one containing diheptyl succinate (DHPS) and one with PCL_{540}-triol, both at 55 phr. The molecular structures of PCL_{540}-Succ-C7 (parent compound), as well as DHPS and PCL_{540}-triol (building blocks) are shown in Figure 4-3b. A one-way ANOVA test followed by a Tukey post-test was performed to determine whether there was any statistically significant change in the number of gas checks for blends made with the building blocks compared to the parent compound. It can be seen in Figure 4-4 that DHPS, one of the building blocks of PCL_{540}-Succ-C7, was not able to prevent the formation of gas checks when blended with PVC at 55 phr, with an average of 6241 gas checks per m^2 of film, which is significantly higher than PCL_{540}-Succ-C7 ($P<0.05$), but showed no decrease compared to the DINP control ($P>0.05$). PCL_{540}-triol, on the other hand, was found to be incompatible with PVC which was evidenced by several observations including: (i) significantly delayed film formation rate on the mill compared to other blends; (ii) extremely poor quality of the final film, which was very brittle, with many cracks and holes, and exhibited similar physical properties to unplasticized PVC; (iii) phase separation, i.e., the material coming off the mill was covered in a thick oily layer, further suggesting the immiscibility of PCL_{540}-triol with PVC. Therefore, we added acetate groups to cap the ends of the PCL_{540}-triol, producing PCL_{540}-Acet, a known compound that is compatible with PVC [23, 30]. Due to the similarity in structure between PCL_{540}-Acet and PCL_{540}-triol, PCL_{540}-Acet was used as a compatible substitute to investigate the contribution of the PCL_{540}-triol group to gas check removal. Upon blending PCL_{540}-Acet with PVC at 55 phr, it was observed that film formation occurred during regular time frames, resulted in no oily residue on the film, and the film was flexible, thereby confirming its compatibility with PVC, as reported by Choi et al. [30]. However, similarly to DHPS, PCL_{540}-Acet did not remove gas checks, producing films with an average of 6122 gas checks per m^2 of film (Figure 4-4), which is significantly higher than PCL_{540}-Succ-C7 ($P<0.05$), but also showed no decrease compared to the DINP control ($P>0.05$). Taken together, these results suggest that the observed phenomenon

of gas check-free films had arisen due to the unique chemical structure of PCL_{540}-Succ-C7 as a whole, and not due to its individual constituents.

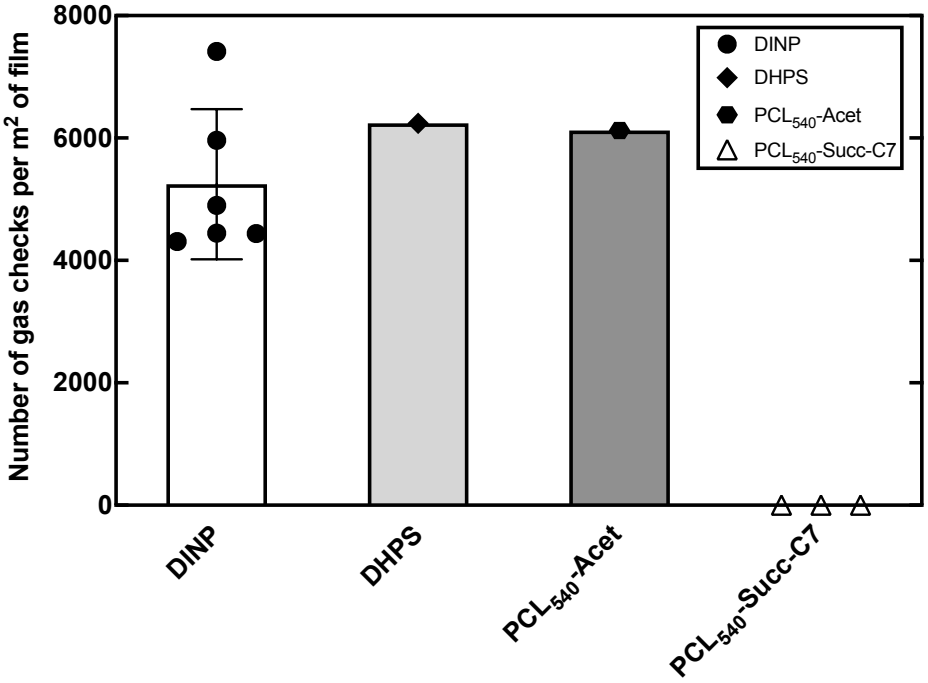


Figure 4-4. Number of gas checks per m^2 of calendered film with DINP, DHPS, PCL_{540}-Acet and PCL_{540}-Succ-C7 blended at 55 PHR. Film gauge was 0.4 mm +/- 0.05 mm for all films.

4.5.2 Additive concentration

To investigate the effect of PCL_{540}-Succ-C7 concentration on eliminating gas checks, we blended the additive at increasing concentrations from 4 phr to 55 phr. All blends (except for the 55 phr PCL_{540}-Succ-C7 blend) contained 55 phr DINP as a primary plasticizer with PCL_{540}-Succ-C7 added at concentrations of 4 phr (2.3wt%), 8 phr (4.5wt%), and 10 phr (5.6wt%), shown in Figure 4-5. A one-way ANOVA and Tukey post-test were performed to determine whether the observed reduction in gas checks with concentration was statistically significant. It was found that at 4 phr there was no significant effect of the PCL_{540}-Succ-C7 on gas check removal ($P>0.05$), with an average of 4807 gas checks per m^2 counted on the film. At 8 phr, there was a significant reduction in the number of gas checks compared to the DINP control and 4 phr films, with an average of 877 gas checks per m^2 ($P<0.05$; $P=0.0013$ and $P=0.0098$, respectively). There was no statistically significant difference in the number of gas checks between the 10 phr and 55 phr films ($P>0.05$),

with virtually no gas checks in any of the films. Therefore, it was established that PCL_{540}-Succ-C7 could be used as a processing aid at concentrations of 10 phr and above in conjunction with a primary plasticizer to effectively remove gas checks.

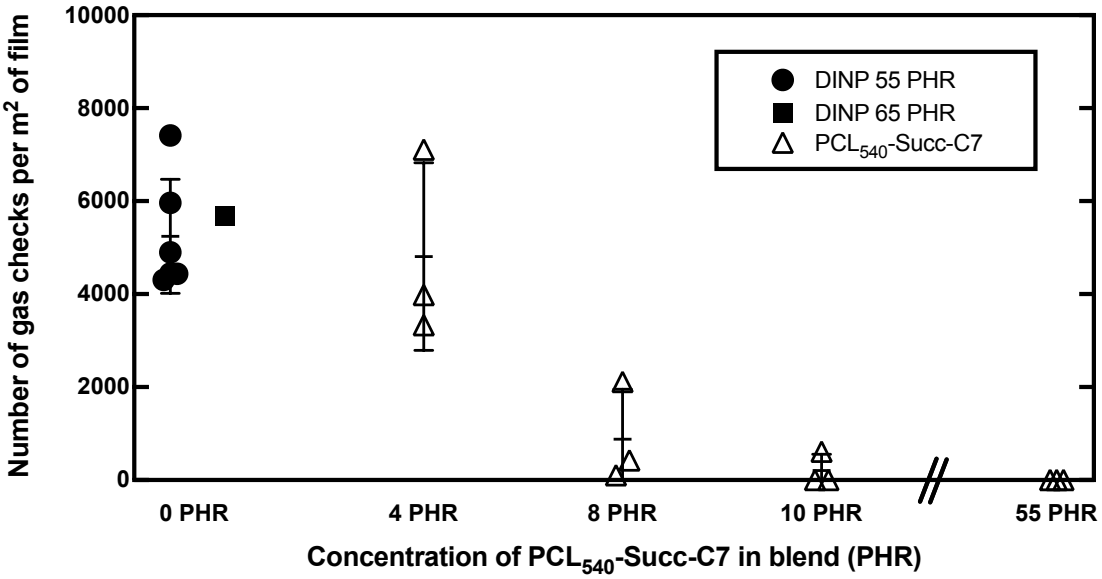


Figure 4-5. Effect of concentration of PCL-Succinate-C7 on gas check removal.

A film with 65 phr DINP was also calendered for comparison, in order to determine whether the simple addition of an extra 10 phr of additive could be the reason for gas check removal. It was found that the 65 phr DINP film still contained an average of 5680 gas checks per m^2 of film (Figure 4-5). Therefore, the observed effects in blends where PCL_{540}-Succ-C7 was incorporated as an additive are due to PCL_{540}-Succ-C7 specifically rather than the presence of extra compound.

4.5.3 Molecular structure

Having demonstrated the efficacy of PCL_{540}-Succ-C7 in preventing gas checks at concentrations as low as 10 phr, while its constituents showed no effects, we wanted to further investigate the structural features responsible for this observed effect. We aimed to perform a structure-function analysis by synthesizing a small library of structural analogs. A total of 9 novel additives were synthesized, shown in Figure 4-3c. A series of star-shaped and linear PCL analogs were made using commercially available PCL-triols (M_n = 300, 540, 900) and PCL-diol (M_n = 530) as

building blocks to study the effect of molecular weight and degree of branching. Several diacids were screened as ester linkers. 1-butanol, *n*-heptanol, and 1-decanol were screened as end-capping agents to study the effect of carbon chain length. The performance of these additives in preventing gas checks was compared with previously known compatible additives: DINP, PCL_{540}-Acet, and DHPS.

We found that both PCL_{300}-Succ-C7 and PCL_{900}-Succ-C7, which have molecular structures identical to PCL_{540}-Succ-C7 (Figure 4-3), but different molecular weights, completely prevented the formation of gas checks in calendered films at 55 phr (see Table 4-3) with no difference in effectiveness at 4, 8, and 10 phr compared to PCL_{540}-Succ-C7 (see Supporting Information, Figure 4-S1). Therefore, we conclude that at values between 300 and 900 g/mol, the molecular weight of the PCL-triol oligomer core had no effect on gas check removal during calendering.

Next, the central PCL-triol (with an M_n of 540 g/mol) was kept constant, while the diacid group was varied from a succinate group to a fumarate, oxalate, or adipate group, shown in red in Figure 4-3c. All of the new molecules that were synthesized (PCL_{540}-Fum-C7, PCL_{540}-Oxa-C7 and PCL_{540}-Adi-C7) completely removed gas checks at 55 phr, as shown in Table 4-3. Therefore, between the analogs tested, the type of diacid did not influence their activity.

Previous studies have shown that succinate and maleate performance as plasticizers was correlated with the alkyl chain length of the molecules [17]. Optimal performance was observed at chain lengths of six to eight carbons, with decreasing performance noted at ten carbons. Thus, the chain length of the alkyl group at the end of our PCL molecule was modified to determine whether chain length also has an effect on gas check removal. The alkyl chain length was modified from its original C_7 (heptanol) to C_4 (butanol) and C_{10} (decanol), as shown in blue in Figure 4-3, while keeping the PCL_{540}-triol core and succinate elements constant. This resulted in the synthesis of two additional analogs, namely PCL_{540}-Succ-C4 and PCL_{540}-Succ-C10, both of which removed all gas checks at 55 phr and behaved similarly to PCL_{540}-Succ-C7, shown in Table 4-3. Therefore, we conclude that within this range, alcohol chain length did not influence the prevention of gas check formation.

The final structural element that was investigated was the role of branching in the additive molecule. All of the aforementioned structures, including the original PCL_{540}-Succ-C7 have a 3-armed star shaped structure (Figure 4-3c). We synthesized a new linear molecule from a PCL-diol core, keeping the succinate diacid and heptanol end groups constant (Figure 4-3c). We observed that the Linear-PCL_{530}-Succ-C7 removed all gas checks at 55 phr, shown in Table 4-3, similarly to the star-shaped molecules, suggesting that branching was not the reason for gas check removal.

Table 4-3. Number of gas checks per m^2 of film for all of the calendered blends.

Additive	Concentration	Average number of gas checks per m^2
DINP	55 phr	5115
DINP	65 phr	5680
PCL_{540}-triol	55 phr	9864
PCL_{540}-Acet	55 phr	6122
DHPS	55 phr	6241
PCL_{540}-Succ-C7	55 phr	0
	10 phr	204
	8 phr	879
	4 phr	4807
PCL_{300}-Succ-C7	55 phr	0
	10 phr	0
	8 phr	0
	4 phr	5193
PCL_{900}-Succ-C7	55 phr	0
	10 phr	0
	8 phr	227
	4 phr	5941
PCL_{540}-Fum-C7	55 phr	0
PCL_{540}-Oxa-C7	55 phr	0
PCL_{540}-Adi-C7	55 phr	0
PCL_{540}-Succ-C4	55 phr	0
PCL_{540}-Succ-C10	55 phr	0
Linear-PCL_{530}-Succ-C7	55 phr	0

Thus, it was concluded that a molecular arrangement consisting of a PCL core structure with an attached diacid and alcohol effectively prevented gas check formation, whereas, remarkably, each component on its own did not. We discovered a series of additives with varying molecular weights of the PCL central group, different acid linkers (succinic, fumaric, adipic and oxalic) and alcohol

capping units of varying lengths (n-butyl to n-decyl) that are effective at removing gas checks during calendering when blended with PVC.

4.5.4 Viscosity

We sought to investigate whether the inclusion of the ester linkage along with the alkyl chain and PCL core altered the viscosity of our compounds, which could produce favorable pressures to remove gas checks. Bourgeois et al. previously reported that the occurrence of gas checks in calendered film was related to the presence of air inclusions in the calender bank, which was in turn related to pressure [10]. They found that at pressures below 120 bar the calender bank contained air inclusions in the backflow and distributed along the flow streams, which corresponded to gas check defects in the final calendered sheets. At pressures above 120 bar, only a few microbubbles were observed in the calender bank, and the corresponding PVC sheets were found to be free of gas checks. Pressure in the calender bank is related to shear rate and consequently melt viscosity [31] and, hence, Bourgeois et al. hypothesized that calendering under conditions of high calender speed, small nip opening, and high apparent viscosity of the polymer would avoid the formation of gas check defects. Since we maintained constant calender speed and nip opening in the production of all our films yet saw a significant decrease in the number of gas checks depending on our film composition, we sought to investigate the effect of viscosity on gas check removal.

As a first step, the viscosities of our novel additives were measured at 25°C, shown in Figure 4-6. It can be seen that the viscosities of the additives that remove gas checks when blended with PVC are higher than those of the additives that do not remove gas checks. DINP, DHPS, and PCL_{540}-Acet (which do not remove gas checks) have viscosities that range from approximately 10 cP to 115 cP. The viscosities of the PCL-based additives (which all remove gas checks) range from approximately 315 cP for Linear-PCL_{530}-Succ-C7 to 3100 cP for PCL_{540}-Fum-C7. This trend suggests that viscosity plays a role in the additives' ability to prevent gas checks from forming. It is worth noting that PCL_{540}-triol, which was found to be incompatible with PVC, has a high viscosity. Despite having a viscosity within the 'favorable' range, it is not a suitable additive to

remove gas checks since it does not blend well with PVC and drastically reduces film quality, making the resulting product unusable.

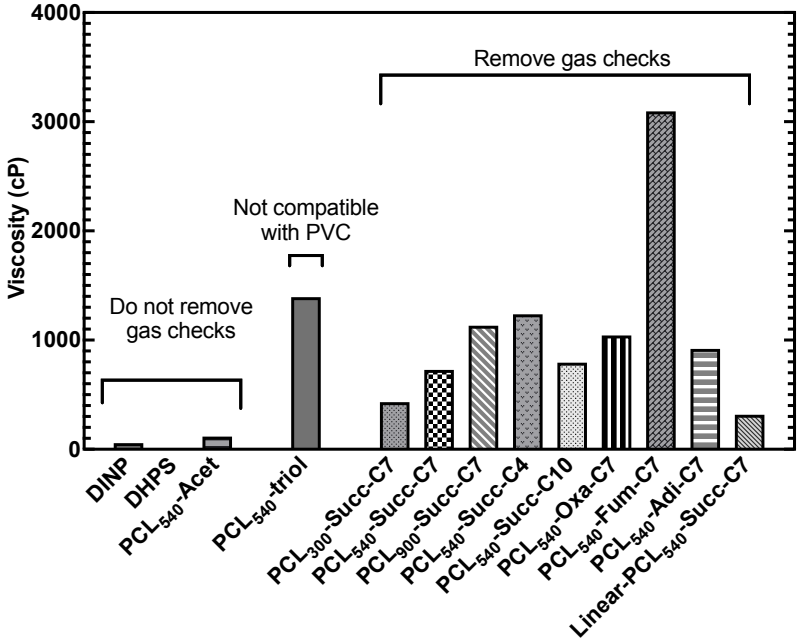


Figure 4-6. Liquid viscosities of additives at 25°C. Steady-shear measurements were taken between 0.1 and 100 s^{-1}.

We subsequently performed rheological tests, shown in Figures 4-7 and 4-8, on the PVC blend melts at 170°C to see if the melt viscosities also corresponded with the prevention of gas check formation. Figure 4-7 shows the complex viscosities of blends made with additives that do not prevent gas checks. It can be seen that DHPS has the highest complex viscosity of this group. Figure 4-8 shows the complex viscosities of blends made with additives that prevent gas checks. It is notable that all of these blends have higher complex viscosities when compared to the blends that do not prevent gas checks, using DHPS as a visual comparison. G′, G″, and tanδ also followed a similar trend and are shown in Figures 4-S2 - 4-S7 of the Supporting Information. Both G′ and G″ were higher for the blends that were found to prevent gas checks. The melt rheology of the blends further supports our hypothesis that these additives alter the apparent viscosity of the polymer blends during calendering, resulting in higher pressures in the calender bank, thus preventing gas check formation in films produced under the same processing conditions of temperature, nip distance, and roller speed.

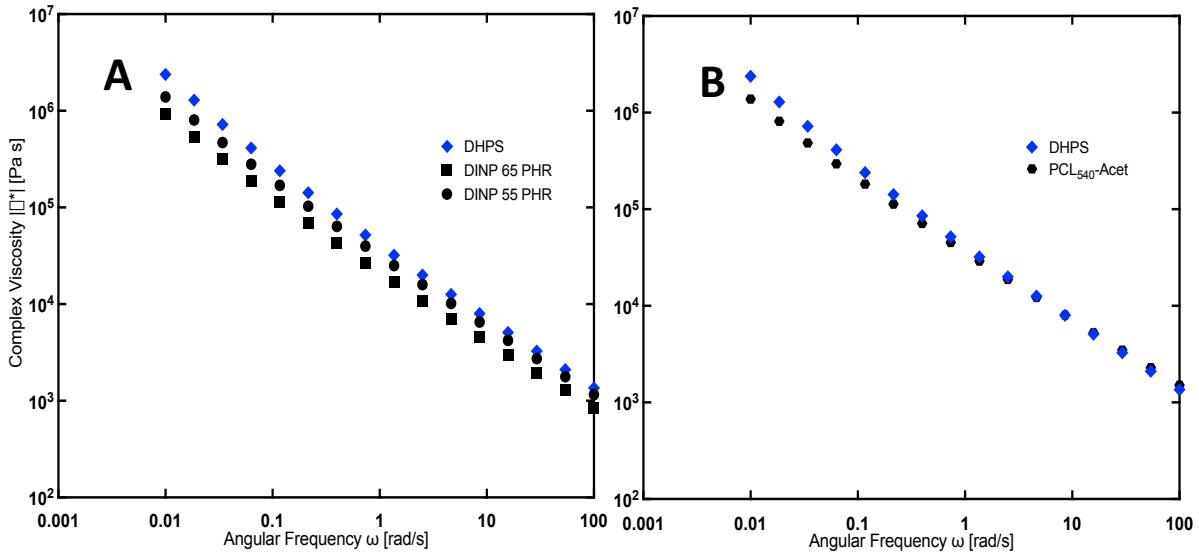


Figure 4-7. Complex viscosity as a function of frequency at 170°C for PVC melts made with additives that do not prevent gas check formation: (A) DINP at 55 and 65 phr and (B) PCL_{540}-Acet at 55 phr. All additives are shown in comparison to DHPS at 55 phr (shown in blue) which also does not prevent gas check formation.

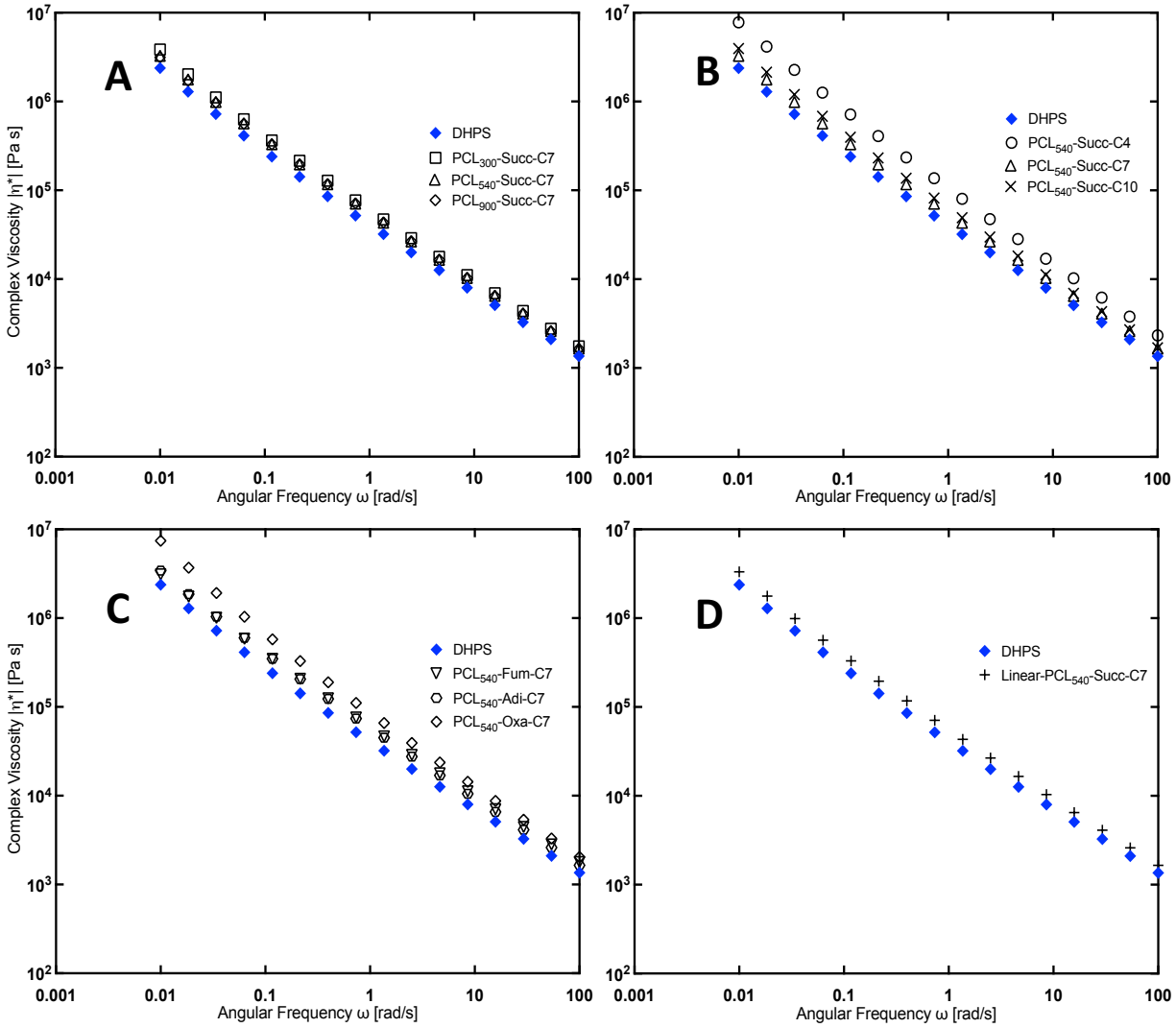


Figure 4-8. Complex viscosity as a function of frequency at 170°C for PVC melts made with additives that effectively prevent gas check formation: (A) PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, PCL_{900}-Succ-C7 (B) PCL_{540}-Succ-C4, PCL_{540}-Succ-C7, PCL_{540}-Succ-C10 (C) PCL_{540}-Fum-C7, PCL_{540}-Adi-C7, PCL_{540}-Oxa-C7 (D) Linear-PCL_{530}-Succ-C7. All curves are shown in comparison to DHPS (shown in blue, which does not prevent gas check formation). All additives were blended at 55 PHR.

4.5.5 Surface tension

Due to the prominent influence of surface tension in the bubble dissolution model developed by Kontopoulou et al. [32], we measured the surface tension of two of our additives, DHPS (an additive that does not prevent gas checks) and PCL_{540}-Succ-C7 (an additive that prevents gas checks), in air at 25°C. DHPS was found to have a surface tension of 30 dynes/cm, and PCL_{540}-

Succ-C7 was found to have a surface tension of 33 dynes/cm. Similarly to Bourgeois et al. [10], Kontopoulou et al. [32] reported that applying higher pressures accelerated bubble dissolution, in this case due to a hypothesized increased driving force for diffusion. Based on their model, they concluded that the factors that significantly affect bubble dissolution are initial bubble size, surface tension, and air concentration in the melt. Based on the similarity in our measured surface tension values between an additive that does not prevent gas checks and one that does, we suggest that the effect of our additives on preventing gas check formation is more strongly influenced by viscosity than surface tension. In altering melt viscosity, and thus pressure, during calendering, we believe that less air becomes entrapped in the polymer melt during processing. Less entrapped air would lead to fewer defects caused by the escaping air. This is consistent with the findings reported by Kontopoulou et al. [32] that correlate air concentration in the melt with bubble dissolution.

4.6 Conclusion

A series of PCL-based additives was developed that can be used to prevent the formation of gas check surface defects during PVC calendering. We found that combining a PCL oligomer core with a diacid linker and alcohol cap consistently produced additives capable of removing gas checks for a range of PCL molecular weights, acid types, and alkyl chain lengths. Viscosity was found to be an important factor in preventing gas check formation; that is, all of the additives that were successful in preventing gas checks had higher viscosities than additives that did not prevent gas check formation. Additionally, we showed that at higher temperatures typically used during processing polymer blends made with additives that prevented defects had higher complex viscosities than blends made with additives that did not prevent defects. Interestingly, it was found that PCL-triol, a high-viscosity oligomer, was not a suitable additive for gas check removal, indicating that viscosity alone is not enough to prevent these defects. Good compatibility with PVC is also an essential feature of any gas check removal additive. Preliminary surface tension mesurements suggested that the influence of bulk viscosity in removing gas checks is stronger than the influence of surface tension-related diffusion. Further investigation of these additives for their plasticizing performance will be important to determine whether incorporating them into blends at low concentrations with a different primary plasticizer is preferable or whether their performance

would allow them to be used independently as plasticizers that can also remove defects. We have shown that, as far as removing gas checks is concerned, both of these options would be viable since defect removal was observed at concentrations as low as 10 phr.

4.7 Acknowledgments

Funding was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC; Collaborative Research and Development Grants, CRDPJ 543853-2019 and Discovery Grants Program, RGPIN 05948-2019, RGPIN 06161-2018) and the James McGill Chair program of McGill University. Student support was provided through McGill Engineering Doctoral Awards (MEDA) of the Faculty of Engineering of McGill University and through a Mitacs Accelerate (IT07985). The authors acknowledge Canadian General-Tower Limited for their donation of materials and use of their laboratory equipment, specifically their lab-scale polymer mill and calender.

4.8 References

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4.9 Supporting information

The following appeared as supporting information made available with the published article:

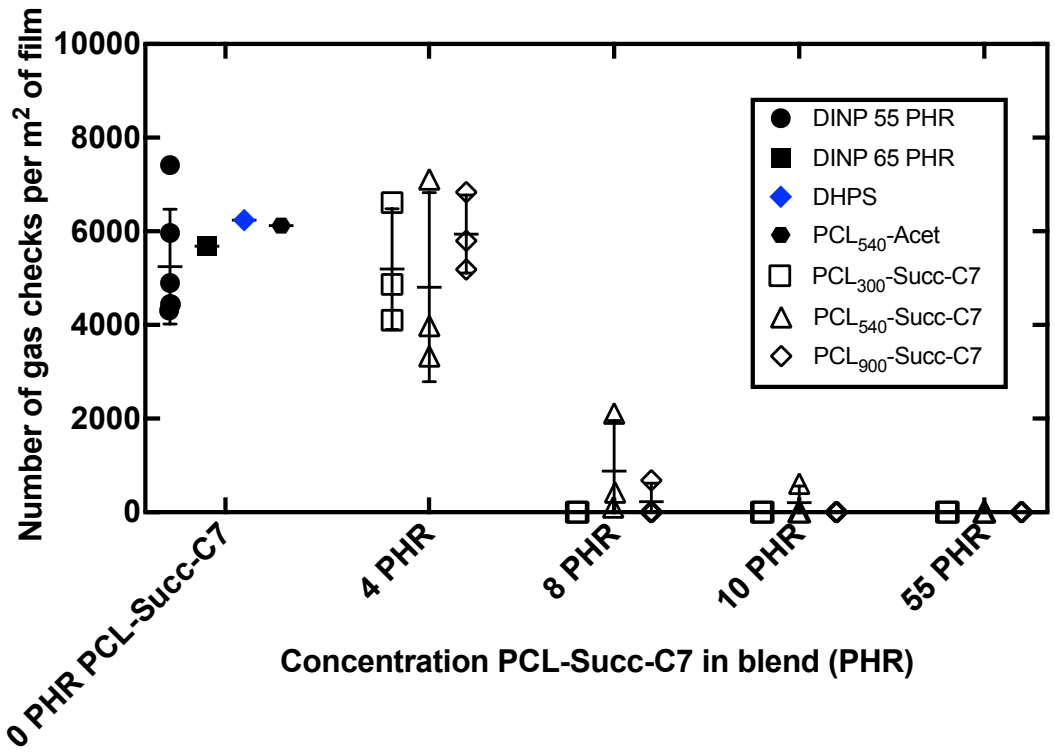

Figure 4-S1. Number of gas checks per m^2 of film for blends made with PCL-Succ-C7 of different molecular weights, at increasing concentrations of PCL-Succ-C7, as compared with DINP, DHPS, and PCL_{540}-Acet

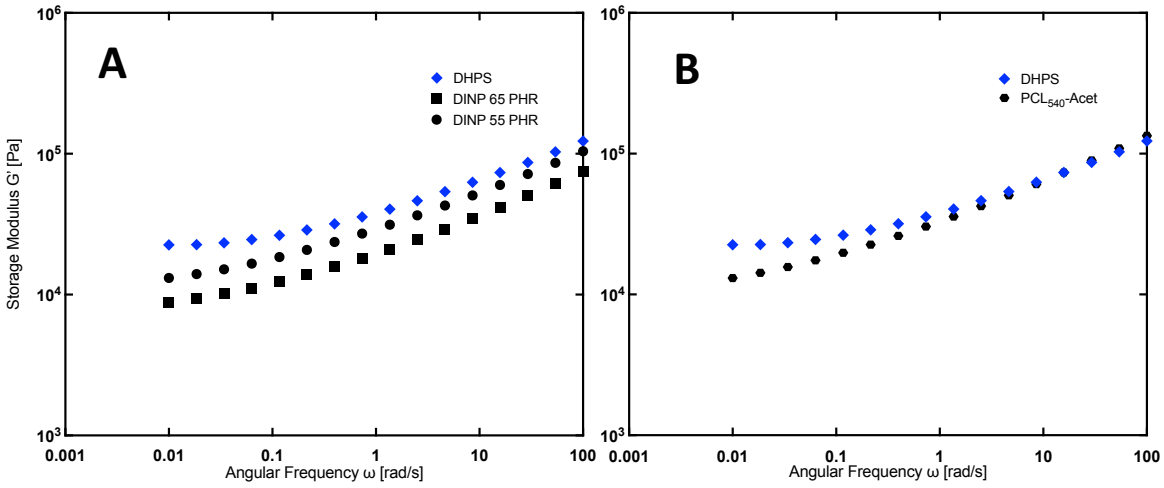

Figure 4-S2. Storage modulus as a function of frequency at 170°C for PVC melts made with additives that do not prevent gas check formation: (A) DINP at 55 and 65 phr and (B) PCL_{540}-Acet at 55 phr. All additives are shown in comparison to DHPS at 55 phr (shown in blue) which also does not prevent gas check formation.

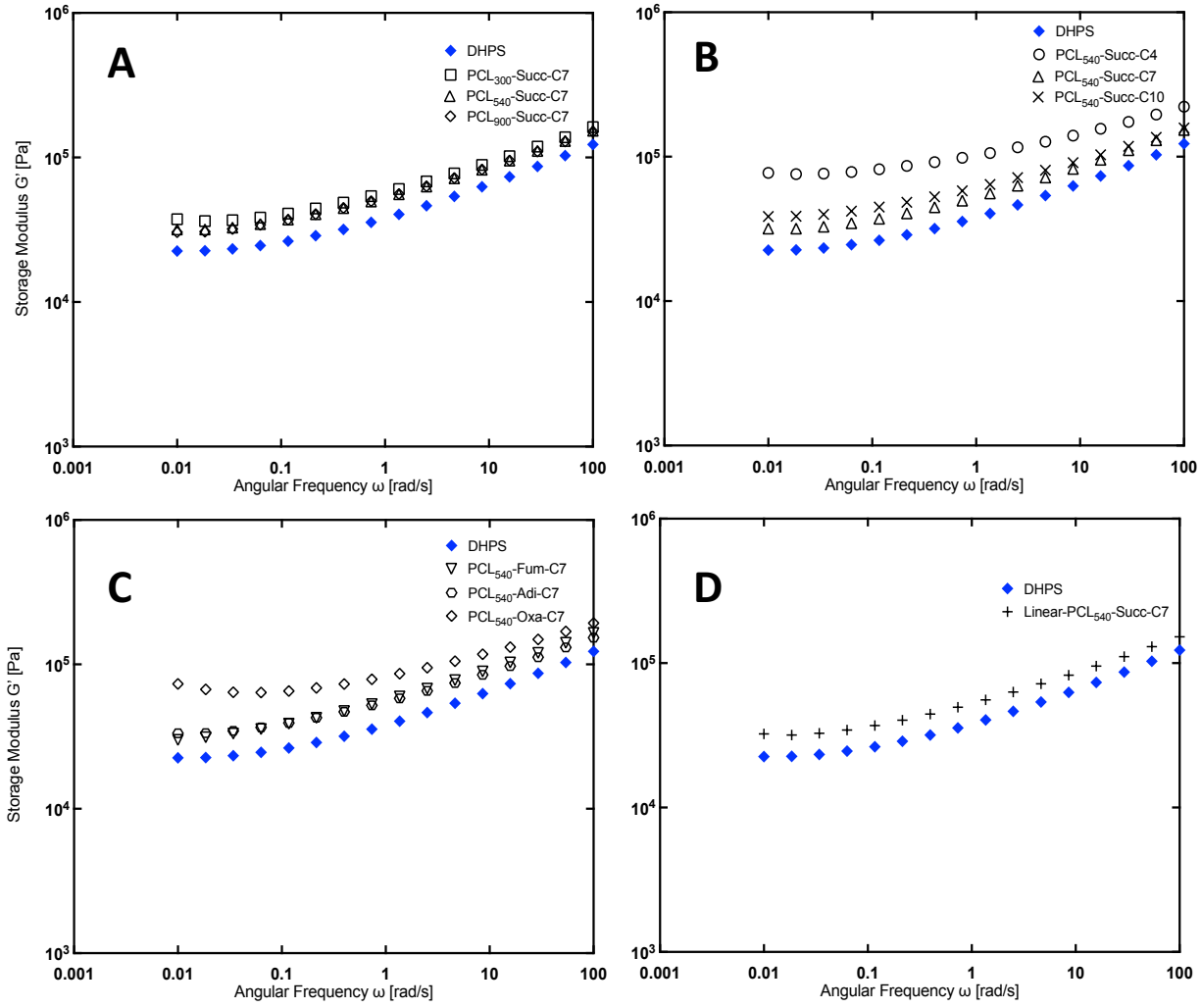

Figure 4-S3. Storage modulus as a function of frequency at 170°C for PVC melts made with additives that effectively prevent gas check formation: (A) PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, PCL_{900}-Succ-C7 (B) PCL_{540}-Succ-C4, PCL_{540}-Succ-C7, PCL_{540}-Succ-C10 (C) PCL_{540}-Fum-C7, PCL_{540}-Adi-C7, PCL_{540}-Oxa-C7 (D) Linear-PCL_{530}-Succ-C7. All curves are shown in comparison to DHPS (shown in blue, which does not prevent gas check formation). All additives were blended at 55 PHR.

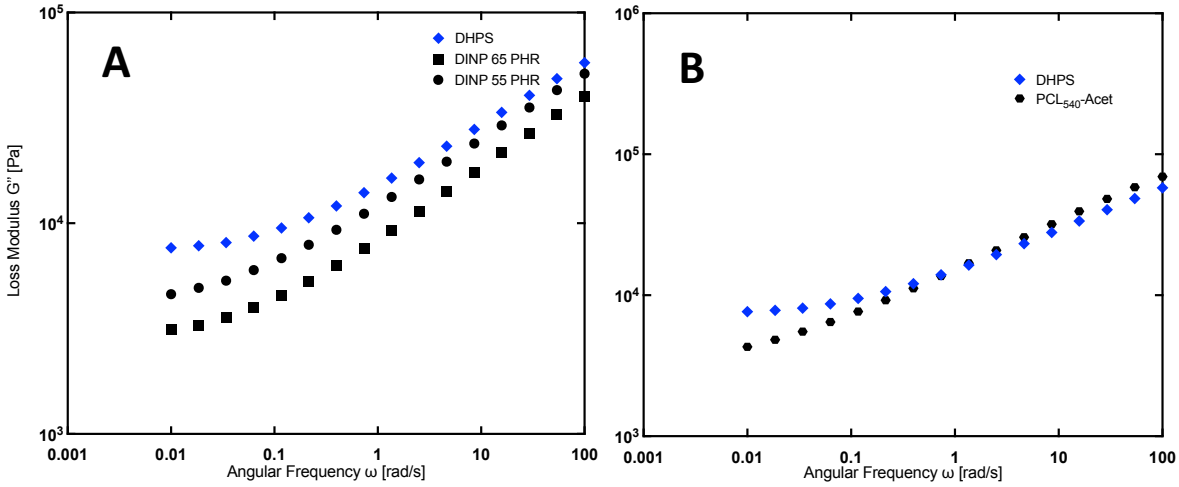

Figure 4-S4. Loss modulus as a function of frequency at 170°C for PVC melts made with additives that do not prevent gas check formation: (A) DINP at 55 and 65 phr and (B) PCL_{540}-Acet at 55 phr. All additives are shown in comparison to DHPS at 55 phr (shown in blue) which also does not prevent gas check formation.

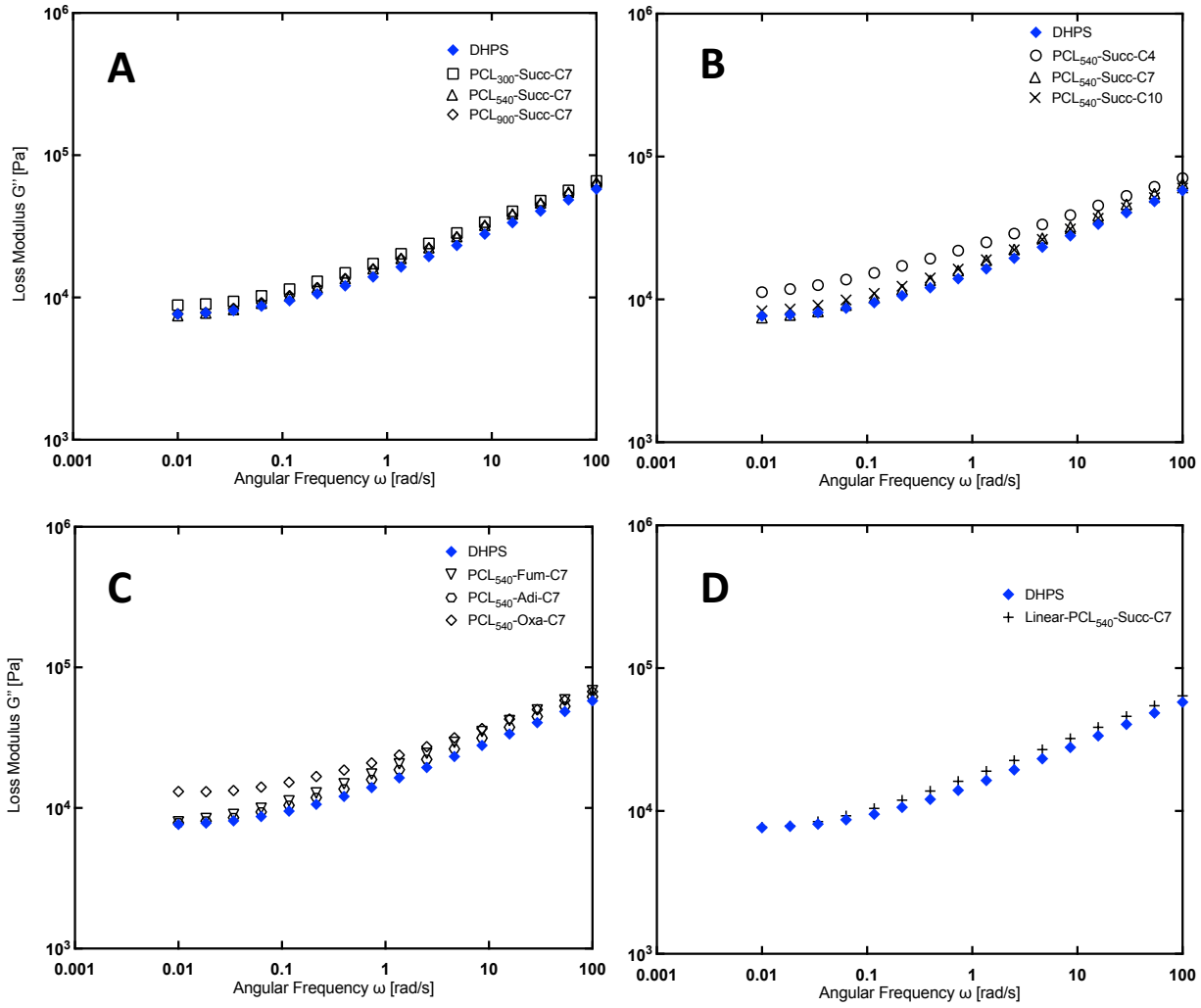

Figure 4-S5. Loss modulus as a function of frequency at 170°C for PVC melts made with additives that effectively prevent gas check formation: (A) PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, PCL_{900}-Succ-C7 (B) PCL_{540}-Succ-C4, PCL_{540}-Succ-C7, PCL_{540}-Succ-C10 (C) PCL_{540}-Fum-C7, PCL_{540}-Adi-C7, PCL_{540}-Oxa-C7 (D) Linear-PCL_{530}-Succ-C7. All curves are shown in comparison to DHPS (shown in blue, which does not prevent gas check formation). All additives were blended at 55 PHR.

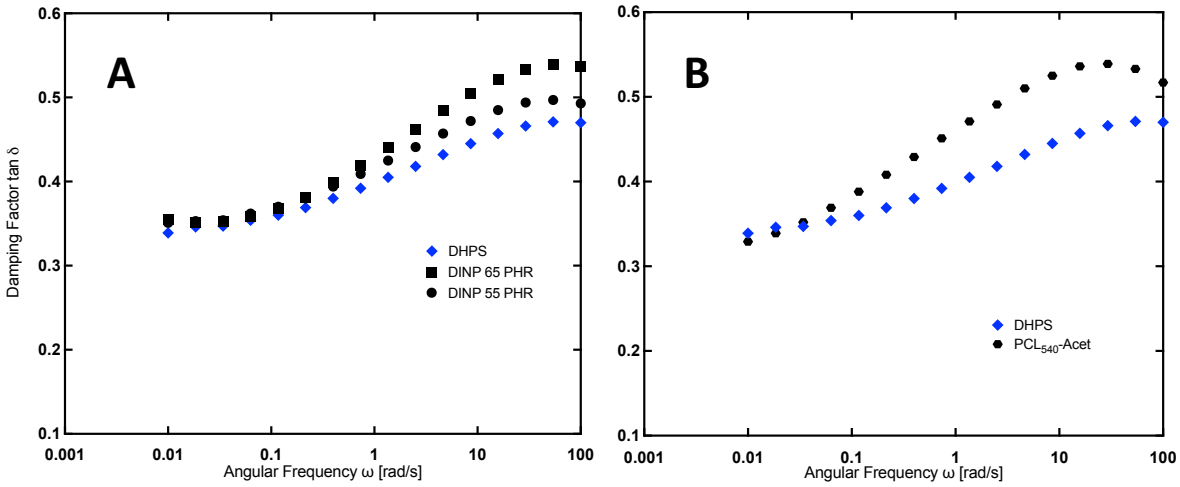

Figure 4-S6. Damping factor as a function of frequency at 170°C for PVC melts made with: additives that do not prevent gas check formation (A) DINP at 55 and 65 phr and (B) PCL_{540}-Acet at 55 phr. All additives are shown in comparison to DHPS at 55 phr (shown in blue) which also does not prevent gas check formation.

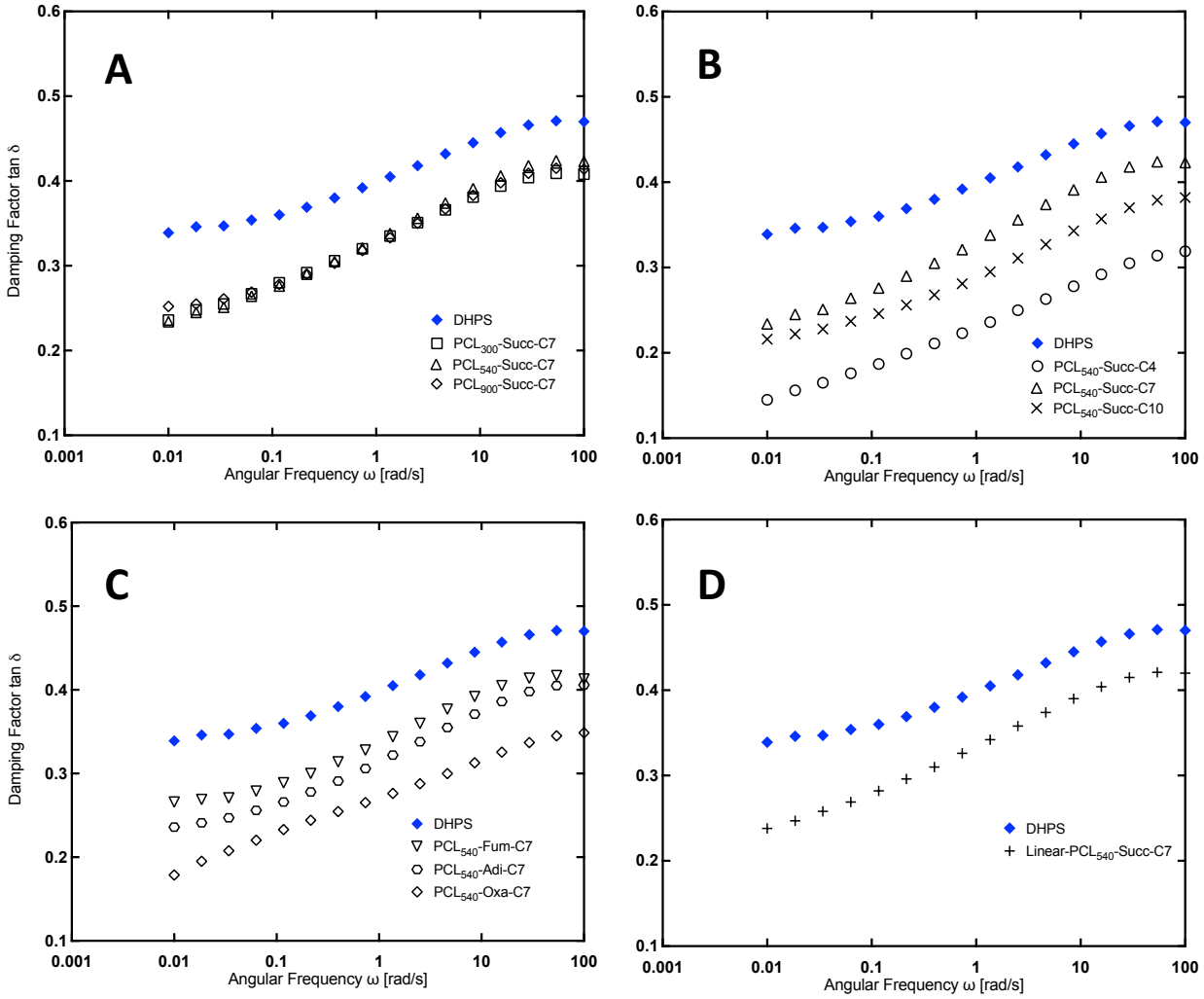

Figure 4-S7. Damping factor as a function of frequency at 170°C for PVC melts made with additives that effectively prevent gas check formation: (A) PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, PCL_{900}-Succ-C7 (B) PCL_{540}-Succ-C4, PCL_{540}-Succ-C7, PCL_{540}-Succ-C10 (C) PCL_{540}-Fum-C7, PCL_{540}-Adi-C7, PCL_{540}-Oxa-C7 (D) Linear-PCL_{530}-Succ-C7. All curves are shown in comparison to DHPS (shown in blue, which does not prevent gas check formation). All additives were blended at 55 PHR.

5

Poly(ε-caprolactone)-based additives: plasticization efficacy and migration resistance[4]

5.1 Preface

This chapter was published online in 2021 in the *Journal of Vinyl & Additive Technology* and presents a rigorous evaluation of the family of additives presented in Chapter 4 as primary plasticizers for PVC. The objective of this work was to study the efficacy of these additives with respect to their mechanical and thermal properties, using both calendered films and extruded and molded bars. Their leaching behavior was also evaluated since the oligomeric star-shaped structures were designed and expected to improve migration resistance.

This article provides an important addition to the previously published work (Chapter 4) about this family of chemicals and their industrial relevance. It establishes that these additives can indeed be used as a new class of primary plasticizers that provide high plasticizing efficiency and improved migration resistance, while still being able to improve film quality during calendering. Being able to use a single additive, especially one designed to be sustainable, for multiple functions, such as plasticization and surface defect removal, presents an advantage during polymer processing. Additionally, since the green chemistry principles outlined in Chapter 3 were used in the design of these additives, and since we improved our synthesis methods in this study to be solvent-free

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and to use bio-based reagents where possible, this family presents a more sustainable alternative to existing plasticizers.

5.2 Abstract

A family of poly(caprolactone) (PCL)-based oligomeric additives was evaluated as plasticizers for poly(vinyl chloride) (PVC). We found that the entire family of additives, which consist of a PCL core, diester linker, and alkyl chain cap, were effective plasticizers that improve migration resistance. The elongation atbreak and tensile strength of the blends made with the PCL-based additives were comparable to blends prepared with diisononyl phthalate (DINP), a plas- ticizer typically used industrially, and diheptyl succinate (DHPS), an alterna- tive biodegradable plasticizer. Increasing concentration was found to decrease glass transition temperature (T_g) and increase elongation at break, confirming their role as functional plasticizers. We found that all of the PCL-based plasti- cizers exhibited significantly reduced leaching into hexanes compared to DINPand DHPS. The PCL-based plasticizers with shorter carbon chain lengthsreduced leaching more than those with longer carbon chain lengths.

5.3 Introduction

Plasticizers are additives that are incorporated into polymeric materials to lower their glass transition temperatures (T_g) and modify their mechanical properties, especially to improve flexibility and melt processability [1, 2]. They can be classified as either internal or external. Internal plasticizers are incorporated into a resin during the polymerization process in the form of grafted or copolymerized groups that improve flexibility. External plasticizers are mixed mechanically with a polymer during processing, and are not covalently bound [3]. While external plasticizers have the advantage of giving manufacturers the liberty to select from a wide variety of plasticizers and to tune blend compositions based on desired properties, they can be lost by evaporation, migration, or extraction since they are not chemically bound to the polymer [4, 5].

Approximately 90% of all plasticizers produced globally are used with poly(vinyl chloride) (PVC), which is one of the most important and widely used commodity thermoplastics [6]. Most PVC plasticizers are external with phthalate plasticizers such as di-(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) accounting for 92% of the total plasticizers produced globally [6]. Extensive work has shown that phthalate plasticizers are pervasive in the environment, with DEHP detected in house dust [7-9], air [10], soil [11], watersheds [12], and animals [13], with resulting exposure to humans. This is problematic given that many studies have linked phthalates to reproductive and developmental toxicity in animals and humans [14-18], which has led to their regulation and prohibition in some consumer items, such as children's toys, in various countries around the world [19-22]. As a result of their tendency to leach into the environment and concerns over their toxicity, there has been considerable research on developing safer non-phthalate plasticizers [23].

Numerous important factors need to be considered when developing a safe plasticizer [24]. From a performance standpoint, compatibility, efficiency, and permanence are key criteria that must be satisfied [25]. Increasingly, principles of sustainability and green chemistry have been incorporated in the design of new plasticizers with the goal of avoiding "regrettable substitution," which is defined as the replacement of toxic chemicals with ones of equal or greater toxic effects [26]. Thus, green design elements such as biodegradation, leaching and low-hazard synthesis are needed in addition to traditional performance considerations. In particular, permanence, or resistance to migration, addresses both performance and sustainable design criteria. Improving plasticizer permanence prevents the reduction of material properties over time that occurs when external plasticizers leach out of the polymer, and it is also the main factor in mitigating environmental and human exposure.

Previous studies have shown that polymeric and oligomeric plasticizers tend to resist migration better than low molecular weight ester plasticizers [6, 27-29]. Poly(ε-caprolactone) (PCL)-based plasticizers have been found to exhibit good compatibility with PVC [30, 31], have increased migration resistance (i.e., less leaching) [32-34], and are also biodegradable [35, 36], non-toxic [37], and biocompatible [38]. Recently, a new family of oligomeric additives (see Figure 5-1) consisting of a PCL core with ester linkers and alkyl chain caps was shown to be effective at

removing surface defects during PVC calendering at concentrations as low as 8 parts per hundred resin (phr, 4.5 wt%) [39]. The previous work investigated the mechanism of surface defect removal; however, the performance of the additives as potential plasticizers has not been evaluated.

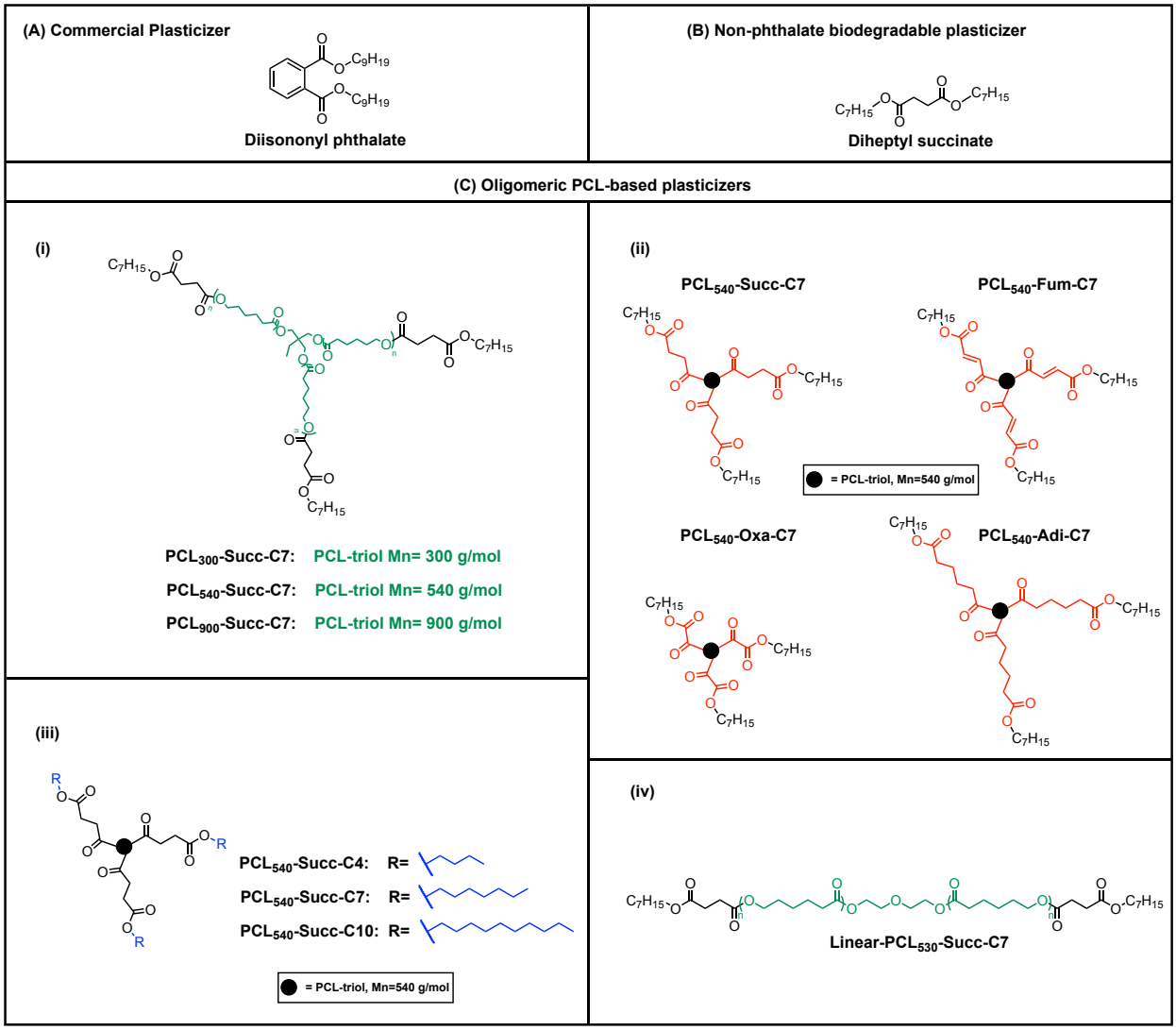

Figure 5-1. Molecular structures of additives evaluated as plasticizers: (A) diisononyl phthalate (DINP) (B) diheptyl succinate (DHPS) (C) oligomeric PCL plasticizers with (i) different PCL core sizes, (ii) different ester groups, (iii) different alkyl caps, and (iv) linear structure.

Therefore, the aim of this work is to assess the effectiveness of these PCL-based additives as primary plasticizers for PVC. Having a single additive serving as both a plasticizer and defect

eliminator provides an important added function and would simplify the process of blending and compounding. We assessed the performance of the additives as plasticizers by investigating their mechanical and thermal properties when blended with PVC as well as their resistance to migration. Specifically, elongation at break, tensile strength and T_g were used as measures of plasticizer efficiency and compared against DINP, a widely used commercial plasticizer, and DHPS, a biodegradable, non-phthalate alternative [40] (see Figure 5-1). Migration resistance was investigated by comparing the leaching of PVC blends made with the PCL-based additives to DINP and DHPS blends. To determine which molecular features of the additives contributed to their plasticization and migration resistance properties, we compared the performance of structural analogs made using different molecular weights of PCL-triol (M_n = 300, 540, 900) and PCL-diol (M_n = 530), different diacid reagents as ester linkers (succinic acid, fumaric acid, adipic acid, oxalic acid), and different alcohols (1-butanol, *n*-heptanol, and 1-decanol) as end-capping agents (see Figure 5-1).

5.4 Experimental

5.4.1 Materials

Poly(ε-caprolactone) (PCL) triol (M_n = 300, 540) (99%) was purchased from Scientific Polymer Products (NY, USA). PCL triol (M_n = 900) (99%), PCL diol (M_n = 530) (99%), fumaric acid (99%), oxalic acid (98%), adipic acid (99%), 1-butanol (99%), and 1-decanol (98%) were purchased from Sigma Aldrich (Missouri, USA). Renewably sourced succinic acid (99%) was purchased from Roquette (Lestrom, France). Renewably sourced Oleris *n*-heptanol (99%) was purchased from Arkema (Pennsylvania, USA). Sulfuric acid (96%), hexanes (99%), and stearic acid were purchased from Fisher Scientific (Montreal, Canada). Epoxidized soybean oil was purchased from Galata Chemicals (Louisiana, USA). Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), antimony oxide Hi-Tint (99.68%), silica (99%), stearic acid (99%), barium/zinc stabilizer (1.046 specific gravity at 20°C), and acrylic processing aid (99.8%) were supplied by Canadian General-Tower Limited (CGT Ltd., Ontario, Canada). Unplasticized PVC

pellets (K58, product code: IH014/G045/AA) were provided by Solvay Benvic (Chevigny-Saint-Sauveur, France). All chemicals and reagents were used as received without further purification.

5.4.2 Plasticizer synthesis

Diheptyl succinate (DHPS) was synthesized in a one-step, solvent-free reaction, as previously reported [40]. Tributylsuccinate-terminated poly(caprolactone) (PCL_{540}-Succ-C4) was synthesized using the same method described previously [39]. The remainder of the star-shaped PCL analogs were synthesized using a two-step reaction method similar to a previously described method [39], but modified to remove any use of the solvent benzene, and subsequent solvent removal steps through rotary evaporation. In a first step, PCL triol (one stoichiometric equivalent) and the diacid reagent (three equiv.) were added to a three-necked round bottom flask fitted with a Dean-Stark trap and a condenser. The mixture was then stirred at room temperature for 5 min. A catalytic amount of sulfuric acid (0.15 equiv.) was added to the reaction mixture and the mixture was heated to 110 °C and stirred continuously. Once at temperature, nitrogen gas was bubbled through the mixture for 90 min to promote the removal of water. The mixture was then cooled to room temperature. The alcohol reagent (three equiv.) was then added directly to the flask and the mixture was re-heated to 110 °C, at which point nitrogen gas was again bubbled through the mixture for 90 min. The mixture was then cooled to room temperature. The resulting viscous oils were not further purified. The reaction was monitored by measuring the amount of generated water collected in the Dean-Stark apparatus. Additionally, ^{1}H-NMR spectroscopy was used to verify the reaction had gone to completion. ^{1}H-NMR spectra were obtained using a Bruker AVIIIHD 500 MHz and Varian Inova 400 MHz spectrometer with an average of 16 scans using deuterated chloroform ($CDCl_3$) as the solvent.

Table 5-1 shows the reagents used to synthesize each plasticizer as well as the abbreviated plasticizer names that will be used hereinafter. The linear PCL analog was synthesized using the same procedure as the star-shaped PCLs except for the use of two stoichiometric equivalents of diacid and alcohol reagents, respectively, instead of the three equivalents used for the star-shaped molecules. The resulting linear-PCL_{530}-Succ-C7 was obtained as a viscous oil and was not further purified.

Table 5-1. Reagents used for the synthesis of each plasticizer.

Plasticizer	Abbreviation	PCL core	Diacid reagent	Alcohol
Diheptyl succinate	DHPS	Not applicable	Succinic acid	Heptanol
Triheptylsuccinate-terminated poly(caprolactone)	PCL_{300}-Succ-C7 PCL_{540}-Succ-C7 PCL_{900}-Succ-C7	PCL-triol (M_n=300) PCL-triol (M_n=540) PCL-triol (M_n=900)	Succinic acid	Heptanol
Tributylsuccinate-terminated poly(caprolactone)	PCL_{540}-Succ-C4	PCL-triol (M_n=540)	Succinic acid	Butanol
Tridecylsuccinate-terminated poly(caprolactone)	PCL_{540}-Succ-C10	PCL-triol (M_n=540)	Succinic acid	Decanol
Triheptyloxalate-terminated poly(caprolactone)	PCL_{540}-Oxa-C7	PCL-triol (M_n=540)	Oxalic acid	Heptanol
Triheptylfumarate-terminated poly(caprolactone)	PCL_{540}-Fum-C7	PCL-triol (M_n=540)	Fumaric acid	Heptanol
Triheptyladipate-terminated poly(caprolactone)	PCL_{540}-Adi-C7	PCL-triol (M_n=540)	Adipic acid	Heptanol
Diheptylsuccinate-terminated poly(caprolactone)	Linear-PCL_{530}-Succ-C7	PCL-diol (M_n=530)	Succinic acid	Heptanol

5.4.3 Blending of Plasticizers with PVC

5.4.3.1 Roll Milling and calendering

Plasticized PVC films were produced by initial mixing of blend components on a lab-scale two-roll mill followed by calendering to produce films [39]. A Hartek two-roll mill HTR-300 (d=120 mm, T=160°C, 45 rpm) was used to melt and mix the blend components for 7 min, starting from the time of film formation on the rolls.

The milled film was then fed into a lab-scale calender (d=180 mm, T=160-170°C, P=45 psi hps, 50 rpm) for 1 min, set to achieve a film gauge of 0.4 mm +/- 0.05 mm. All plasticized PVC films were prepared to a final concentration of 55 phr (32.5 wt%) plasticizer. Each blend contained 100

phr PVC 70K suspension resin, 55 phr plasticizer, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid.

5.4.3.2 Extrusion and compression molding

Plasticized PVC pellets were prepared to final concentrations of 20 phr (16.67 wt%), 40 phr (28.57 wt%) and 60 phr (37.50 wt%) using a conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation) with a screw diameter of 5/14 mm, a screw length of 109.5 mm, and a batch size of 3 g. The extruder was operated at 140 °C using a rotation speed of 30 min^{-1}. Blends were prepared using the following stepwise sequence. Initially, UPVC was combined with 20 phr plasticizer, 4 phr epoxidized soybean oil as a thermal stabilizer, and 5 phr stearic acid as a lubricant and fed into the extruder. The resulting extrudate was manually cut into small pellets and then recycled through the extruder. In the second step, another 20 phr plasticizer was added and extruded to achieve a total concentration of 40 phr plasticizer. The resulting blend was again recycled through the extruder. In the final step, another 20 phr plasticizer was added (to the 40 phr blend) and extruded to achieve a final concentration of 60 phr. The resulting blend was again recycled through the extruder and the extrudate was manually cut into pellets.

The extruded PVC pellets were pressed into tensile bars using a heat press (Carver Manual Hydraulic Press with Watlow Temperature Controllers) at 165°C. The dimensions of the tensile bars were 1.5 mm thickness, 3.25 mm width of narrow section (*W*), 15.5 mm length of narrow section (*L*), 32.5 mm distance between grips (*D*), 63.5 mm overall length (LO), and 10 mm width overall (WO), which correspond to the type V sample described in ASTM D-638-03, and were previously reported by Erythropel et al. [41]. The samples were pressed at 5 tons of clamping force for 10 min, 10 tons of clamping force for 10 min, and finally at 20 tons of clamping force for 30 min, and then cooled to room temperature using cooling water. Once cooled, the pressure was released and the bars were removed from the mold and placed in a desiccator (Drierite, Fisher Scientific) for a minimum of 48 h before tensile testing.

5.4.4 Tensile testing

Tensile testing of film samples was performed using an Instron Tensile Tester 3365 equipped with a Bluehill Universal 5 kN load cell following the ASTM D882-12 protocol. Test bars were punched from films into dimensions of 1 x 6 in with a thickness of 0.016 in., and a testing speed of 20 in·min^{-1} was used with an initial gap of 2 in. Percent elongation and maximum stress (tensile strength) were automatically recorded by the attached computer. Three bars were punched from each film and the data reported is an average of the three tests.

Tensile testing of the extruded samples was performed using a Yamazu Easy Test tensile tester with a load cell of 500 N in a procedure adapted from ASTM D-638-03 [41]. The exact dimensions (thickness and width) of the test bar were measured using electronic calipers (Electronic Outside Micrometer, Fowler Tools & Instruments) and a testing speed of 5 mm·min^{-1} was used. Force and distance were automatically recorded by the attached computer until break of the test bar. Maximum stress was computed and reported by the software and percent elongation was calculated using Eq. (i).

$$Elongation = \frac{L-L_o}{L_o} \times 100 \quad \text{(i)}$$

where L_o represents the initial gap distance between the clamps and L represents the elongation distance between the clamps, as recorded by the instrument. Three tensile bars were produced from three separate batches of extruded material and the reported data is the average of three tests.

5.4.5 Differential scanning calorimetry (DSC)

The glass transition temperature of plasticized PVC blends was measured using a TA Instruments Q2000 differential scanning calorimeter. A previously-established temperature-modulated differential scanning calorimetry (MDSC) protocol was used [41]. Briefly, between 5-10 mg of sample was weighed and loaded into a Tzero Hermetic aluminum pan then into the DSC sample holder. The MDSC protocol comprised two cool-heat cycles. In the first cycle, the sample was cooled to -90°C and held isothermally for 5 min. The cooled sample was then exposed to a linear

heating ramp of 2°C·min^{-1} with a superimposed modulated heating (amplitude=1.27°C, period=60s) until it reached 100°C and was held isothermally for 5 min. This cycle was repeated a second time. DSC results were analyzed using TA Universal Analysis software (V4.5A). Glass transition temperature was determined from the reversible heat flow curve of the second heating cycle using the T_g tool.

5.4.6 Leaching

The disks that were used for the leaching tests were prepared from the previously calendered PVC films (55 phr plasticizer). A circular punch (d=25mm) was used to cut film samples that were layered into stacks of eight and placed in a circular mold with a thickness of 1 mm. A heat press (Carver Manual Hydraulic Press with Watlow Temperature Controllers) was used to press the films at 165°C for 1 min under 5 tons of force and 4 min under 20 tons of force. The samples were cooled under pressure using circulating cold water. They were then removed from the mold and placed in a desiccator (Drierite, Fisher Scientific) for a minimum of one week before the leaching tests.

Leaching tests were performed using a protocol adapted from ASTM D1239-98. Each disk was weighed prior to the start of the test then suspended in a 250 ml Erlenmeyer flask using an aluminum wire. The flasks were filled with 200 ml of hexanes, stoppered, and set in a shaker at 100 rpm and 50°C for 6 h. At the end of this time, the disks were removed from the flasks and dried under vacuum at 35°C for 7 days and then weighed. The percent weight loss of the plasticizer was calculated using Eq. (ii).

$$Plasticizer\ loss = \frac{m - m_o}{0.325 \times m} x\ 100 \qquad \text{(ii)}$$

where m represents the final mass of the disk after the leaching test and m_o represents the initial mass of the disk before the leaching test. Since the concentration of plasticizer is known to be 55 phr, or 32.5 wt%, of the PVC blend, the initial mass of plasticizer was calculated by multiplying the mass of the disk by 0.325. Three separate leaching tests were performed for each plasticizer and the results shown are presented as the mean and standard deviation of the three tests.

5.4.7 Statistics

Statistical analyses were performed using GraphPad Prism 8 software. The measured values for elongation at break (Figure 5-3), glass transition temperature (Figure 5-5) and percent plasticizer loss (Figure 5-6) of the plasticizers in this study were compared against controls (DINP and DHPS) using a one-way analysis of variance (ANOVA) followed by Dunnett's post-test. Differences among the PCL plasticizers in each of these aforementioned experiments were analyzed by one-way ANOVA followed by the Holm-Sidak multiple comparison test. The effect of plasticizer concentration on elongation at break and tensile strength (Figure 5-4) was determined by two-way ANOVA since there were two independent variables, molecular weight and concentration. In all comparisons, $P<0.01$ was considered statistically significant.

5.5 Results & discussion

5.5.1 Synthesis

We aimed to optimize the synthesis of the PCL-based additives [39] by avoiding the use of organic solvent with the goal of developing a set of conditions that reduced reaction waste and were amenable to large-scale production. Figure 5-2 shows the successful incorporation of the heptyl-succinate groups onto the PCL core of PCL_{540}-Succ-C7, as observed through ^{1}H NMR, using our modified one-pot method that was based on the solvent-free method previously described by Elsiwi et al. [39]. Thus, we showed that this was a viable method of synthesizing the plasticizers in this study.

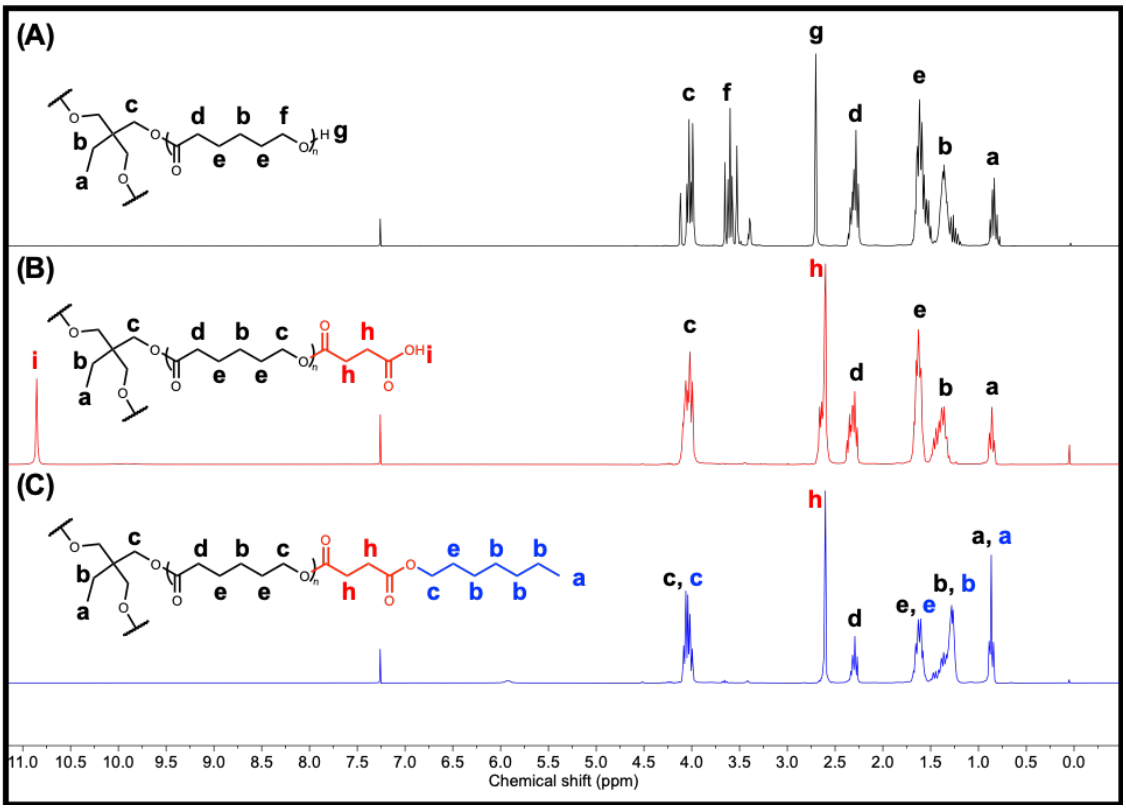

Figure 5-2. ^{1}H-NMR spectra showing the reaction progress of PCL_{540}-Succ-C7: (A) commercially available PCL-triol (M_n of 540 g/mol); (B) reaction intermediate after first step; (C) PCL_{540}-Succ-C7.

5.5.2 Mechanical properties

Calendered PVC blends made with the PCL-based additives all demonstrated comparable elongation at break to the control plasticizers (DINP and DHPS) when blended at the same concentrations, with no statistical difference in their means ($p > 0.01$), as shown in Figure 5-3. Shi et al. previously reported no effect of molecular weight or branching on the tensile properties of PCL-based plasticizers [33], which is in agreement with our findings. The tensile strength of all PCL-based blends was also found to be comparable with the DINP blend, with the only significant difference observed between PCL_{540}-Fum-C7 and DHPS, with the PCL_{540}-Fum-C7 blend exhibiting a higher tensile strength than DHPS ($p<0.01$). Erythropel et al. previously reported an increase in modulus, which represents a decrease in plasticizing performance, of fumarate plasticizers compared with succinate and adipate plasticizers due to the double bond in the fumarate molecule which leads to decreased plasticizer mobility [42, 43]. We hypothesize that this

double bond also accounts for the increased tensile strength that was observed in comparison to DHPS. However, the significant structural differences between DHPS and PCL_{540}-Fum-C7 make it difficult to perform a direct comparison.

The film formulations did not include any secondary plasticizers so the influence of the target compounds could be assessed without interference from other plasticizing agents. Additionally, incompatibility can be observed qualitatively during hot compounding when phase separation is observed with the plasticizer exuding from the surface of the compounded material, forming fine oil droplets or an oily film, as well as through the observation of poor mechanical properties of the final blend [44, 45]. In our case, no phase separation or exudation from the PVC polymer matrix was observed for any of the additives, film formation occurred on the roll mill within acceptable timeframes (<2 min), and the blends exhibited superior mechanical properties suggesting no incompatibility. These observations are consistent with several previous studies, summarized by Hubbell et al., establishing the compatibility between PVC and PCL theoretically and experimentally [45]. Thus, the mechanical performance of the family of PCL additives suggests that they can all function effectively as primary plasticizers for PVC, producing flexible calendered films with comparable tensile properties to existing PVC blends with commercial plasticizers. Among the different PCL additives, no significant differences in performance were observed.

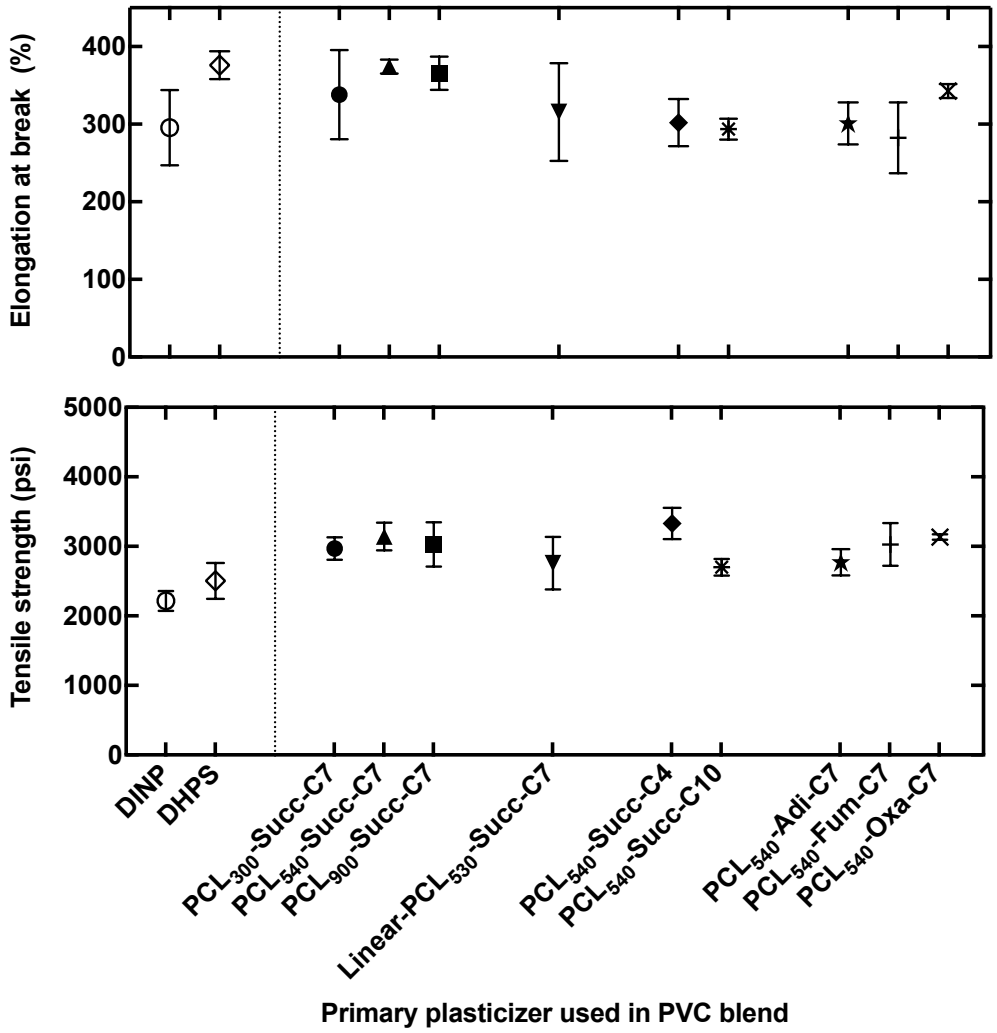

Figure 5-3. Elongation at break and tensile strength of calendered poly(vinyl chloride) (PVC) films prepared with 55 phr of various poly(caprolactone) (PCL) plasticizers, and compared to diisononyl phthalate (DINP) and diheptyl succinate (DHPS) controls.

The effect of concentration of the PCL-based additives on mechanical properties was assessed on extruded PVC blends. A family of three additives (Figure 5-1 C) of increasing molecular weight (PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, and PCL_{900}-Succ-C7) were blended with PVC at concentrations of 20, 40 and 60 phr. Figure 5-4 shows a trend of increasing elongation at break and decreasing tensile strength with increasing plasticizer concentration for all three compounds. There was no effect of molecular weight over the range studied ($p>0.01$) however concentration had a significant effect ($p<0.0001$). These results are consistent with multiple previous reports of increasing elongation and decreasing tensile strength with increasing plasticizer concentration for

various polymer-plasticizer systems [46-49]. This finding is important in establishing the feasibility of using these additives commercially given the need to be able to quickly fine-tune material properties by altering plasticizer concentration [50]. The elongation at break of the 40 phr blends (94%-113%) was shown to be comparable with previously published elongations for DEHP (96%)[43] and DHPS (93%)[40] blends of the same formulation with PVC (Figure 5-4). Therefore, we have shown that the PCL-based plasticizers exhibit equivalent efficiency in controlling PVC mechanical properties by altering concentration when compared with DEHP and DHPS. We also demonstrated the successful blending of the additives with PVC using a second compounding technique (extrusion) under the same conditions used for phthalate plasticizers, with no observation of phase separation or exudation. Furthermore, we found no significant effect of molecular weight on elongation, with all three plasticizers performing comparably, seen in Figure 5-4.

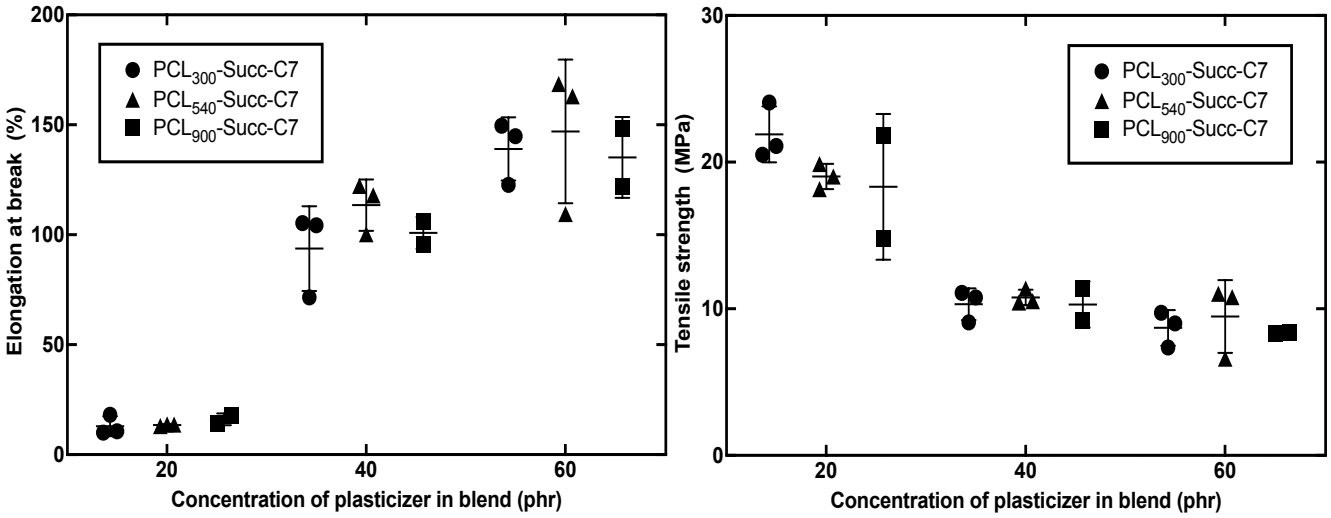

Figure 5-4. Effect of plasticizer concentration on elongation at break and tensile strength of extruded poly(vinyl chloride) (PVC) blends.

5.5.3 Thermal properties

To investigate the effect of additive concentration on the thermal properties of PVC, the T_g of blends prepared with PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, and PCL_{900}-Succ-C7 was evaluated at concentrations of 20, 40, 55 and 60 phr. A decrease in T_g with increasing additive concentration

was seen for all the additives, as shown in Figure 5-5. This trend holds true even when comparing samples that were prepared by different techniques and with different blend formulations. For example, the T_g of the 55 phr PCL_{540}-Succ-C7 blend prepared by calendering (-13°C) falls between the T_g of 10°C for the 40 phr and the T_g of -16°C for 60 phr blends prepared by extrusion and compression molding. The DSC curves for the polymer-plasticizer blends can be found in the Supporting Information. The thermal properties of the plasticized blends agree with the mechanical findings (see Figs. 5-3 and 5-4), and support previous work that shows the T_g of plasticized PVC to be correlated with tensile properties such as elongation at break [41]. Similarly to the mechanical properties, the effect of concentration on T_g is significant while the effect of molecular weight, within our studied range, is not.

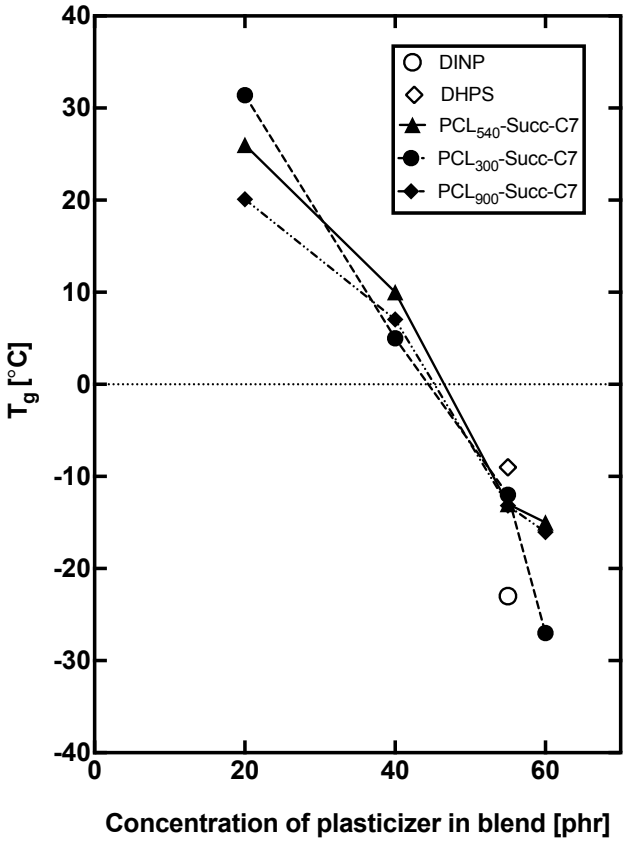

Figure 5-5. Effect of plasticizer concentration on glass transition temperature (T_g).

The T_g of the blends at 40 phr (5 to 10°C), 55 phr (-9 to -23°C) and 60 phr (-15 to -27°C) were all found to be below room temperature. Since polymer blends are expected to be flexible at

temperatures above T_g and rigid below T_g, the T_g results coupled with the elongation results obtained at room temperature suggest that at concentrations between 40 and 60 phr the PCL-based additives are effective plasticizers. Additionally, the T_g of the blends prepared with PCL-based additives were found to be between the T_g for DINP and DHPS. Therefore, the thermal behavior of PVC blends prepared with the PCL-based additives further supports their efficacy as primary plasticizers.

5.5.4 Leaching

Having established the efficiency of the PCL-based additives in altering mechanical and thermal properties of PVC blends, we sought to investigate their resistance to migration. Hexane was chosen as an extraction medium as it is a good solvent for the plasticizers (as opposed to less aggressive aqueous extraction agents such as water or saline solution), providing a fast preliminary indication of the leaching behavior of the new plasticizers compared to DINP and DHPS. It was found that all the PCL-based plasticizers demonstrated significantly lower leaching into hexanes after 6 h compared with DINP and DHPS controls (p<0.01, Figure 5-6). While DINP and DHPS blends demonstrated 41% and 28% plasticizer loss, respectively, the leaching of PCL-based plasticizers ranged from 2%-14%.

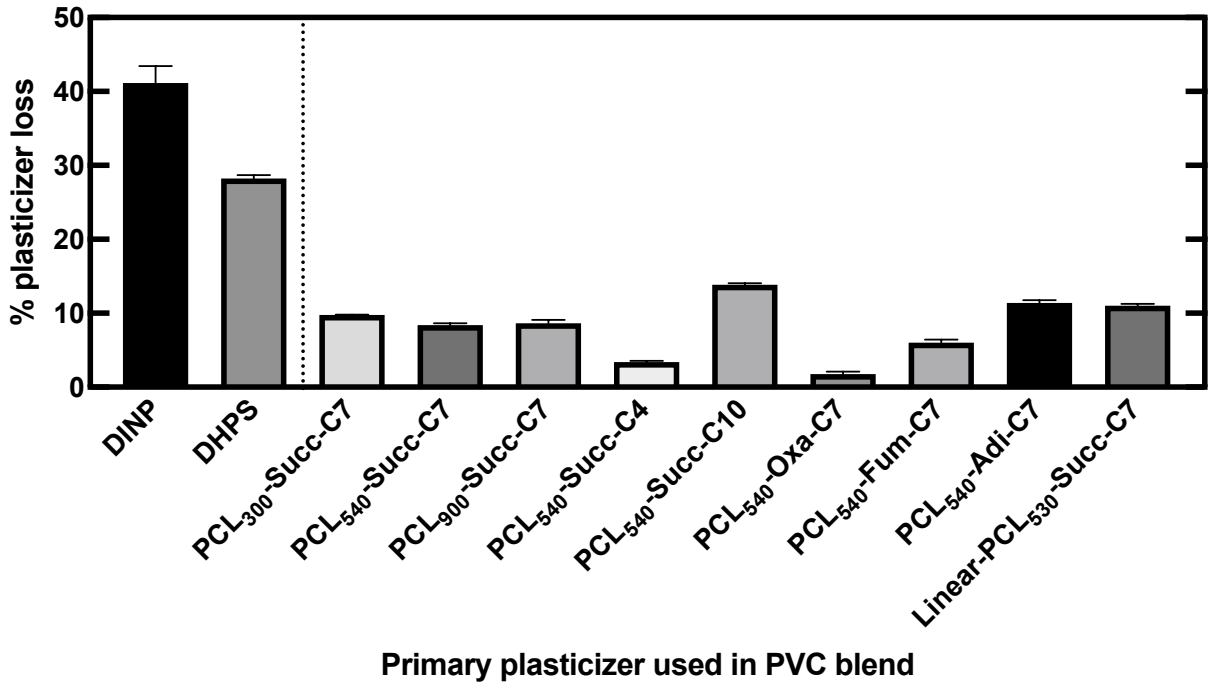

Figure 5-6. Leaching of plasticizers into hexanes after 6 hrs at 50°C. All blends were prepared with a plasticizer concentration of 55 phr.

5.5.4.1 Effect of molecular weight

There was no difference in the amount of plasticizer leached between PCL_{300}-Succ-C7, PCL_{540}-Succ-C7 and PCL_{900}-Succ-C7, with all three plasticizers exhibiting leaching between 8%-10%, all significantly lower than DINP and DHPS. The three plasticizers are comprised of a PCL-triol core (of increasing molecular weights of 300, 540, and 900 g/mol), a succinic acid linker and a 7-carbon alkyl cap (see Figure 5-1 C). However, despite their differences in molecular weight, these three analogs displayed similar leaching behavior. This finding conflicts with previous studies of PCL-based plasticizers, which describe a noticeable effect of molecular weight on plasticizer leaching [32]. That being said, in previous studies, this trend had been investigated and established over a broad range of molecular weights (between 1300-4000 g/mol), whereas our studied range was much narrower (900-1500 g/mol). In line with this, we suspect that had we investigated a broader range of molecular weight species, this trend would have been apparent.

5.5.4.2 Effect of alkyl chain length

A significant effect of alkyl chain length on migration was found when comparing PCL_{540}-Succ-C4, PCL_{540}-Succ-C7, and PCL_{540}-Succ-C10 (molecular structures shown in Figure 5-1 C). We observed a trend of increasing leaching (3%, 8%, and 14%) with increasing alkyl chain length from four to ten carbons ($p < 0.01$, see Figure 5-6). All three additives contained an identical PCL-triol core, with M_n of 540 g/mol, and a succinic acid linker; however, they were synthesized using alcohols of increasing chain lengths (i.e., butanol, heptanol, decanol). Many plasticization theories exist to describe how plasticizers function when combined with a polymer matrix. The reader may refer to reviews on the subject by Daniels and Czogala et al. [51,52]. All of these theories imply existing chemical interactions between the plasticizer and polymer. Here, we focused on the electrostatic interactions (e.g. Van der Waals forces, specifically dipole-dipole interactions) between the polar groups of the plasticizer, such as the carbonyl groups of the ester linkages, and the polarized carbon-chlorine bond on the polymer. While interactions between the polar groups on the plasticizer and the chlorine atoms of PVC allow the plasticizer to remain associated with the polymer and prevent exudation, the non-polar aliphatic segments of the plasticizer act as spacers to effectively push away from the polymer matrix, acting as lubricants for the polymer chains, as suggested by the lubricity theory of plasticization. A balance between polar and non-polar groups is required in order for a plasticizer to exhibit high permanence and function effectively. The increase in leaching with alkyl chain length is likely the result of a decrease in the relative proportion of polar groups on the plasticizer, which provide strong points of interaction with the polymer through the formation of solvating dipoles on the PVC chain [2,51]. Thus, having longer non-polar aliphatic functional groups on the plasticizer means that fewer points of attraction exist between polymer and plasticizer, resulting in increased migration. This agrees with previously reported findings for dibenzoate, succinate, maleate, and monoglyceride plasticizers that report lower migration of plasticizers with shorter alkyl chain groups [53, 54].

5.5.4 3 Effect of acid type

Similarly, a significant effect of the dicarboxylic acid on migration resistance was observed ($p < 0.01$, see Figure 5-6), with increasing leaching with the increasing length of aliphatic group within the acid. All four structures, PCL_{540}-Oxa-C7, PCL_{540}-Succ-C7, PCL_{540}-Fum-C7, and PCL_{540}-Adi-

C7, are comprised of two ester functional groups, with differing carbon chain lengths between the esters. PCL_{540}-Oxa-C7, which is made from oxalic acid, the smallest dicarboxylic acid, is comprised of two adjoining esters with no aliphatic group between them and exhibited the lowest leaching of the four plasticizers at 2%. Conversely, PCL_{540}-Adi-C7, made from adipic acid, which contains two carboxylate groups separated by four methylene groups, has the longest aliphatic linker of the four plasticizers, and exhibited the highest leaching at 11%. There was no statistical difference in the amount of plasticizer leached between PCL_{540}-Succ-C7 and PCL_{540}-Fum-C7, which demonstrated 6-8% leaching, and both contain two linking carbons. Succinic acid, which contains a C-C single bond is simply the saturated analog of fumaric acid which contains a C=C double bond. While previous studies have reported differences between the performance of some fumarate and succinate plasticizers due to the stiffness imparted by the fumarate double bond [41, 43], this does not appear to play a significant role in their resistance to migration. The use of different acids modifies the ratio of polar to non-polar groups in each plasticizer, with an increase in the ratio of non-polar groups (i.e., longer aliphatic chains) corresponding to higher levels of leaching, which is consistent with the trend observed for the different alkyl capping groups.

5.5.4.4 Effect of branching

Finally, the effect of branching on migration resistance was investigated using linear-PCL-$Succ_{530}$-C7 (Figure 5-1 C). All of the other PCL-based additives in this study were synthesized from a PCL-triol core, resulting in a three-armed star structure, while linear-PCL-$Succ_{530}$-C7 was synthesized from a PCL-diol, resulting in a linear structure. Leaching of the linear analog was compared to PCL_{540}-Succ-C7 and PCL_{300}-Succ-C7 since all three additives were synthesized from an oligomeric PCL core, succinic acid, and heptanol, and have similar molecular weights. We found no significant difference between the leaching of linear-PCL-$Succ_{530}$-C7 and the two branched analogs, with all three additives leaching between 8-11%. These findings support previous results that found no correlation between the degree of branching of PCL-based plasticizers on leaching [33].

5.6 Conclusion

We established that a family of oligomeric PCL-based additives can be used as primary plasticizers for PVC. We demonstrated their synthesis using a solvent-free approach. All of the additives functioned comparably to DINP and DHPS as primary plasticizers. Specifically, elongation at break of blends produced with the PCL-based additives were found to be equivalent to blends produced with DINP and DHPS. Similarly, the tensile strengths of blends produced with the additives were found to be comparable to the DINP blend, with only the fumarate-based PCL_{540}-Fum-C7 exhibiting a statistically higher tensile strength compared to DHPS. Generally, increasing additive concentration resulted in higher elongation at break, confirming the ability to modify PVC material properties by varying the concentration of plasticizer in the blends. Similarly, T_g decreased with increasing additive concentration, verifying that the additives contribute to the reduction of T_g of PVC, as is commonly seen with other plasticizers. T_g values were found to be between those of blends prepared with DINP and DHPS. No significant effects of molecular structure on mechanical or thermal properties were found. Leaching tests determined that all of the PCL-based additives demonstrated significantly improved migration resistance compared to DINP and DHPS. Carbon chain length of the additives, controlled through the use of different carboxylic acid and alcohol reagents, was found to have the greatest effect on leaching, while molecular weight and branching did not have significant effects in the ranges studied. Plasticizers made with shorter chained alcohols and acids, such as PCL_{540}-Succ-C4 and PCL_{540}-Oxa-C7, exhibited the lowest leaching while those made with higher chained alcohols and acids, such as PCL_{540}-Succ-C10 and PCL_{540}-Adi-C7, exhibited the highest leaching. Therefore, we established a new application for additives that were previously used for surface defect removal by showing that they can also be used as primary plasticizers with low leachability.

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6

Conclusions and Original Contributions

6.1 Summary of conclusions and outlook

Some plastic additives, like phthalates, are pervasive environmental contaminants that have been shown to have negative health effects in humans and animals. With global plastic production on the rise and with growing recognition of the accumulating impacts of plastics on the environment in the long term, it is important to take great care in the design of new additives to replace the problematic compounds that are currently available. In this thesis, a new family of additives was developed for PVC that prevented the formation of surface defects during calendering, demonstrated good plasticization performance, and significantly reduced leaching compared to traditional phthalate plasticizers.

Chapter 3 presented a guiding framework based on the principles of green chemistry for developing new, safe plasticizers. The importance of the design choices made early in the development of new chemicals was emphasized along with a review of the experimental techniques that can be used to evaluate green plasticizers. The use of design heuristics, predictive models, and chemical toxicological databases were suggested as starting points in the development of biodegradable, non-toxic, and permanent plasticizers.

Chapter 4 presented a new family of additives that were designed using the principles outlined in Chapter 3. The additives were designed to include an oligomeric PCL core structure since PCL had previously been found to be highly compatible with PVC, non-toxic, biodegradable, and was expected to exhibit lower leaching compared to traditional plasticizers due to its oligomeric nature. The incorporation of heptyl succinate groups was based on previous research showing them to be

non-toxic, biodegradable, and effective plasticizers. In Chapter 4, we established that these additives were extremely effective at removing gas check surface defects during PVC calendering. Their broad range of efficacy, from concentrations as low as 8 phr up to 55 phr, was established. Additive viscosity was found to influence polymer melt viscosity, and was identified as an important factor in preventing the defects from forming. The hypothesis that the unique molecular arrangement consisting of a PCL core, diester linker, and alkyl chain cap was able to prevent defects was confirmed by showing that the "building blocks" alone, PCL and DHPS, were ineffective in preventing gas checks. Future work investigating the relationship between calendering process parameters and surface defects produced on films made with these additives will be important in identifying their capacity for usage in industrial applications.

Chapter 5 built on the results of Chapter 4 with an evaluation of the family of additives as primary plasticizers for PVC. This study showed that all of the additives behaved effectively as primary plasticizers, displaying elongation at break and tensile strength values comparable to DINP and DEHP. The relationship between plasticizer concentration and mechanical and thermal properties was investigated, showing increasing elongation and decreasing T_g with increasing plasticizer concentration. This confirmed that polymer material properties could be tuned by altering plasticizer concentration which is important for their industrial applicability. This study also included experiments based on the principles of green chemistry outlined in Chapter 3. All of the additives were shown to have significantly lower leaching into hexanes compared to DINP, confirming that designing an oligomeric additive would improve permanence. The structure of the additives was found to have a significant effect on their leaching properties, with additives having shorter carbon chain lengths exhibiting the lowest amount of leaching. This structure-property study contributed to advancing the understanding of polymer-plasticizer interactions for this system. Additive synthesis was modified to eliminate the use of solvent and incorporate bio-based reagents. These results provide an excellent foundation from which to expand the study of these additives, however more work is required to assess plasticizer performance for specific applications, and, importantly, to validate the hypothesis of sustainability by testing toxicity and biodegradation.

These findings are significant since they represent the first reported use of chemical additives to control gas check surface defects. Previous research focused exclusively on eliminating defects by controlling calendering processing parameters. Having a chemical means to control surface defects would provide compounders with greater flexibility in controlling the final product properties, without having to alter the process. For example, operators would not be limited to modifying parameters such as nip distance, which directly correlates to final film thickness, to avoid the occurrence of gas checks.

Furthermore, these findings demonstrate that designing additives to meet sustainability criteria does not require the sacrifice of performance or functionality. Starting at the earliest stages of development of the new additives, we looked to previous studies of biodegradation and toxicity to guides us in the molecular design and choice of reagent for the new additives. We showed that these additives were highly effective as primary plasticizers, with comparable performance to phthalates, and significantly lower leaching, in addition to being effective in eliminating surface defects.

The multiple functionalities established for these additives include being: (i) general purpose plasticizer; (ii) specialty plasticizer to reduce leaching; and (iii) processing-aid to remove surface defects. Since the potential to use these additives in wide concentration ranges was demonstrated, the results of this thesis provide manufacturers with flexibility to choose how to incorporate them into existing formulations. It is also significant that the efficacy of the additives was established under realistic processing conditions, using techniques such as extrusion, milling, and calendering. Some existing plasticizer research involves the use of solvent casting, which is only practical at the laboratory scale while extrusion is the preferred method for high-throughput production [40,41,42,43]. Thus, our findings also have important implications for the commercial viability of these additives.

Taken together, the work in this thesis shows that the newly developed PCL additives can serve as low-leaching replacements for phthalate plasticizers and as processing aids to improve film surface finish during PVC calendering. While these additives were designed with principles of sustainability in mind, it should be noted that validation of toxicity and biodegradation properties

is still required. This will be a crucial step before the commercialization of these additives. It is also important to note that the effectiveness of these additives was only investigated with PVC. PVC, a petroleum sourced polymer, is known to persist in the environment and contribute to the accumulating plastic waste on our planet. This raises questions about the long-term implications of ongoing research to improve PVC blends. While developing additives that are less harmful to humans, animals, and ecosystems is of highest importance, will making safer plasticizers that allow PVC products to be marketed as "green" or "phthalate-free" ultimately discourage manufacturers from switching to more sustainable plastics? Will making PVC easier to process into films delay its replacements with other polymers in the future? Will greener compounds serve an important step in transitioning to long-term sustainability, or will they hinder it? There are no simple answers to these questions, however it is important to approach issues of sustainability with a wide and long-term view. We hope that this work can serve as an important starting point for future research into the development of fully bio-sourced and biodegradable plastics. A holistic approach that combines functionality and sustainability, and considers optimization with respect to several parameters, can serve as a template for others seeking to develop safer, industrially useful chemicals.

6.2 Original contributions

The work presented in this thesis consist of a number of significant contributions to the body of literature on safer PVC additives. The original contributions arising from this work include the following:

1) **A new family of PCL-based additives was developed using the principles of green chemistry to drive the design of the new additives.** This involved the production of eleven new additives and the adaptation of their synthesis to eliminate the use of solvent and incorporate bio-based reagents.

2) **The effectiveness of the new additives in eliminating gas check surface defects during PVC calendering was demonstrated.** This marked the first reported use of chemical

additives to treat gas check surface defects. These results established a concentration range for defect removal and showed that there were no significant differences in the ability to eliminate surface defects based on molecular weight, acid group, or alkyl chain length within the additives studied.

3) **Additive viscosity and blend viscosity were shown to play a crucial role in the ability to remove surface defects.** The results demonstrated that all of the additives that were successful in eliminating surface defects had higher viscosities than those that were not. However, viscosity alone was necessary but not sufficient in describing the effect, since additives of high viscosity that had poor compatibility with PVC could not achieve defect removal.

4) **The structural features of the PCL-based additives that contribute to their effectiveness were identified.** The arrangement of a PCL core, with a diester linker, and alkyl chain cap was found to be uniquely suited to removing gas check surface defects.

5) **The efficiency of the additives as primary plasticizers was established.** The additives were shown to have comparable efficacy to existing plasticizers, DINP and DEHP, at concentrations ranging from 40 phr to 55 phr.

6) **Mechanical and thermal properties of the additives blended with PVC were reported for the first time.** The results showed decreases in T_g and increases in elongation at break with increasing plasticizer concentration.

7) **The PCL-based additives were shown to significantly reduce leaching.** The results showed that all of the additives reduced leaching into hexanes compared to DINP, with additives with shorter carbon chain lengths resulting in the lowest leaching.

6.3 Recommendations for future work

Based on the conclusions of the work in this thesis, the following recommendations for areas for further investigation are made:

1) The relationship between polymer flow properties and calendering processing parameters (such as nip distance, speed of rotation, temperature) with the addition of the PCL-based additives should be investigated. This data can be used to model the formation of the gas checks during calendaring with respect to the thermodynamics and mechanical stresses in the system. This would be useful in gaining a better understanding of how these additives can be used industrially to optimize the processing of these additives into PVC formulations.

2) Experiments should be performed to validate the hypothesis of sustainability that was based on the molecular structure of the PCL-based additives. Specifically: (a) Conduct biodegradation tests to identify degradation metabolites and establish the stability of metabolites; (b) Conduct toxicity tests, including *in vitro* and *in vivo* testing of the parent compounds and any stable metabolites, should they be discovered; and (c) Expand the preliminary leaching tests into different media, specifically aqueous media, which will have important environmental implications for the fate of the additives after disposal of the plastic products.

3) The compatibility of the newly-developed additives with PVC should be evaluated experimentally. This will provide a fundamental understanding of the polymer-additive interactions.

4) Rapid, standardized techniques to validate claims of sustainability should be developed. In Appendix A, exploratory results of a radiocarbon analysis on DHPS and its reactants are summarized, showing which chemicals were bio-sourced and which were petroleum-sourced. This approach can be expanded to test the other PCL-based additives.

5) The use of the PCL-based additives with biopolymers, such as poly(hydroxyl alkanoate) (PHA) and poly(lactic acid) (PLA), should be investigated with the goal of developing an entirely biodegradable plastic blend with comparable performance to PVC blends. Specifically, this should include (a) Determining whether the additives are compatible with the biopolymers; (b) Investigating their efficacy as plasticizers; (c) Investigating their ability to eliminate surface defects; and (d) Testing their biodegradability and toxicity.

6) Life cycle assessments should be conducted to compare the sustainability of different plasticizers and polymer-plasticizer systems. This would take into account the overall energy requirements from raw material extraction to waste disposal and provide a broader picture of the sustainability of using certain additives are compared to others.

7

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Appendix

Appendix A1. Radiocarbon dating report

While many alternative plasticizers have reportedly been developed using renewable resources, it is possible for chemicals with identical chemical structures to be synthesized using fossil fuel-derived starting materials. As such, we wanted verify the bio-based content of a given plasticizer. Thus we designed a preliminary study in collaboration with Dr. Peter Douglas to use radiocarbon analysis to determine the amount of biomass carbon content in a plasticizer in order determine whether it was synthesized using bio-based or petroleum-based reagents.

Diheptyl succinate plasticizer was tested in this study along with the reactants, succinic acid and heptanol, used to make the plasticizer. The results of the radiocarbon dating, presented in table A-1, show that this analysis could be used to identify a fully bio-based plasticizers as well as a plasticizer synthesized from a combination of bio-based and petroleum-based starting materials.

The following report was provided by the A. E. Lalonde AMS Laboratory in Ottawa, Canada. The sample preparators were Sarah Murseli and Christabel Jean, and the AMS analyst was Dr. Xiao-Lei Zhao.

Sample Processing

Sample pretreatment techniques and definitions of media codes can be found in Crann et al. (2017). For more information about the equipment used for sample preparation, please see St- Jean et al. (2017) and Crann et al. (2017). Both manuscripts can be found at www.ams.uottawa.ca/Research.

Reporting of Data

In this analysis report, we have followed the conventions recommended by Millard (2014).

Radiocarbon Analysis

Radiocarbon analyses are performed on a 3MV tandem accelerator mass spectrometer built by High Voltage Engineering (HVE). $^{12,13,14}C^{+3}$ ions are measured at 2.5 MV terminal voltage with Ar stripping. The fraction modern carbon, $F^{14}C$, is calculated according to Reimer et al. (2004) as the ratio of the sample $^{14}C/^{12}C$ ratio to the standard $^{14}C/^{12}C$ ratio (in our case Ox-II) measured in the same data block. Both $^{14}C/^{12}C$ ratios are background-corrected and the result is corrected for spectrometer and preparation fractionation using the AMS measured $^{13}C/^{12}C$ ratio and is normalized to δ13 C (PDB). Radiocarbon ages are calculated as $-8033\ln(F^{14}C)$ and reported in 14 C yr BP (BP=AD 1950) as described by Stuiver and Polach (1977). The errors on 14C ages (1σ) are based on counting statistics and $^{14}C/^{12}C$ and $^{13}C/^{12}C$ variation between data blocks. We do not report δ13 C as it is measured on the AMS and contains machine fractionation.

D14C (defined as per mil Depletion or Enrichment Relative to Standard Normalized for Isotope Fractionation) is calculated as: (F14C – 1) · 1000

Δ14C (defined as the absolute amount of 14C in the sample in the year it was measured) is calculated as: (F14C·e(1950-y)/8267) – 1) · 1000

Please note: If Year of Collection "z" and Measurement "y" are not the same, multiply by e(y-z)/8267

Table A-1. Radiocarbon results. Material codes and protocols are described in Crann et al. (2017).

Lab ID	Submitter ID	Material	Mat code[a]	^{14}C yr BP	±
UOC 6527	DHPS (bio SA + bio hep)	plasticizer	D	>Modern	–
UOC 6528	DHPS (bio SA + bio hep)	plasticizer	D	>Modern	–
UOC 6529	DHPS (petroleum-based SA + bio hep)	plasticizer	D	1876	27
UOC 6530	Bio SA	Succinic acid	D	>Modern	–
UOC 6531	Petroleum-based SA	Succinic acid	D	43989	930
UOC 6532	Bio hep	alcohol	D	>Modern	–

References

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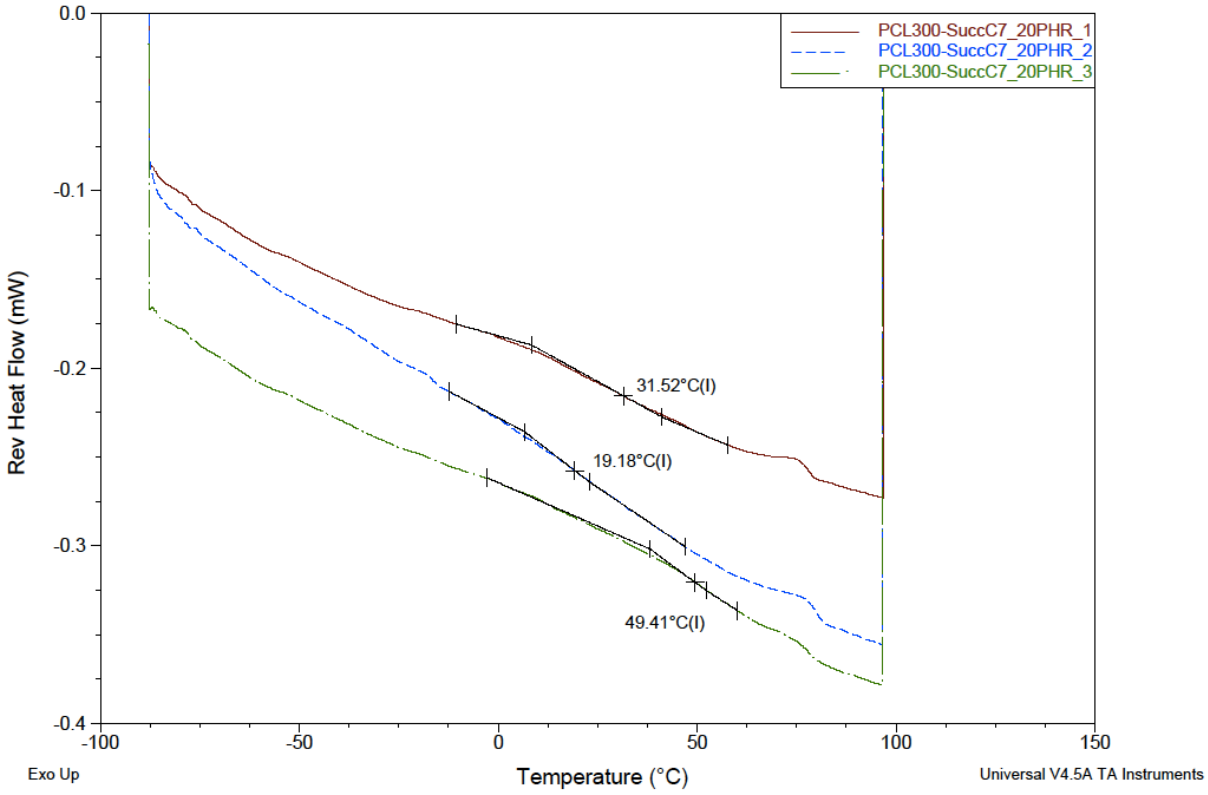
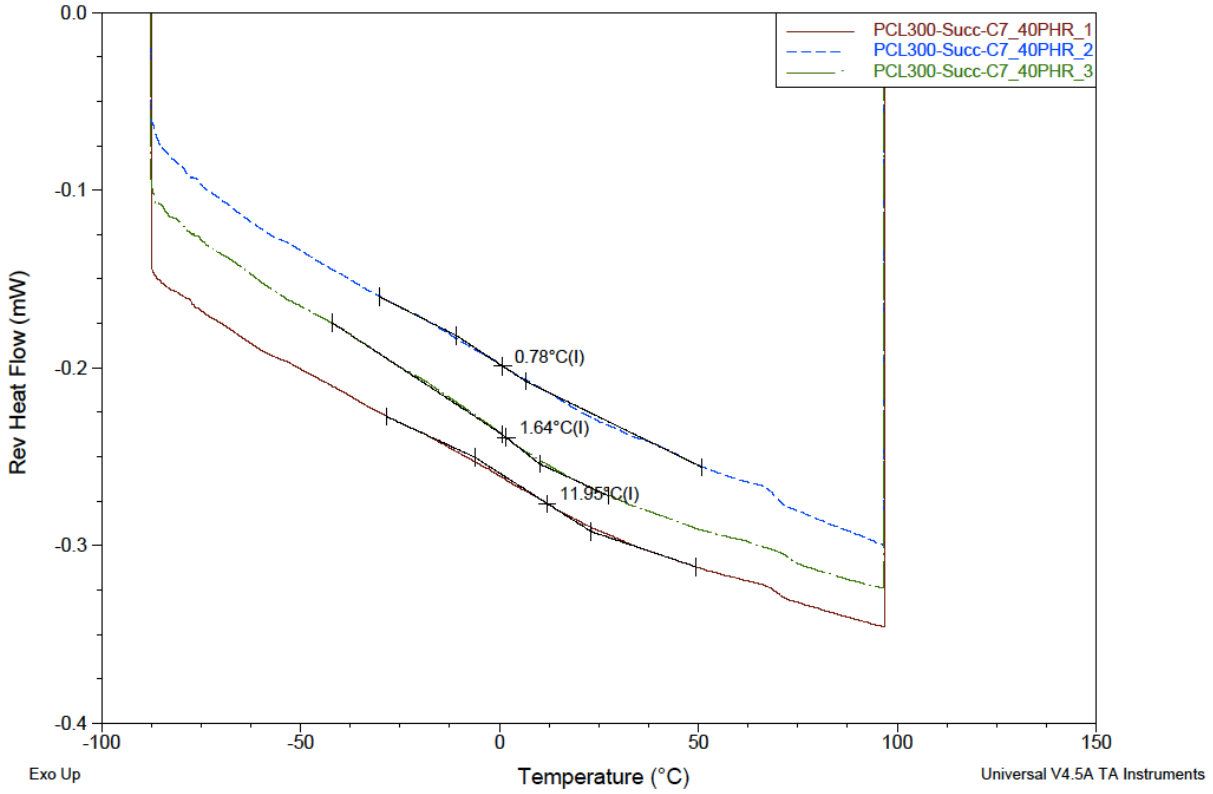
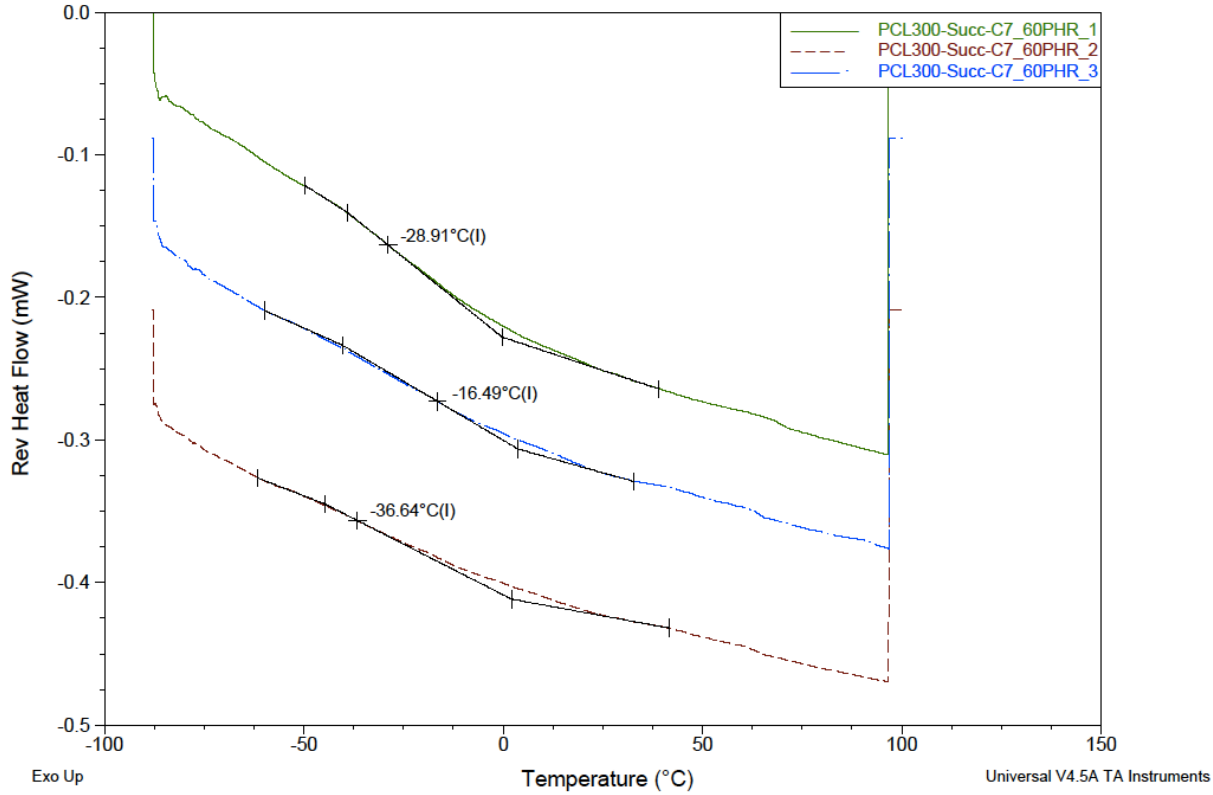
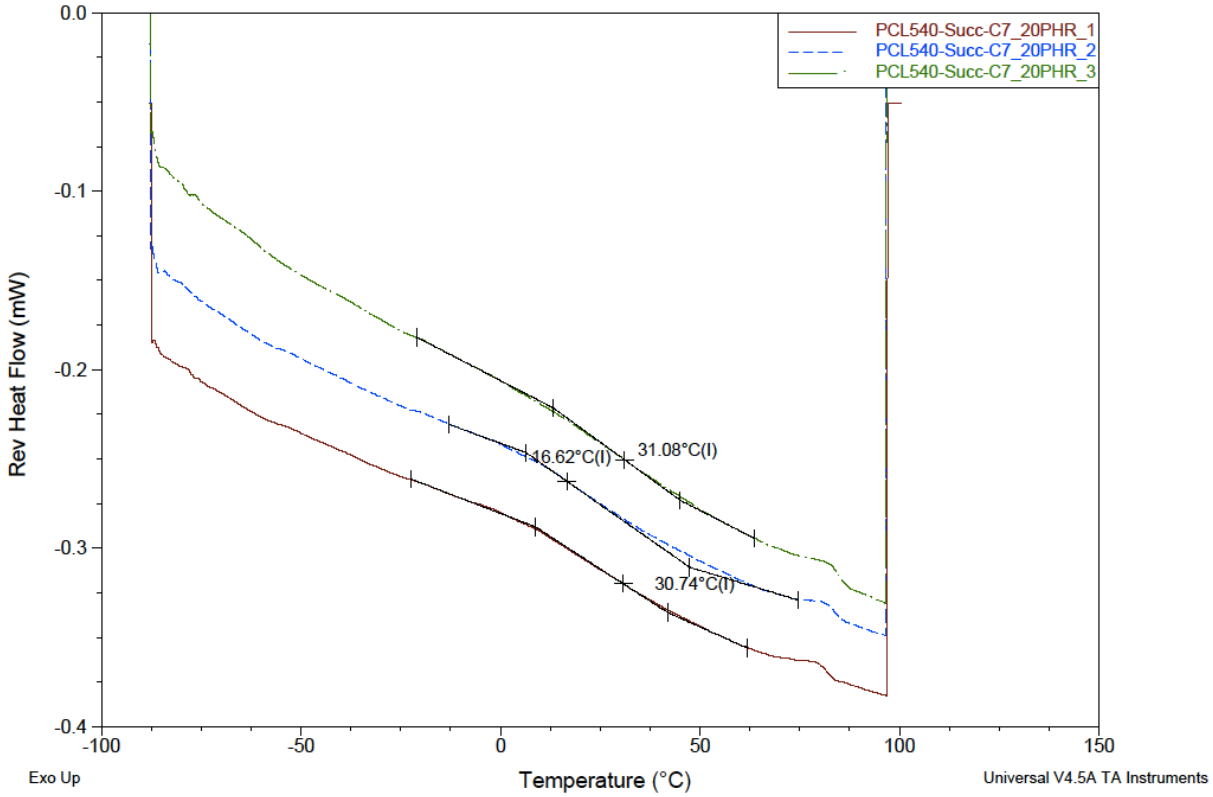
Appendix A2. Differential Scanning Calorimetry Curves

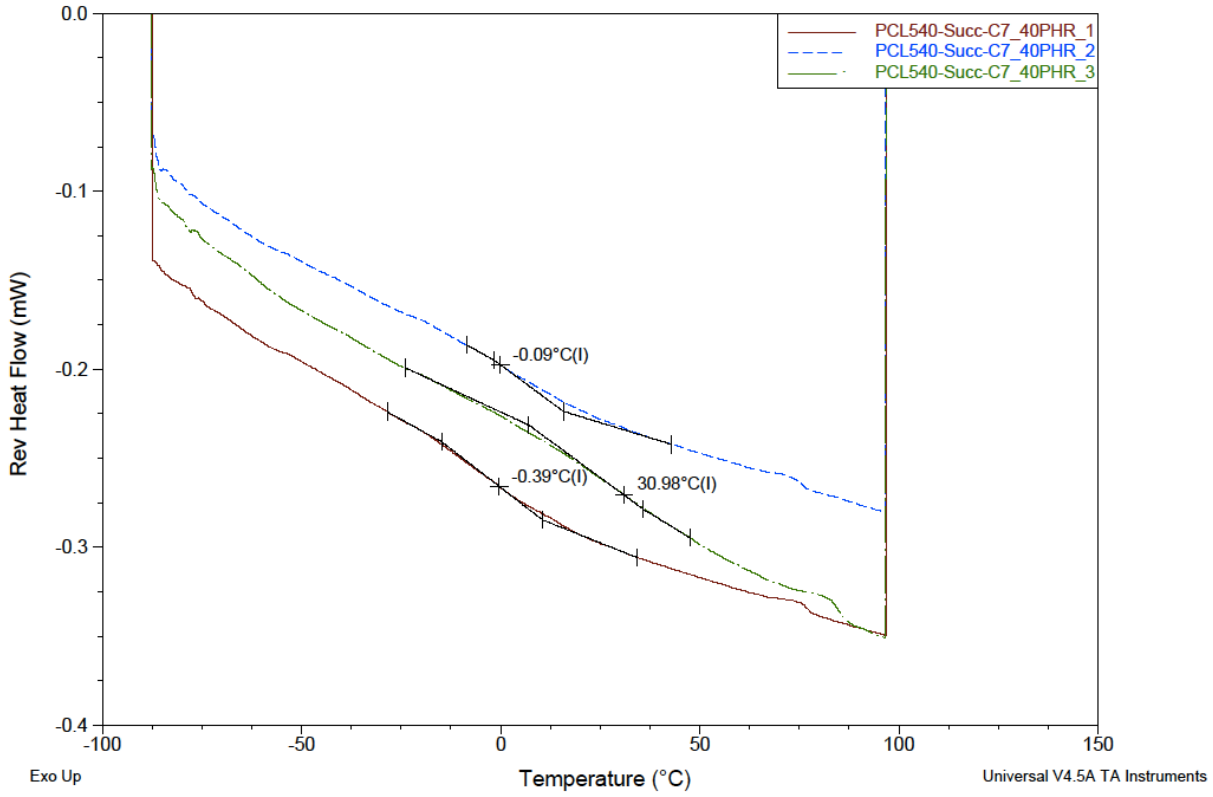
The following DSC curves appeared as Supporting Information with the article *Poly(ε-caprolactone)-based additives: plasticization efficacy and migration resistance*.

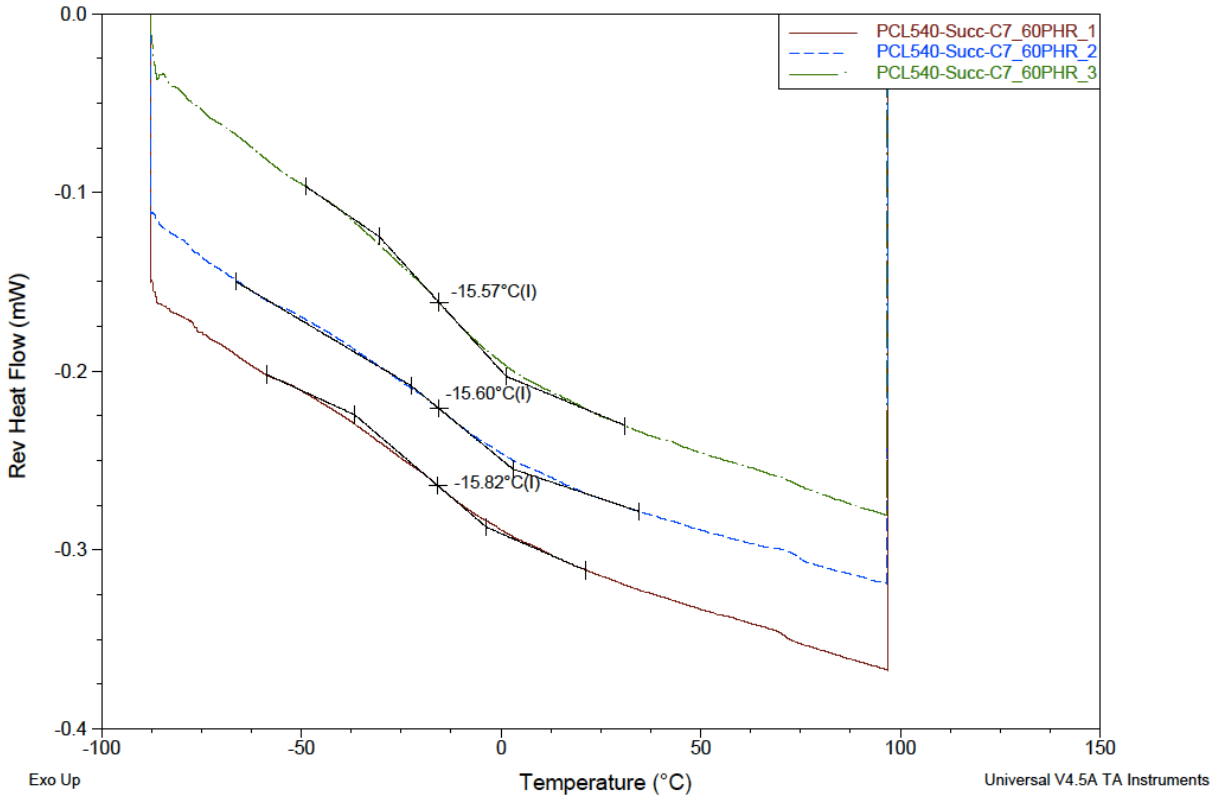


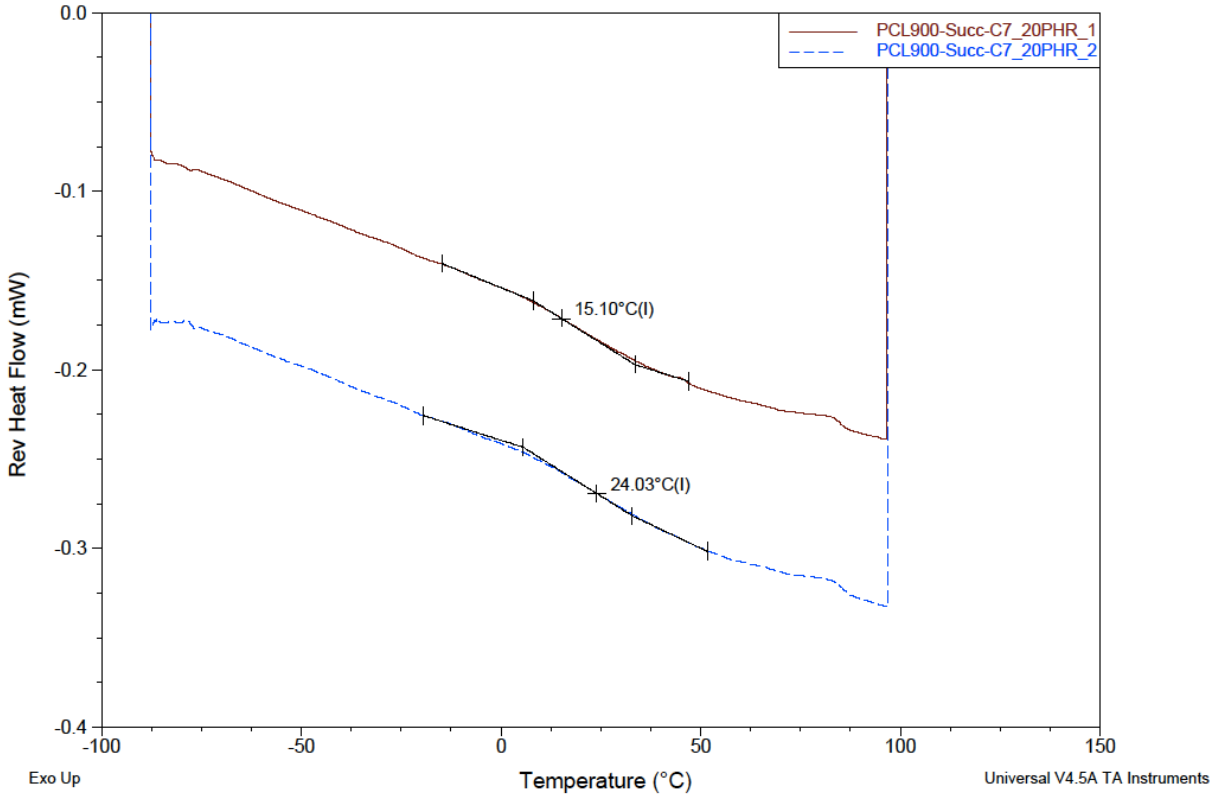

PCL300-Succ-C7_40PHR_1
PCL300-Succ-C7_40PHR_2
PCL300-Succ-C7_40PHR_3
0.78°C(I)
1.64°C(I)
11.95°C(I)
Rev Heat Flow (mW)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

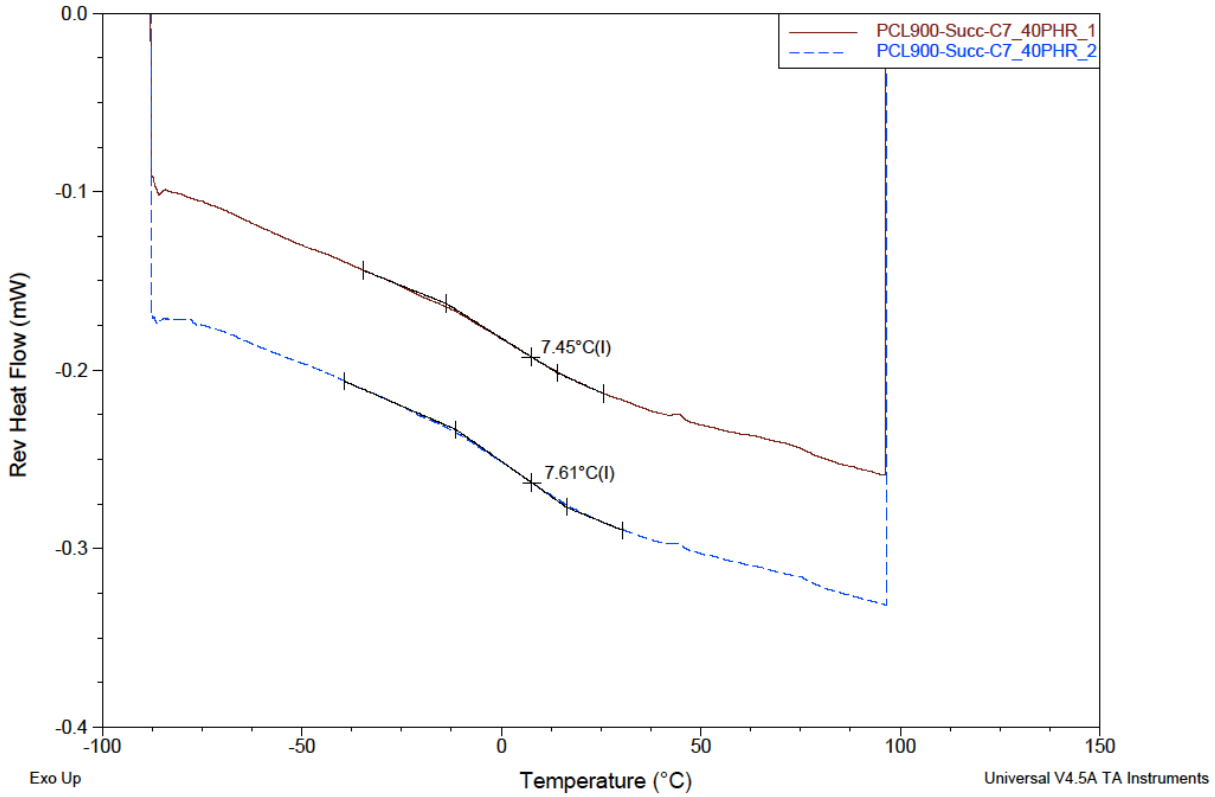

PCL300-Succ-C7_60PHR_1
PCL300-Succ-C7_60PHR_2
PCL300-Succ-C7_60PHR_3
-28.91°C(I)
-16.49°C(I)
-36.64°C(I)
Rev Heat Flow (mW)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

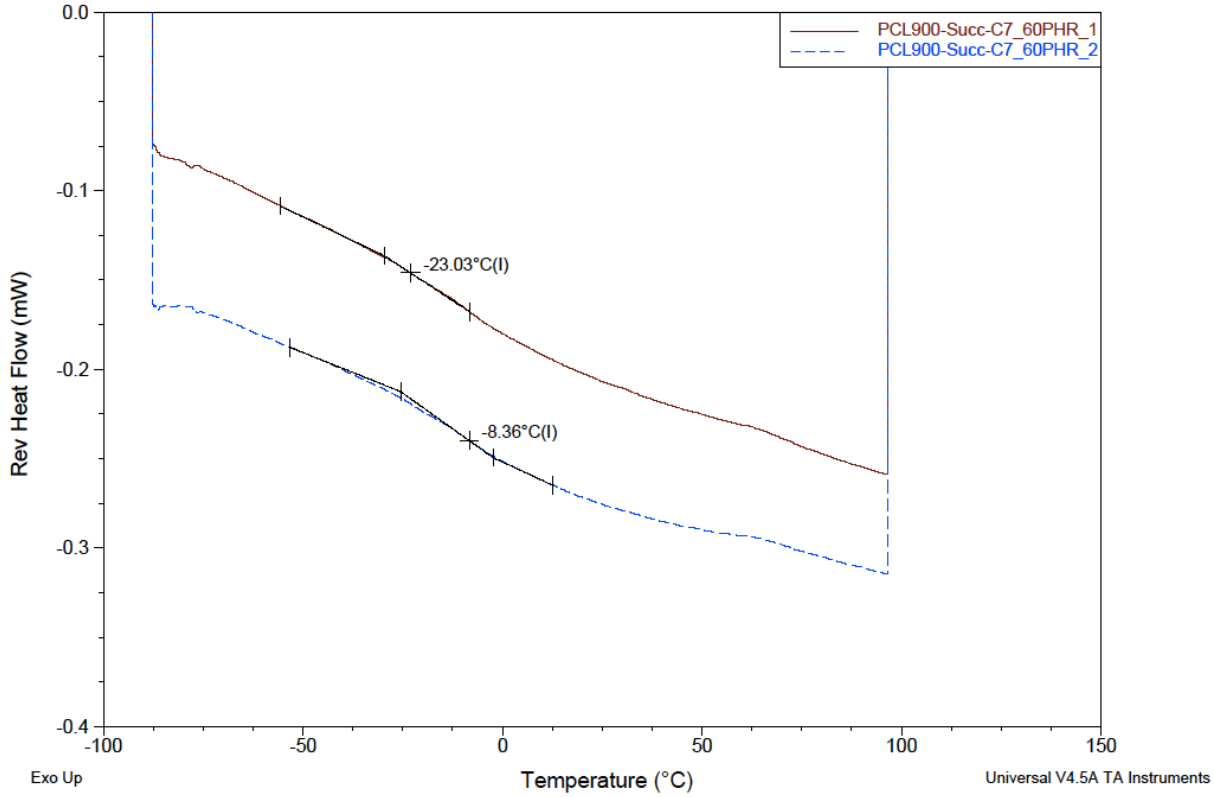

PCL540-Succ-C7_20PHR_1
PCL540-Succ-C7_20PHR_2
PCL540-Succ-C7_20PHR_3
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
16.62°C(I)
31.08°C(I)
30.74°C(I)
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

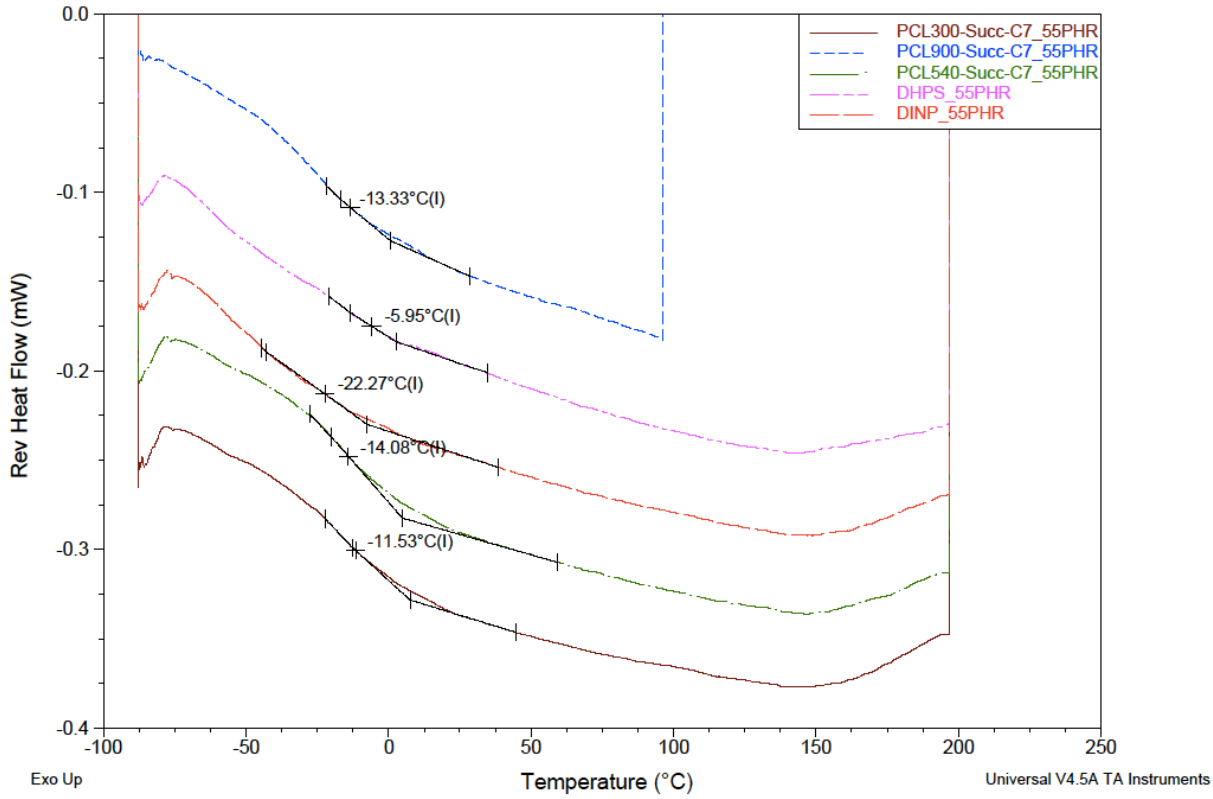

PCL540-Succ-C7_40PHR_1
PCL540-Succ-C7_40PHR_2
PCL540-Succ-C7_40PHR_3
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
-0.09°C(I)
-0.39°C(I)
30.98°C(I)
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments


PCL540-Succ-C7_60PHR_1
PCL540-Succ-C7_60PHR_2
PCL540-Succ-C7_60PHR_3
-15.57°C(I)
-15.60°C(I)
-15.82°C(I)
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments


PCL900-Succ-C7_20PHR_1
PCL900-Succ-C7_20PHR_2
15.10°C(I)
24.03°C(I)
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments


PCL900-Succ-C7_40PHR_1
PCL900-Succ-C7_40PHR_2
7.45°C(I)
7.61°C(I)
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments


PCL900-Succ-C7_60PHR_1
PCL900-Succ-C7_60PHR_2
-23.03°C(I)
-8.36°C(I)
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments


PCL300-Succ-C7_55PHR
PCL900-Succ-C7_55PHR
PCL540-Succ-C7_55PHR
DHPS_55PHR
DINP_55PHR
-13.33°C(I)
-5.95°C(I)
-22.27°C(I)
-14.08°C(I)
-11.53°C(I)
Rev Heat Flow (mW)
0.0
-0.1
-0.2
-0.3
-0.4
-100
-50
0
50
100
150
200
250
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

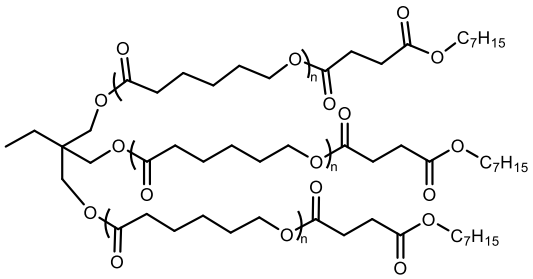
Appendix A3. Expanded methodology

Solvent-free synthesis of PCL-based additives

General synthesis of star-shaped additives

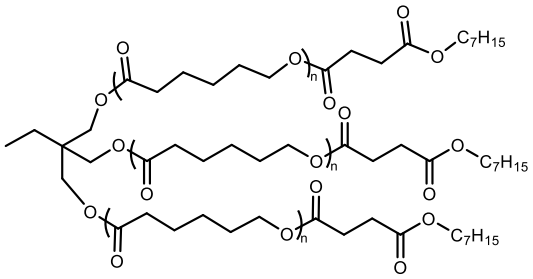
Synthesis of the star-shaped PCL analogs was performed via a two-step reaction sequence in a single three-necked round-bottom flask fitted with a Dean-Stark trap and a condenser. PCL triol (1 equiv.) was massed directly into a 1 L round-bottom flask followed by the addition of the appropriate diacid (3 equiv.). The mixture was stirred at room temperature for 5 minutes. Catalytic amounts of sulfuric acid (0.15 equiv.) were then added dropwise to the reaction mixture and the mixture was heated at 110 °C and stirred continuously. Once at temperature, nitrogen gas was bubbled through the mixture for 90 min to promote the removal of water. The mixture was then cooled to room temperature. The appropriate alcohol (3 equiv.) was then added to the same flask equipped with the Dean-Stark apparatus and condenser, and the mixture was re-heated to 110 °C, at which point nitrogen gas was again bubbled through the mixture for 90 min. The mixture was then cooled to room temperature. The resulting viscous oils were not further purified.

i. PCL_{300}-Succ-C7:



The compound was prepared according to the general procedure described above using 169.5 g (0.565 mol, 1 equiv.) of PCL-triol (M_n = 300), 200.2 g (1.695 mol, 3 equiv.) of succinic acid, 196.9 g (1.695 mol, 3 equiv.) of *n*-heptanol, and 4.7 mL (0.088 mol, 0.15 equiv.) of H_2SO_4 to afford 495.5 g (0.554 mol) of PCL-300-C7 as a viscous light orange oil in a 98% yield.

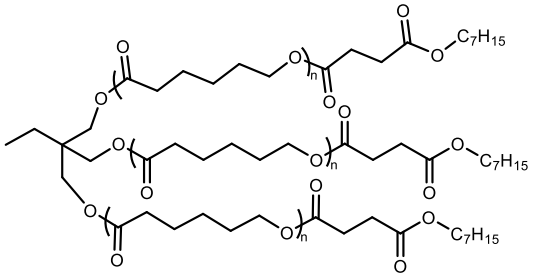
ii. PCL_{540}-Succ-C7:



The compound was prepared according to the general procedure described above using 240.0 g (0.444 mol, 1 equiv.) of PCL-triol (M_n = 540), 157.5 g (1.333 mol, 3 equiv.) of succinic acid, 154.9 g (1.333 mol, 3 equiv.) of *n*-heptanol, and 3.7 mL (0.069 mol, 0.15 equiv.) of H_2SO_4 to afford 489.3 g (0.431 mol) of PCL-540-C7 as a viscous brown oil in a 97% yield.

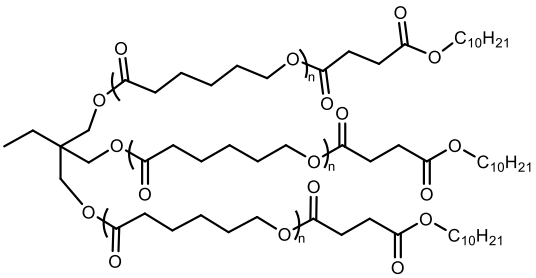
IR (neat) v = 2929.81, 2858.36, 1731.23, 1152.17 cm^{-1}.

iii. PCL_{900}-Succ-C7:



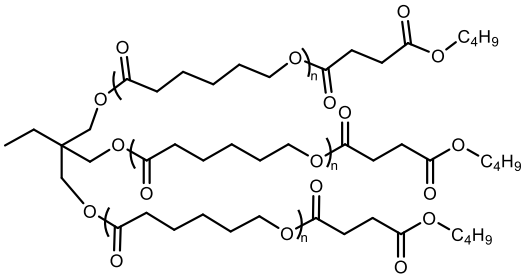
The compound was prepared according to the general procedure described above using 310.0 g (0.344 mol, 1 equiv.) of PCL-triol (M_n = 900), 122.0 g (1.033 mol, 3 equiv.) of succinic acid, 120.1 g (1.033 mol, 3 equiv.) of *n*-heptanol, and 2.8 mL (0.054 mol, 0.15 equiv.) of H_2SO_4 to afford 499.4 g (0.334 mol) of PCL-900-C7 as a viscous yellow oil in a 97% yield.

iv. PCL_{540}-Succ-C10:



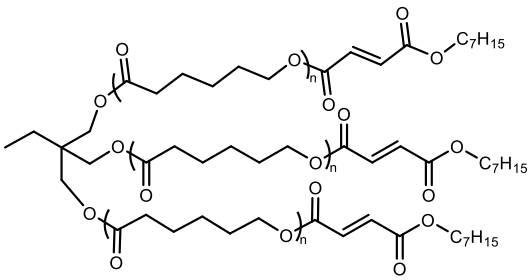
The compound was prepared according to the general procedure described above using 86.40 g (0.160 mol, 1 equiv.) of PCL-triol (M_n = 540), 56.68 g (0.480 mol, 3 equiv.) of succinic acid, 75.97 g (0.480 mol, 3 equiv.) of 1-decanol , and 1.27 mL (0.024 mol, 0.15 equiv.) of H_2SO_4 to afford 195.7 g (0.155 mol) of PCL-540-C10 as a viscous brown oil in a 97% yield.

v. PCL_{540}-Succ-C4:



The compound was prepared according to a procedure similar to that described above, using 108 g (0.200 mol, 1 equiv.) of PCL-triol (M_n = 540), 70.85 g (0.600 mol, 3 equiv.) of succinic acid, 1.6 mL (0.030 mol, 0.15 equiv.) of H_2SO_4 and 44.47 g (0.600 mol, 3 equiv.) of 1-butanol to afford 199.7 g (0.198 mol) of PCL-540-C4 as a viscous brown oil in a 99% yield. For the synthesis of PCL_{540}-Succ-C4, 250 mL of Benzene was used as a solvent and added in the first step of the reaction. After completion of the reaction, the product was concentrated to remove Benzene and afford the star-shaped analog as a viscous oil.

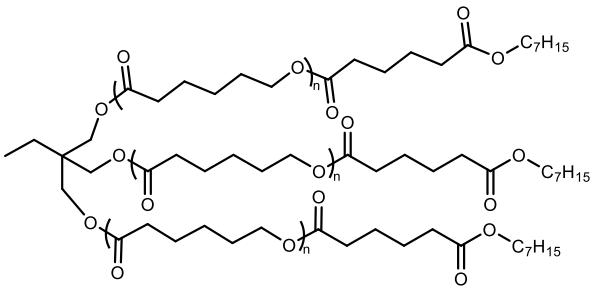
vi. PCL_{540}-Fum-C7:



The compound was prepared according to the general procedure described above using 99.90 g (0.185 mol, 1 equiv.) of PCL-triol (M_n = 540), 64.40 g (0.555 mol, 3 equiv.) of fumaric acid, 64.49 g (0.555 mol, 3 equiv.) of *n*-heptanol, and 1.48 mL (0.027 mol, 0.15

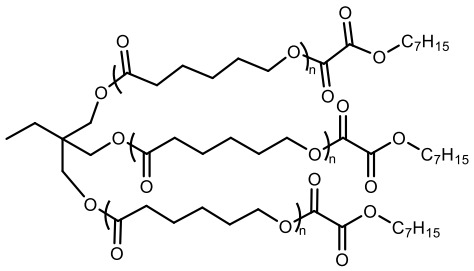
equiv.) of H_2SO_4 to afford 204.6 g (0.181 mol) of PCL-Fumarate-C7 as a viscous brown oil in a 98% yield.

vii. PCL_{540}-Adi-C7:



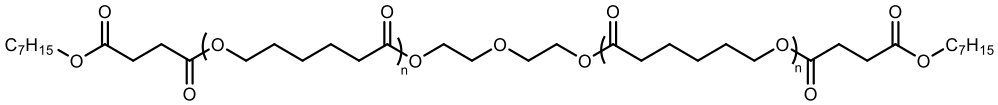
The compound was prepared according to the general procedure described above using 91.80 g (0.170 mol, 1 equiv.) of PCL-triol (M_n = 540), 74.53 g (0.510 mol, 3 equiv.) of adipic acid, 59.26 g (0.510 mol, 3 equiv.) of *n*-heptanol, and 1.36 mL (0.026 mol, 0.15 equiv.) of H_2SO_4 to afford 198.9 g (0.163 mol) of PCL-Adipate-C7 as a viscous brown oil in a 96% yield.

viii. PCL_{540}-Oxa-C7:



The compound was prepared according to the general procedure described above using 114.38 g (0.212 mol, 1 equiv.) of PCL-triol (M_n = 540), 57.21 g (0.635 mol, 3 equiv.) of oxalic acid, 73.83 g (0.635 mol, 3 equiv.) of *n*-heptanol, and 1.69 mL (0.032 mol, 0.15 equiv.) of H_2SO_4 to afford 216.1 g (0.206 mol) of PCL-Oxalate-C7 as a viscous brown oil in a 97% yield.

ix. Linear-PCL530-Succ-C7



The compound was prepared according to the general procedure described above using 114.48 g (0.216 mol, 1 equiv.) of PCL-diol (M_n = 530), 51.01 g (0.432 mol, 3 equiv.) of

succinic acid, 50.2 g (0.432 mol, 3 equiv.) of *n*-heptanol, and 1.7 mL (0.032 mol, 0.15 equiv.) of H_2SO_4 to afford 190.1 g (0.205 mol) of Linear PCL-C7 as a viscous orange oil in a 95% yield.