Synthesis and Application of Poly(caprolactone)-based Additives for Gas Check Prevention during the Calendering of Poly(vinyl chloride) Films

by

Luis Fernando Alvarez de la Garma

Department of Chemical Engineering

McGill University

Montreal, Quebec, Canada

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

Abstract

Poly(vinyl chloride) (PVC) is the third most produced polymer globally. In its pure form, PVC exhibits brittleness, hardness, and inflexibility. Consequently, plasticizers are needed to enhance the polymer's flexibility, processability, and a reduction in the glass transition temperature (T_g). Phthalate-based plasticizers, owing to their commendable plasticization efficacy and cost-effectiveness, have dominated the market. Unfortunately, these plasticizers are susceptible to leaching from the polymer matrix, persisting in ecosystems and precipitating adverse effects on both the environment and human health. Phthalate-based plasticizers are recognized as endocrine disruptors and a source of toxic metabolites. Acknowledging these concerns, there is a need to develop more sustainable and bio-based alternatives to traditional plasticizers.

In this thesis, a biodegradable alternative plasticizer derived from poly(caprolactone), chemically bonded to a diacid reagent (succinic acid) and capped with hydrophobic end-groups (n-heptanol), was studied as a plasticizer in the calendering process of PVC films. This strategy aimed to mitigate the leaching of phthalate plasticizers. Unexpectedly, the introduction of PCL-based additives exhibited a unique behavior, effectively preventing surface defects caused by air entrapment in PVC calendering films, commonly referred to as gas checks. Gas checks are known to impact film properties, leading to perforations during the subsequent thermoforming process.

The examination of calendering PVC films involved the evaluation of physical and chemical properties. Three distinct molecular weight variants (540, 900, and 2000 g/mol) of PCL-based additives were incorporated as secondary plasticizers at concentrations of 5 and 10 parts per hundred of resin (phr), alongside DINP as the primary plasticizer at 55 phr. This investigation aimed to elucidate the connection between PCL-based additives and the prevention of gas checks. Surprisingly, the mechanical properties of the films remained largely unaffected by the PCL-based additives. This is in contrast to the thermal and rheological properties assessed through dynamic mechanical thermal analysis, which exhibited notable changes. However, despite these alterations, a discernible correlation between thermal and rheological properties was not identified.

The evaluation of chemical properties included the titration of end-groups to determine the acid value of PCL-based additives. Interestingly, a correlation emerged between the acid value and the occurrence of gas checks in the PVC calendering films. Higher acid values were associated with a reduced number of gas checks, indicating that the effectiveness of the additive in preventing gas checks diminishes as hydrolysis occurs, removing the capping groups. This insight underscores the role of acid value as a crucial factor influencing the efficacy of PCL-based additives in mitigating gas checks during the calendering process.

Résumé

Le poly(chlorure de vinyle) (PVC) est le troisième polymère le plus produit dans le monde. Sous sa forme pure, le PVC est fragile, rigide et démontre un manque de flexibilité. Par conséquent, des plastifiants sont nécessaires pour améliorer la flexibilité du polymère, sa facilité de traitement et la réduction de la température de transition vitreuse (T_g). Les plastifiants à base de phtalates ont dominé le marché en raison de leur efficacité de plastification et de leur rentabilité. Malheureusement, ces plastifiants sont susceptibles d'être lessivés de la matrice polymère, de persister dans les écosystèmes et d'avoir des effets néfastes sur l'environnement et la santé humaine. Les plastifiants à base de phtalates sont reconnus comme des perturbateurs endocriniens et une source de métabolites toxiques. Compte tenu de ces préoccupations, il est nécessaire de mettre au point des solutions de remplacement des plastifiants traditionnels qui seront plus durables et d'origine biologique.

Dans cette thèse, un plastifiant alternatif biodégradable dérivé du poly(caprolactone), chimiquement lié à un réactif diacide (acide succinique) avec des groupes terminaux hydrophobes (n-heptanol), a été étudié en tant que plastifiant dans le processus de calandrage de films en PVC. Cette stratégie visait à atténuer la lixiviation des plastifiants à base de phtalates. De manière inattendue, l'introduction d'additifs à base de PCL a présenté un comportement unique, empêchant efficacement les défauts de surface causés par l'emprisonnement de l'air dans les films de calandrage en PVC, communément appelés "gas checks". Ces derniers sont connus pour avoir un impact sur les propriétés des films, entraînant des perforations au cours du processus de thermoformage qui s'ensuit.

L'examen du calandrage de films de PVC impliquait l'évaluation des propriétés physiques et chimiques. Trois variantes distinctes de poids moléculaire (540, 900 et 2000 g/mol) d'additifs à base de PCL ont été incorporées comme plastifiants secondaires à des concentrations de 5 et 10 parties par cent de résine (phr), aux côtés du DINP comme plastifiant primaire à 55 phr. Cette étude visait à élucider le lien entre les additifs à base de PCL et la prévention des "gas checks". Il est surprenant de constater que les propriétés mécaniques des films n'ont pas été affectées par les additifs à base de PCL. Cela contraste avec les propriétés thermiques et rhéologiques évaluées par l'analyse thermique mécanique dynamique, qui a montré des changements notables. Cependant, malgré ces modifications, aucune corrélation perceptible entre les propriétés thermiques et rhéologiques n'a été identifiée.

L'évaluation des propriétés chimiques comprenait le titrage des groupes terminaux afin de déterminer l'indice d'acidité des additifs à base de PCL. Il est intéressant de noter qu'une corrélation est apparue entre l'indice d'acidité et l'apparition de défauts dans les films de calandrage en PVC. Des indices d'acidité plus élevés ont été associés à un nombre réduit de défauts, ce qui indique que l'efficacité de l'additif dans la prévention des "gas checks" diminue au fur et à mesure que l'hydrolyse se produit, éliminant les groupes terminaux. Cette constatation souligne le rôle de l'indice d'acidité en tant que facteur crucial influençant l'efficacité des additifs à base de PCL dans l'atténuation des défauts d'étanchéité au cours du processus de calandrage.

Acknowledgments

First and foremost, I would like to thank Professors Richard Leask, Milan Maric and Jim Nicell for giving me the opportunity to study under their supervision. Even though they didn’t know me, they trusted that I was the correct person to work on this project. Their guidance, enormous patience, and support were crucial for me to achieve this important goal in my personal and professional life.

I would also like to thank all the members in the Leask and Maric labs for all the help and advice they kindly provided me when I requested, as well as all my friends who supported me on this new experience and for all the new friendships I made during the journey.

Finally, I am forever grateful to my family for always supporting and believing in me in every decision I have taken in my life. Without their love, encouragement and prayers, this could not have been possible.

Table of Contents

List of Figures

List of Tables

Contribution of Authors

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

Luis F. Alvarez, Kushal Panchal, Jim A. Nicell, Richard R. Leask, Milan Maric. (2023). "Investigation of Additives for Preventing the Formation of Gas Checks during Calendering of Poly(vinyl chloride) calendaring Films." (Chapter 4).

Luis Alvarez planned and performed the experiments in this article and was responsible for interpreting and analyzing the results other than the calendering which was carried out by Kushal Panchal at our industry collaborators facility. Luis Alvarez also prepared and edited the manuscript. My co-authors, Richard Leask, Jim Nicell, and Milan Maric were responsible for funding acquisition, supervision of the research project, and editing of the manuscript. Kushal Panchal contributed to the experimental design and editing of the manuscript.

1. Introduction

The total production of plastics worldwide was approximately 367 million tonnes in 2020 and it is increasing every year [1]. Poly(vinyl chloride) (PVC), is one of the most used polymers throughout the world [2] due to its outstanding properties and low production cost [3], approximately, the production of PVC is close to 57 million tonnes per year. After polyethylene and polypropylene, PVC is the most produced plastic, representing 13% of the global plastic production [1, 4]. Some of the properties that make this plastic so versatile are its wear and chemical resistance, flame retardancy, freedom in design, recyclability, UV-stability among others [1, 5]. PVC is used in rigid and soft applications, the later of these representing 60% of total products made [6].

Alone, PVC is a brittle and hard material. Therefore, additives called plasticizers are blended with PVC to improve its flexibility and to enable its processing [7]. Plasticizers are essential to the plastic industry and are present in PVC blends in proportions as high as 80% weight of the final product [8]. However, many of these small molecules are not chemically bound to the plastic [9] and have been shown to have adverse effects on ecosystems and human health [10] thereby becoming an important, and fairly persistent, source of environmental contamination [11]. Some of the most widely used plasticizers are phthalate based [12] and include bis(2-ethylhexyl) phthalate (DEHP), bis(isononyl) phthalate (DINP) and bis(isodecyl) phthalate (DIDP). Countless studies have shown that phthalates are toxic, and prone to migrate from PVC blends into the environment where they can act as endocrine disruptors, interfering with hormone regulation and reproduction in living organisms [6, 7, 9].

Plasticizers are additives that are used to modify the properties of polymer blends, decreasing the glass transition temperature, and making the plasticized polymer easier to handle owing to its being softer and more flexible [13]. It is estimated that around 90% of plasticizers worldwide are used to make with PVC processable [14, 15, 16]. Lately, alternative plasticizers have been researched and developed with the goal of reducing the environmental damage caused by phthalate plasticizers, while being functionally equivalent [17]. Some of these new additives are derived from agricultural feedstocks like, fruits, cereals, trees or even waste agricultural material [6].

Plasticized PVC films or sheets are typically produced by calendering, a process that consists of passing melted polymer through two heated and pressured rolls to produce a film with a controlled and specific thickness [18]. Unfortunately, surface defects are often produced in calendered films, affecting the mechanical properties of the films and their quality, resulting in delays in production lines, waste of resources, or even the disposal of poor-quality films [18]. In particular, gas check defects, which are seen as pits of shallow tears in the surface of the film, are believed to be caused by the incorporation of air into the films, during calendering [19]. Preventing the formation of the gas checks typically requires a high skill level of the operational staff to tweak the process operating parameters in order to avoid the entrapment of air [20].

Recent research has focused on in the development of a series of sustainable sourced plasticizers [21]. Work has lately focused on investigating the migration resistance of a plasticizer based on a biodegradable polyester, poly(caprolactone) (M_n = 540 g/mol), with succinic acid and capped with n-heptanol: abbreviated as PCL_{540}-Succ-C_7 [21]. It was discovered that this PCL-based additive, when mixed with PVC even at low concentrations as a secondary plasticizer, can prevent gas check surface defects in the production of PVC films/sheets in a lab scale calendering process [21, 20]. However, while having great potential to improve the production of PVC films using calendering, thereby avoiding some of the negative impacts mentioned above, the mechanism by which gas checks are prevented remains unknown. It is hypothesized that both chemical and physical effects of the PCL-based additives, lead to the prevention of the gas checks.

Three chemical additives of different PCL core molecular weight (540, 900 and 2000 g/mol) were tested. Beyond investigating the effect of PCL molecular weight, we investigate the effect of acid value, since could be directly related to gas checks. The foundation of this connection lies in the chemical relationship between the plasticizer and the matrix. As observed earlier, incorporating a capping molecule to the PCL core was crucial to transform the molecule into an effective gas check preventer, unlike PCL alone which was proved ineffective preventing gas checks.

Therefore, the focus of this research reported herein was to explore how this PCL-based additive reduces gas checks. Specifically, this research investigates the impact of PCL molecular weight on gas check suppression while monitoring mechanical, thermal, and chemical properties of plasticized PVC blends in order to develop insights into how PCL-based additives prevent gas checks. In particular a series of PCL-based additives that prevent the formation of gas checks were synthesized from different molecular weights PCL cores, i.e., 540, 900 and 2000 g/mol. The impact of molecular weight of the additive on the chemical and physical properties of blends were measured by quantifying the acid value, mechanical, thermal, and rheological properties and compared the number of gas checks obtained in plasticized PVC films during the calendering process. The scope of the work includes the following:

1. Assessment of the effectiveness of the PCL-based additives at molecular weights of 540, 900 and 2000 g/mol, at concentrations of 5 and 10 parts per hundred of resin (phr) to establish a relation to the reduction or prevention of gas checks in PVC plasticized calendering films.
2. Evaluation of the chemical and physical properties of the calendered films with PCL-based additives samples at molecular weights of 540, 900 and 2000 g/mol.
3. Evaluation of the chemical and physical properties of extruded PVC with the PCL-based additives as a primary plasticizer at concentrations of 20, 40 and 60 phr.

This thesis is presented in a series of chapters including this Introduction (Chapter 1), followed by a Literature Review (Chapter 2), and Materials and Methods (Chapter 3). Chapter 4 consists of a manuscript that has been prepared for submission for publication and includes all, results, discussion, and the main conclusions arising from this work. Chapter 5 consist of measured physical properties of PVC extruded samples with PCL-based additives at concentrations of 20, 40 and 60 phr. A general discussion of the results along with suggestions for future work is detailed in Chapter 6 followed by Chapter 7 where a high-level summary of the conclusions of the work and their implications is detailed.

2. Literature Review

2.1 Poly(vinyl chloride)

PVC was first used in the early 19th century when V. Regnault made the first vinyl halides [22, 23], but it was not until the early 20th century when Fritz Klatte found that it was possible to synthesize vinyl chloride monomer by reacting acetylene with hydrochloric acid and then produce PVC via free-radical initiation [24] (see Figure 2.1). In the mid-20th century PVC was shown to be an effective replacement for rubber [14]. From this point onwards, many developments have been made to enhance production processes and properties and develop new applications of PVC [14].

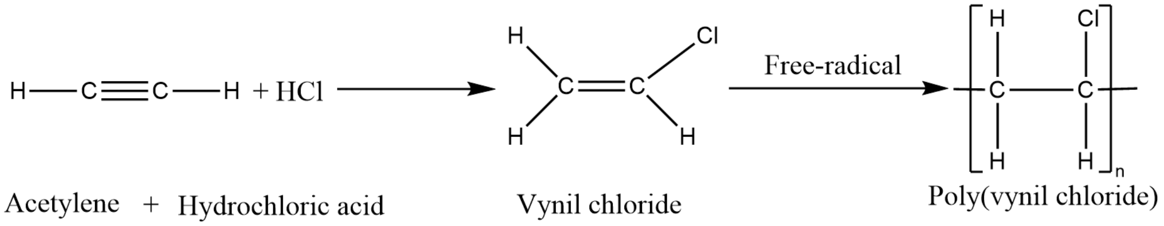

FIGURE 2.1 Synthesis of poly(vinyl chloride).

Currently PVC is mainly produced through three different polymerization processes: i.e., suspension polymerization, emulsion polymerization and bulk polymerization. Suspension polymerization encompasses approximately 80% of the production of PVC worldwide due to the efficiency of the process and affordable production cost [25].

Despite the advantages associated with the use of plasticized PVC, it also has some key disadvantages, mainly arising from the fact that the most widely used plasticizers are phthalate-based and these plasticizers tend to leach out from PVC, because they are not covalently bound to the polymer matrix [9]. Some studies concerning this problem have shown that these plasticizers have highly adverse effects on ecosystems and human health and are currently found throughout the environment [26]. Because of these effects, various jurisdictions worldwide (e.g. Japan, Canada, European Union, Argentina, Brazil) [27], have taken steps in recent years to restrict, ban or phase out their use in many products. Consequently, this has triggered the need to develop alternative plasticizers that avoid these negative effects, while being sustainably sourced from renewable feedstocks [28].

2.2 Plasticizers

Through a mechanism called plasticization [29], low molecular weight chemical additives called plasticizers are used to modify polymer properties, such as increasing flexibility to make them less brittle, improve processability, and ductility. Specifically, in terms of material properties, these substances are expected to reduce the modulus, glass transition temperature, tensile strength, hardness among others, while at the same time increasing flexibility, elongation at break, etc. [12]

The origins of plasticizers dates to 1862 when Alexander Parkes manufactured the first man-made plasticizer, however, it was not until the late 19th century that the concept known today as "plasticizer" was established [12]. The first additives used as plasticizers were natural camphor and castor oil but produced unsatisfactory results. In the early 20th century, phthalic acid esters became the most widely used and produced family of plasticizers and remain the largest class of plasticizers in use in the 21st century [12]. The most widely used phthalate-based plasticizers are, bis(2-ethylhexyl) phthalate (DEHP), bis(isononyl) phthalate (DINP) and bis(isodecyl) phthalate (DIDP), since these plasticizers have excellent plasticization performance and a, relatively low cost compared to other similar additives [30]. Figure 2.2 shows the synthesis of phthalate-based plasticizers by the esterification of phthalic anhydride and alcohol.

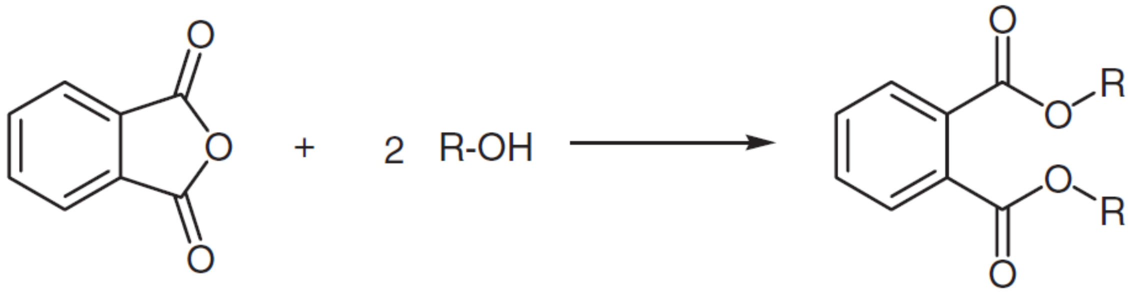

FIGURE 2.2 Synthesis of phthalate-based plasticizers [12].

Since then, many scientists have developed theories to explain how these chemical compounds work. The three leading theories accepted by the polymer science community are: the Lubrication Theory, the Gel Theory, and the Free Volume Theory [12].

Lubrication theory (1940) is based on the idea that in the presence of a plasticizer, the polymer becomes more flexible due to the diffused plasticizer molecules in the polymer matrix, reducing polymer-polymer interactions and thus, weakening the rigid structure of the polymer [31 ,32]. The gel theory (1944) is based on the hypothesis that the plasticizer interacts with the matrix of the polymer resulting in a weak three-dimensional network thereby increasing flexibility by overcoming external stress [33, 34, 35]. Finally, the free volume theory (1950) postulates that the addition of plasticizers modifies the polymer backbone by adding more end groups and side chains that enable the backbone to move and rotate, thus, improving flexibility in the polymer [36, 37].

Plasticization can arise through two different mechanisms: namely internal plasticization and external plasticization. Internal plasticization is the most complex of these two plasticization processes, since in order to increase the flexibility of the final product, the polymer must be chemically modified to induce chain separation by generating stable chemical bounds [12]. One of the main reasons this plasticization process is less used is because of the high costs of compatible plasticizers [33, 36]. In contrast, through the process of external plasticization, the polymer does not chemically change, because the additive is not chemical bound to the polymer and is just mixed at desirable process conditions [33, 16].

Plasticized polymers can be made of primary and secondary plasticizers. Primary plasticizers are mainly added to a polymer to enhance flexibility, whereas secondary plasticizers (also known as extenders) are other chemical compounds added to the matrix of the polymer, but not with the objective of increasing flexibility, but to improve other properties depending on the application of the polymer [24]. Examples include acrylonitrile-butadiene rubber to increase oil, solvent, and chemical resistance; calcium carbonate to avoid decreased elongation after heat aging; antimony oxide for flame self-extinguishing; and aluminum trihydrate for flame-retardant properties [38].

Traditional plasticizers are considered to be potentially harmful substances due to their toxicological impacts, potential for bioaccumulation, tendency to disrupt endocrine functions and potential carcinogenic effects [39, 40]. Plasticizers are prone to leach out from plastics, leading to their ubiquitous distribution in the environment [26]. According to some studies from the European Union Environmental Risk Assessment, the presence of plasticizers has been found in alarming concentrations, showing these substances do not easily degrade, tend to persist, and contaminate all compartments of the environment (i.e., soil, sediments, water, etc.) for long times [26]. Contamination by plasticizers can lead to several health problems such as, ovarian toxicity [41], endocrine disruption [42], neurotoxicity [42], cytotoxicity [43], DNA damage [43], and metabolic toxicity [44].

The lifespan of plastics is short; for example, it is estimated that 40% of plastics have a service life of less than one month [45]. Thus, recycling has been used as a means of reducing the quantities of these products and prevent them from ending up in the environment [46]. In the last three decades, significant advances in management and recycling have been accomplished [46]. Despite these efforts, most plastic waste still ends up in landfills or is incinerated, resulting in the emission of contaminants such as carbon monoxide (CO) and carbon dioxide (CO_2). Europe and Japan have taken significant steps towards making the recycling process more efficient and to raise awareness of environmental issues associated with plastics. Unfortunately, approximately 50% of plastic waste is still directed to landfill disposal [47].

When plasticizers are lost from the polymer matrix through leaching, the properties of the plasticized polymer are affected, leading to poor performance in the final product [48]. However, leaching can have other very important implications. For examples, in the 1960s, DEHP was found to have leached into blood stored in a PVC blood bag and, in response of this finding, exhaustive research has been done to assess the health risk associated with these chemical compounds [49, 50]. Beyond their use in such medical applications, phthalates are used in many products such as wires, cables, baby-care products, toys, etc. [51]. The latter of these is viewed as significant because children can ingest leached-out plasticizer by putting the toy in their mouth. Consequently, some countries have specifically prohibited the use of phthalate-based plasticizers; for example, Canada, Japan, some states in the United States, among others, have restricted the concentration of these chemical compounds, or even in some products banned their use [52, 53].

The health and environmental risks associated with plasticizers have motivated industry and academia to develop alternative compounds that resist leaching, such as through increasing the molecular weight of the plasticizer which can entangle more thoroughly with the matrix of the polymer. However, these additives are less effective in terms of their functional ability to plasticize polymers [51]. Lately, driven by new regulations and legislation [53], researchers are seeking more sustainable and bio-based plasticizers [28]. Efforts to develop new sustainable plasticizers are urgently needed as the demand for plasticizers continues to grow with an expected demand of 9.5 million tonnes in 2024 [48].

Sustainable and bio-based (or renewably sourced) plasticizers are intended to replace traditional plasticizers. Since these new products are still under research and development, most alternative plasticizers are not used as primary plasticizers, but as secondary plasticizers to improve some of the properties of the polymers [54]. According to market studies, the demand of sustainable plasticizers is forecasted to reach around US$2.68 billion dollars by 2025, which represents a significant increase compared to the US$1.112 billion dollars reached in 2016 [51].

2.3 Calendering

The calendering process is used in a wide number of industries, such as in the manufacture of products such as paper, steel and rubber, among others, which require specific or controlled thicknesses of rolled sheets [55]. Calendering is commonly used in the polymer industry, and consists of heated rolls, spinning in opposite directions at a specific velocity, which press a molten polymer, which are set apart by a “nip distance” to produce the desirable product with specific thickness [18]. This process is pictured in Figure 2.3.

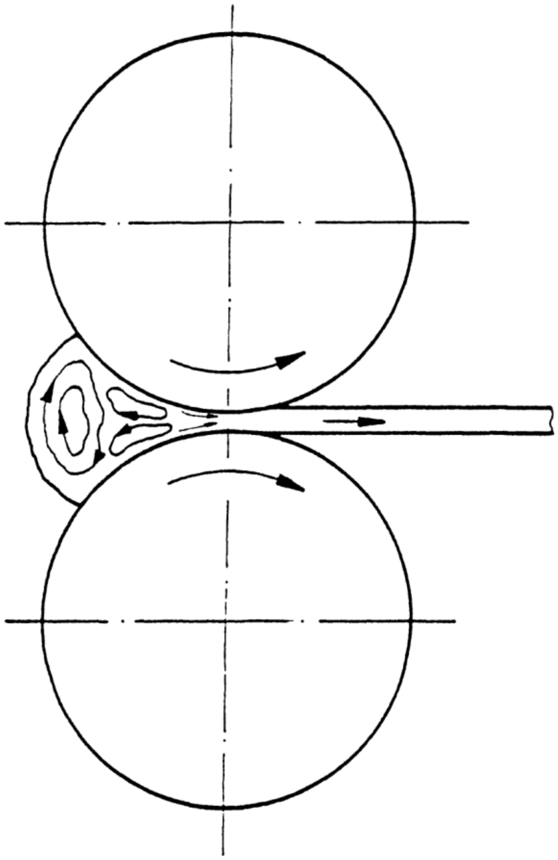

FIGURE 2.3 Molten polymer passing through two heated rolls in the calendering process [56].

The typical number of rolls in a calendering process consists of between three and six rolls, where the thickness of the film is gradually reduced between each roll, and thus the number of rolls used depends on the process and the required thickness. The shear mixing and heat transfer between the rolls is boosted by the friction generated between the rolls in addition to the high temperature of the process [18]. Thus, temperature, velocity and pressure profiles have been studied extensively since 1938 [57].

Various models of this process have been developed and over time these models have become more complex and accurate [58]. Early models tried to explain the thermal effects of the rolls on the processed polymers, as well as attempting to incorporate viscoelastic effects [58, 59]. The assumptions and simplicity of the models limited their application; however, these early studies laid the foundation for more sophisticated modern models which, incorporate viscous dissipation and other effects, provide insight into the pressure profile, and must be solved numerically using methods such as finite element analysis [60].

Models developed prior to 1990 were mainly limited to explaining the calendering process in two dimensions [61]. These models were very useful in explaining at a gross level what was occurring in the calendering process, however, it was not until the 1990s that Luther and Mewes produced and solved a three-dimensional model, providing a more detailed explanation and understanding of this complex process, which aids in our understanding of how different process variables relate to each other [61, 62].

For instance, there are some variables like temperature, velocity, and pressure that are crucial to obtaining high-quality films. High performance heat transfer as well as controlled flow between the rolls is critical to prevent defects on the sheets [55] that lead to poor product quality, delays in production lines, and waste of materials. There are five categories of PVC defects in calendered films [18]:

1. Air bubbles (gas checks): Captured air bubbles that are elongated in the direction of the calender flow between the two rolls [18].
2. V-Shapes: This defect is due to undulating motions occurring in the melt bank between the rolls, the result of this defect is surface thickness irregularities resembling a “V” [63].
3. Mattness: The result of this defect is a small gap in the surface of the film when the film is not in contact with the rolls after leaving the gap between the rolls [18].
4. Dimensional non-uniformities: These dimensional irregularities are differences in the thickness of the films since the rolls can bend due to large separating forces [18].
5. Structural anomalies: These anomalies are because of the crystalline structure change that PVC can exhibit at high temperatures and pressures [18].

This thesis is focused on the entrapment air bubbles termed as gas checks, which affects the properties of the films leading to perforation during the thermoforming process [19]. Gas checks are a common defect in calendered PVC films but are not well understood. In some studies focused on explaining this phenomenon, it has been hypothesized that this problem is related to the pressure in the calendered bank and the velocity of the rolls [19], leading to the supposition that, increasing the pressure and velocity, and reducing the nip distance can prevent the formation of gas checks [19, 64]. However, the disadvantage of preventing the gas checks by modifying the operational conditions is that it requires skilled operators, limits the type of sheet that can be produced (e.g., in thickness) and, even so, this does not guarantee the prevention of such surface defects [20].

Recently, however, a novel and effective method has been developed to prevent the formation of gas checks without modifying the operational conditions in the calender [21]. That is, the use of modified poly(caprolactone) (PCL)-based additives, as a secondary plasticizer has shown an outstanding performance to obtain films free of gas checks. These PCL-based additives, chosen for their biodegradable nature, are modified to ensure compatibility with PVC during the mixing process.

3. Methodology

3.1 Materials

Poly(ε-caprolactone) (PCL) triol of three molecular weights (CAPA 3050, M_n = 540 g/mol; CAPA 3091, M_n = 900 g/mol; CAPA 3201, M_n = 2000 g/mol) of 99% purity were purchased from Ingevity UK Ltd. (UK). Renewable sourced succinic acid (99%) was purchased from Roquette, (Iowa, USA). Sulfuric acid (96%), stearic acid, potassium hydroxide (85%), acetone (99.5%), were purchased from Fisher Scientific (Canada). Renewably sourced n-heptanol (Oleris, 99%) was purchased from Arkema (Pennsylvania, USA). Epoxidized soybean oil was purchased from Galata Chemicals (Louisiana, USA). Unplasticized PVC pellets (K58, product code IH014/G045/AA) were supplied by Solvay Benvic (Chevigny-Saint-Sauveur, France). Isopropanol (>99.99%) was purchased from MilliporeSigma (USA). Phenolphthalein (ACS certified) was purchased from J.T Baker Chemicals (USA). Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), stearic acid (99%), antimony oxide Hi-Tint (99.68%), silica (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.) Stearic acid (99%) was supplied by Canadian General-Tower Limited (CGT; Ontario, Canada). Low molecular weight gas check additive samples for chemical analysis were also supplied by HallStar (Chicago, USA). All chemicals and reagents were used as received without further purification.

3.2 Synthesis of PCL-based additives

The synthesis of the star-shaped PCL-based additives listed in Table 3.1, and all syntheses were performed via a two-step esterification reaction in a single flask. In the first step, 1 stoichiometric equivalent (stoic. equiv.) of PCL triol was massed out into a three-necked round bottom flask, followed by the addition of succinic acid (3 stoic. equiv.) while the mixture was continuously stirred a stirring plate. Catalytic amounts of sulfuric acid (0.156 stoic. equiv.) were then added dropwise to the reaction mixture. The reaction flask was fitted with a Dean-Stark apparatus (to collect generated water from the esterification reactions) and a condenser, then placed on a heating mantle, and heated at 110°C for 90 mins, after which the reaction mixture was cooled to room temperature. In the second step, n-heptanol (3 stoic. equiv.) was added to the same flask equipped with the same Dean-Stark apparatus and condenser and the mixture was reheated to 110°C for 90 mins, after which the reaction mixture was cooled and stored in the fume hood. No purification was done, and all PCL analogs were obtained as viscous oils except for the star-shaped molecule with 2000 g/mol molecular weight for the PCL core. This was a waxy solid at room temperature. The chemical structure of the star shaped PCL-based additive is shown in Figure 3.1.

TABLE 3.1. Synthesized poly(caprolactone) (PCL)-based additives.

PCL additive name	Code	# of PCL branches	Relative M_n (g/mol)
Triheptylsuccinate-terminated poly(caprolactone)	PCL$_{540}$-Succ-C$_7$	3	1000
	PCL$_{900}$-Succ-C$_7$	3	1200
	PCL$_{2000}$-Succ-C$_7$	3	2400

Relative M_n measured with Gel Permeation Chromatography (GPC) relative to linear poly(methyl methacrylate) (PMMA) standard, and HPLC grade THF as an eluent at 40˚C.

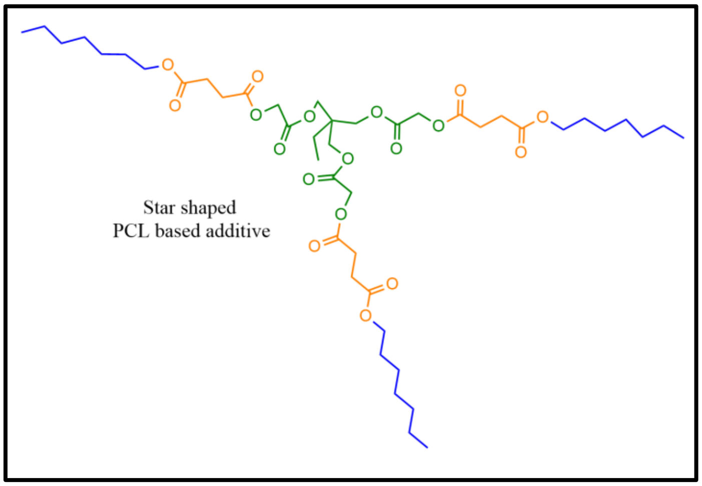

FIGURE 3.1 Poly(caprolactone) (PCL)-based star shaped additives. The green section of the molecule represents the PCL-triol, which is the central part of the molecule, whereas the orange segment represents the succinic acid, and the blue component represents the n-heptanol.

3.3 Gel permeation chromatography

The modified PCL-based additives' molecular weights were analyzed by using gel permeation chromatography (GPC). The number average molecular weight (M_n) was measured using a Waters Breeze instrument and high-performance liquid chromatography (HPLC) grade Tetrahydrofuran (THF) as an eluent at a flow rate of 0.3 mL/min. The GPC had three Waters Styragel HR columns as follows: HR1 which has a molecular weight measurement range of 10^2 to 5×10^3 g/mol; HR2 with a molecular weight measurement range of 5×10^2 to 2×10^4 g/mol; and HR4 with a molecular weight measurement range of 5×10^3 to 6×10^5 g/mol), a guard column, and a refractive index (RI 2414) detector. The columns were heated to 40 ˚C throughout the duration of the analysis. The molecular weights were measured relative to poly(methyl methacrylate) (PMMA) standards. The molecular weights obtained through measurement are relative molecular weights, and achieving absolute values requires universal calibration.

3.4 Film production

Plasticized PVC films were produced by first mixing blend components on a lab-scale two roll mill. A Hartek two-roll mill HTR-300 (D =120 mm, T = 160°C, 45 rpm) was used to melt and mix blend components for 7 mins, starting from the time of film formation on the mill rolls. Secondly, to produce the final films, the resulting milled film was then fed into a lab-scale calender (D = 80 mm, T= 160-170°C, P = 45 psi, 50 rpm) for 1 min and set to achieve a film gauge of 0.4 ± 0.05 mm. All plasticized PVC were made to a final concentration of 55 phr primary plasticizer (DINP), and concentrations of 5 and 10 phr with PCL-based additives as secondary plasticizer. Each blend formulation consisted of 100 phr PVC 70K suspension resin, 55 phr primary 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.

3.5 Counting gas checks

Grids of 7 cm × 7 cm size were used to manually count the gas checks on each film, with four films produced and a grid was made on three sections of each film: top left corner, the middle, and the bottom right corner. The gas checks within each grid were counted and then averaged to obtain the number of gas checks per film. This was done for all four films per blend formulation and then averaged to obtain the number of gas checks per blend formulation. The average number of gas checks was normalized per square meter (m^2) of film.

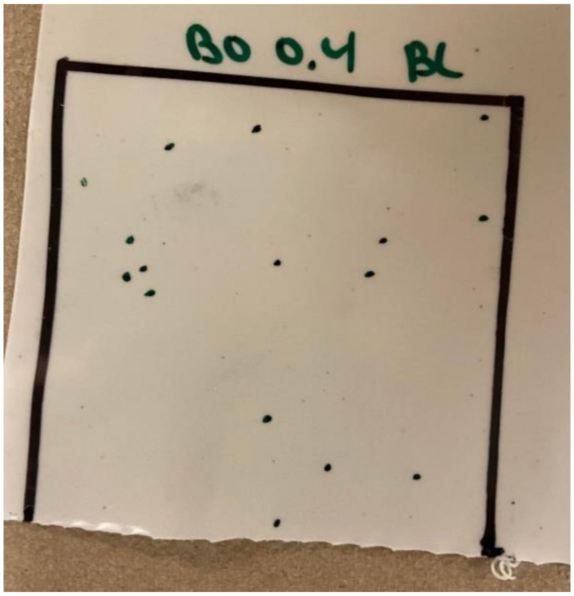

FIGURE 3.2 Gas checks manually counted in a grid of 7 cm × 7 cm size, in a PVC calendered film without PCL-based additives.

3.6 Extrusion

In general, PVC blends were produced in a multiple step extrusion process. Plasticizer concentrations starting at 20 phr (parts per hundred of resin) (16.67 wt%) then 40 phr (28.57 wt%), and final concentrations as high as 60 phr (37.50 wt%) were mixed using a conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation) (Waltham MA USA). The mini extruder was operated at a temperature of 140°C and with a rotation speed of 30 min^{-1}.

The blends presented in the manuscript are described in the paper, For Chapter 5, the following stepwise sequence was used to prepare the blends with the gas check additives used as a primary plasticizer. Firstly, unplasticized PVC was combined with 20 phr gas check additive, 4 phr epoxidized soybean oil as a thermal stabilizer, and 5 phr stearic acid as a lubricant and fed into the mini extruder. The resulting extrudate with a PCL-based additive concentration of 20 phr was cut into small pellets and recycled through the mini extruder to facilitate proper mixing. In the next step another 20 phr PCL-based additive was added to the extrudate from the first step to build up a total PCL-based additive concentration of 40 phr and the resulting extrudate was also recycled.

In the final step, another 20 phr PCL-based additive was added to the 40 phr blend to make up a final concentration of 60 phr. Again, the resulting extrudate from the final step was recycled through the mini extruder to ensure a homogeneous mixture and then manually cut into small pellets for storage.

3.7 Compression molding

The extruded plasticized PVC pellets were pressed into tensile bars, rheology disks, and bar for dynamic mechanical thermal analysis (DMTA) at a temperature of 165˚C using a heat press (Carver Manual Hydraulic Press with Watlow Temperature Controllers) (Wabash IN USA). The dimensions of the tensile bars were 2.9 mm thickness (T), 3.2 mm width of narrow section (W), 13 mm length of narrow section (L), 24.6 mm distance between grips (D), 63.5 mm overall length (LO), and 9.5 mm width overall (WO), which correspond to the type V sample described in ASTM D-638-03 [65]. The dimensions of the disks for rheological testing were 1 mm thick (T) and 25 mm in diameter (D). The DMTA bars had the following dimensions, a thickness (T) of 1.45 mm, a length (L) of 45 mm and a width (W) of 10 mm. Exact measurements of the width and thickness of individual bars were determined using an electronic caliper (Electronic Outside Micrometer, Fowler Tools & Instruments) prior to testing. The samples were pressed at a clamping force of 5 tons for a duration of 10 mins, followed by 10 tons of clamping force for 10 mins and finally a clamping force of 20 tons for 30 mins, then they were brought to room temperature using cooling water. Once cooled, the pressure was released from the samples and they were removed from the mold and placed in a desiccator (Drierite, Fisher Scientific) for a minimum of 48 hours before undergoing tensile, rheology, or DMTA testing.

3.8 Thermal gravimetric analysis

The thermal stability of the plasticizers (PCL-based additives) as well as the plasticized PVC blends were evaluated using thermal gravimetric analysis (TGA) under nitrogen environment using a TA Instruments, Discovery TGA 5500 (New Castle, DE). Samples were run with a nitrogen flow of 25 mL/min from 25 to 700°C at a heating rate of 10°C/min. The onset temperatures at which 5% weight of samples begin to degrade were reported.

3.9 Differential scanning calorimetry

The glass transition temperature (T_g) of plasticized PVC blends was measured using a TA instrument (New Castle, DE), 2500 Discovery Differential Scanning Calorimeter (DSC). A temperature-modulated differential scanning calorimetry (MDSC) protocol previously established by Erythropel et al. was adopted for this analysis [66]. Briefly, 3 to 10 mg of plasticized PVC blends was weighed out and loaded into a Tzero pin hole hermetic aluminum pan and then placed in the DSC sample holder. The MDSC protocol consisted of two cool-heat cycles. In the first cycle, the sample was cooled to -90°C and held isothermally for 5 min, then it was exposed to a linear heating ramp at a rate of 2°C/min to 100°C. The constant heat rate was superimposed by a sinusoidal modulation of 1.27°C amplitude with a period of 60s. This cycle was repeated to make up the second cool-heat cycle. The DSC results were analyzed using TA TRIOS software (V5.1.1). The glass transition temperature was determined through midpoint analysis from the reversible heat flow curve of the second heat cycle using the T_g tool.

3.10 Tensile testing

Tensile testing of the heat pressed tensile bars was performed using a Yamazu (Kyoto, Japan.) Easy Test tensile tester with a load cell of 500 N following a procedure adapted from ASTM D638-03 [1]. Exact measurements of the width and thickness of each test bar were determined using electronic calipers prior to testing. A strain rate of 5 mm/min was used and the force as well as the distance were automatically recorded by software (WinAGS Lite) on the connected computer until the test bar broke. The stress-strain curves were used to obtain the values of tensile strength, strain expressed as a percentage (%) of elongation at break, stress-at-break and modulus.

3.11 Rheology and dynamic mechanical thermal analysis

Plasticized PVC blends heat pressed into 25 mm disks were characterized rheologically by measuring storage modulus (G′), loss modulus (G″), loss factor (tan δ), and complex viscosity (η*), through dynamic oscillatory tests using an Anton Paar MCR 302 strain-controlled rheometer (Anton Paar Canada, St-Laurent, Quebec, Canada). A parallel plate geometry (25 mm diameter), PP25 configuration and a CTD 450 convection oven (operated under nitrogen to prevent PVC degradation) were used. A strain amplitude of 5% within a linear viscoelastic range was applied over a frequency range of 0.01 to 100 rad/s at 170°C.

Dynamic mechanic thermal analysis (DMTA) was conducted on the plasticized PVC blends that had been heat pressed into DMTA bars in order to evaluate transition points and possible post-processing conditions. The SRF12 configuration was used on the same rheometer with the same oven conditions as described above. The DMTA bars were loaded in tension, and a temperature ramp at a rate of 5°C/min was performed from 25°C to 200°C, with an oscillation strain of 0.1% and a frequency of 1 Hz to obtain G′, G″ and tan δ curves. Anton Paar (Germany, Ostfildern), RheoCompassTM software (Version 1.23, 403-Release was used for the analysis of all rheological and DMTA results.

3.12 Acid value

The acid value was determined following a procedure adapted from the American Oil Chemists′ Society (AOCS) Cd3a-63. A plasticizer quantity of 2.0 to 2.5 g was weighed out in an Erlenmeyer flask and dissolved with 50 to 70 ml of a 1:1 isopropanol:acetone mixture. The resulting solution was stirred to complete solvation on a magnetic stirrer and then neutralized using a 0.1 N solution of potassium hydroxide (KOH) to the first pink colour end point (i.e., stable for 30 seconds). Phenolphthalein indicator was used as well as a 50 ml burette for the 0.1 N KOH solution. The acid value (AV) expressed as mgKOH/g was calculated using the following equation (1):

$$AV = \frac{ml\,KOH \times F}{W}, \tag{3.1}$$

where F is the factor of the KOH solution (56.108 g/mol KOH × normality of KOH solution), and W is the weight of the sample in grams.

4. Investigation of Additives for Preventing the Formation of Gas Checks during Calendering of Poly(vinyl chloride) calendaring Films.

Luis F. Alvarez[1], Kushal Panchal[3], Jim A. Nicell[2], Richard R. Leask[1], Milan Maric[1*].

[1]Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, QC, Canada, H3A 0C5.

[2]Department of Civil Engineering, McGill University, 817 Sherbrooke Street West, Montreal, QC, Canada, H3A 0C3.

[3]Canadian General-Tower Ltd, Cambridge, Ontario, Canada, N1R 5T6.

*Corresponding Author

4.1 Preface

Chapter 4 is dedicated to the assessment of PVC calendered films, specifically focusing on their chemical, mechanical, thermal, and rheological properties. In this investigation, PCL-based additives are employed as secondary plasticizers to gauge their efficacy in mitigating gas checks. The synthetic methodology and key characteristics of these PCL-based additives align with the details provided in Chapter 3. The experimentation involved the utilization of DINP as the primary plasticizer at 55 phr, while PCL-based additives served as secondary plasticizers at concentrations of 5 and 10 phr. The primary objective of this comparative analysis is to establish a correlation between the properties of PVC calendered films and the concentration of gas checks in them.

4.1 Abstract

Gas checks on poly(vinyl chloride) (PVC) calendered films are a common but not well understood surface quality defect that causes delays and resource wastage in manufacturing of plastic sheets and films. In this work, three modified poly(caprolactone) (PCL)-based additives of differing molecular weights were used as a secondary plasticizer with the goal of preventing the formation of gas checks without modifying the calendering process conditions. To better understand gas check prevention mechanisms, a series of PCL-based additives that prevent gas checks were synthesized and their effect on the thermal, mechanical, rheological, and chemical properties of blends were extensively assessed. A high molecular weight (2000 g/mol) PCL-based additive was unable to prevent gas checks in PVC blends, unlike the lower molecular weight (540 g/mol and 900 g/mol) additives. The results suggest that chemical and physicochemical properties affect the prevention or reduction of gas checks, whereas the physical properties are not affected by the addition of the secondary plasticizer. The acid value was found to be correlated with gas checks reduction, as hydrolysis removes the capping groups, lowering the effectiveness of the additive in removing the gas checks.

Key words

Acid value, molecular weight, PCL-based additive.

4.2 Introduction

In the polymer industry, calendering is the process of making a continuous film with controlled thickness through compression and smoothing of polymer melt, achieved by passing it through a system of heated cylindrical rolls called calenders [1]. Poly(vinyl chloride) (PVC) films/sheets are commonly made by calendering and are widely used to manufacture commercial products [2,3]. The PVC film global market was valued at US$14.7 billion in 2022 and is projected to be US$19.6 billion by 2032, with PVC films constituting 10% of the global packaging film market [4]. During the calendering process, surface defects widely referred to as “gas checks” can occur thereby spoiling the product [5]. Gas checks are visible fleck-shaped defects that occur due to air entrapment in the calendar bank.

Gas checks cause delays in PVC film production, reduce the film mechanical properties at defect sites and, consequently, often result in wasted films if marketability requirements are not met [5]. Typically, if the PVC films are not wasted, they are recycled [5]. Though the mechanism of gas check evolution in calendering is not well understood, ways have been sought to prevent their occurrence [5]. A common approach used by many manufacturers to avoid gas checks is to produce thinner films and then laminate them together to achieve a desired film thickness [43]. However, this process is not only inefficient, but it can also lead to interfacial instability [43]. Alternatively, it has been shown that the manipulation of processing parameters such as the roll speed and calender nip distance can reduce the occurrence of gas checks, but the downside to this is that products are obtained with less than satisfactory properties [5]. Fortunately, however, the use of chemical additives for gas check prevention has been recently reported. Jamarani et al developed additives based on poly(caprolactone) (PCL) that were used as a secondary plasticizer during calendering of PVC and successfully prevented gas checks [5,6].

It was hypothesized that viscosity plays a major role in the prevention of gas checks [5], by influencing process pressure. Therefore, in undertaking the present work, we started with the hypothesis that PCL precursors of higher molecular weights would be beneficial.

In this work, we report the testing of three chemical additives of different PCL core molecular weight (540 to 2000 g/mol), with a three-arm star-shaped molecular structure, when blended into PVC formulations. The lowest molecular weight (540 g/mol) additive was previously studied and was effective in removing gas checks [5]. Beyond investigating the effect of PCL molecular weight on the material properties of the films, we also investigated the acid value of the additives for potential chemical interactions related to gas checks. This relationship is rooted in the chemical compatibility of the plasticizer with the matrix, as we previously noticed that a capping molecule(s) to the PCL core was necessary to prevent gas checks.

4.3 Experimental

4.3.1 Materials

Poly(ε-caprolactone) triol of three molecular weights (CAPA 3050, M_n = 540 g/mol; CAPA 3091, M_n = 900 g/mol; CAPA 3201, M_n = 2000 g/mol) of 99% purity were purchased from Ingevity UK Ltd. (UK). Renewable sourced succinic acid (99%) was purchased from Roquette, (Iowa, USA). Sulfuric acid (96%), potassium hydroxide (85%), acetone (99.5%), were purchased from Fisher Scientific (Nepean ON, Canada). Renewably sourced n-heptanol (Oleris, 99%) was purchased from Arkema (King of Prussia, PE, USA). Isopropanol (>99.99%) was purchased from MilliporeSigma (USA). Phenolphthalein (ACS certified) was purchased from J.T Baker Chemicals (USA). Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), stearic acid (99%), antimony oxide Hi-Tint (99.68%), silica (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. Cambridge, ON, Canada)

4.3.2 Synthesis of PCL-based additives

The synthesis of the star-shaped PCL-based additives, listed in the previous chapter, Table 3.1, were performed via a two-step esterification reaction in a single flask. In the first step, 1 stoichiometric equivalent (stoic. equiv.) of PCL triol was massed out into a three-necked round bottom flask, followed by the addition of succinic acid (3 stoic. equiv.) while the mixture was continuously stirred a stirring plate. Catalytic amounts of sulfuric acid (0.156 stoic. equiv.) were then added dropwise to the reaction mixture. The reaction flask was fitted with a Dean-Stark apparatus (to collect generated water from the esterification reactions) and a condenser, then placed on a heating mantle, and heated at 110°C for 90 mins, after which the reaction mixture was cooled to room temperature. In the second step, n-heptanol (3 stoic. equiv.) was added to the same flask equipped with the same Dean-Stark apparatus and condenser and the mixture was reheated to 110°C for 90 mins, after which the reaction mixture was cooled and stored in a cool well-ventilated area. No purification was done, and all PCL analogs were obtained as viscous oils except for the star-shaped molecule with 2000 g/mol molecular weight for the PCL core. This was obtained as a waxy solid at room temperature. The chemical structure of the star shaped PCL-based additive is shown in the previous chapter, Figure 3.1.

4.3.3 Gel Permeation Chromatography

The number average molecular weights (M_n) of the modified PCL-based additives reported in Table 4.1 were analyzed by gel permeation chromatography (GPC) using a Waters Breeze instrument and HPLC grade THF as an eluent at a flow rate of 0.3 mL/min. The GPC has three Waters Styragel HR columns (HR1 which has a molecular weight measurement range of 10^2 to 5×10^3 g/mol, HR2 with a molecular weight measurement range of 5×10^2 to 2×10^4 g/mol, and HR4 with a molecular weight measurement range of 5×10^3 to 6×10^5 g/mol), a guard column, and a refractive index (RI 2414) detector. The columns were heated to 40 ˚C throughout the analysis. Molecular weights were measured relative to PMMA.

4.3.4 Film production

Plasticized PVC films were produced by first mixing blend components on a lab-scale two roll mill. A Hartek two-roll mill HTR-300 (D =120 mm, T = 160°C, 45 rpm) was used to melt and mix blend components for 7 mins, starting from the time of film formation on the mill rolls. Secondly, to produce the final films, the resulting milled film was then fed into a lab-scale calender (D = 80 mm, T = 160 to 170°C, P = 45 psi, 50 rpm) for 1 min and set to achieve a film gauge of 0.4 ± 0.05 mm. All plasticized PVC were made to a final concentration of 55 phr primary plasticizer (DINP) and concentrations of 5 and 10 phr with PCL-based additives as secondary plasticizer. Each blend formulation consisted of 100 phr PVC 70K suspension resin, 55 phr primary 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.

4.3.5 | Counting gas checks

Grids of 7 cm × 7 cm size were used to manually count the gas checks on each film, with four films produced and a grid was made on three sections of each film: top left corner, the middle, and the bottom right corner. The gas checks within each grid were counted and then averaged to obtain the number of gas checks per film. This was done for all four films per blend formulation and then averaged to obtain the number of gas checks per blend formulation. The average number of gas checks was normalized per square meter (m^2) of film.

4.3.6 Compression molding

The produced plasticized PVC films were chopped into small pieces and were pressed into tensile bars, rheology disks, and dynamic mechanical thermal analysis (DMTA) bars using a Carver Manual Hydraulic Heat Press (Wabash IN USA) outfitted with Watlow Temperature Controllers (St. Louis, USA) and maintained at a temperature of 165°C. The dimensions of the tensile bars were 2.9 mm thickness (T), 3.2 mm width of narrow section (W), 13 mm length of narrow section (L), 24.6 mm distance between grips (D), 63.5 mm overall length (LO), and 9.5 mm width overall (WO), which correspond to the type V sample described in ASTM D-638-03 [1]. The dimensions of the disks for rheological testing were 1.0 mm thick (T) and 25 mm in diameter (D). The DMTA bars had the following dimensions, a thickness (T) of 1.45 mm, a length (L) of 45 mm and a width (W) of 10 mm. Exact measurements of the width and thickness of individual bars were taken using an Electronic Outside Micrometer caliper (Fowler Tools & Instruments; Massachusetts, USA) prior to testing. The samples were pressed at a clamping force of 5 tons for a duration of 10 mins, followed by 10 tons of clamping force for 10 mins, and finally a clamping force of 20 tons for 30 mins. They were then cooled to room temperature using cooling water. Once cooled, the pressure was released from the samples and they were removed from the mold and placed in a desiccator

(Drierite, Fisher Scientific) for a minimum of 48 hours before undergoing tensile, rheology, or DMTA testing.

4.3.7 Thermal gravimetric analysis

The thermal stability of the plasticizers (PCL-based additives) as well as the plasticized PVC blends were evaluated using thermal gravimetric analysis (TGA) using the Discovery TGA 5500 from TA Instruments (New Castle, DE) under nitrogen environment. Samples were run with a nitrogen flow of 25 mL/min from 25 to 700°C at a heating rate of 10°C/min. The onset temperatures at which 5% weight of samples begin to degrade were recorded.

4.3.8 Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of plasticized PVC blends was measured using differential scanning calorimetry (DSC) using a Q200 Differential Scanning Calorimeter from TA Instruments (New Castle, DE). A temperature-modulated differential scanning calorimetry (MDSC) protocol previously reported by Erythropel et al. was adopted for this analysis [9]. Briefly, 3 to 10 mg of plasticized PVC blends were weighed and loaded into a hermetic aluminum pan and then placed in the DSC sample holder. The MDSC protocol consisted of two cool-heat cycles. In the first cycle, the sample was cooled to -90°C and held isothermally for 5 min, then it was exposed to a linear heating ramp at a rate of 2°C/min to 100°C. The constant heat rate was superimposed by a sinusoidal modulation of 1.27°C amplitude with a period of 60s. This cycle was repeated to make up the second cool-heat cycle. All DSC and MDSC results were analyzed using TA Universal Analysis software (V4.5A). The glass transition temperature was determined through midpoint analysis from the reversible heat flow curve of the second heat cycle using the T_g tool.

4.3.9 Tensile testing

Tensile testing of the heat pressed tensile bars was performed using a Shimadzu (Kyoto, Japan.) Easy Test tensile tester with a load cell of 500 N and following a procedure adapted from ASTM D638-03 [1]. A strain rate of 5 mm/min was used and the force as well as the distance were automatically recorded by WinAGS Lite software on the connected computer until the test bar broke. The stress-strain curves were to obtain the values of tensile strength, strain expressed as percentage (%) elongation at break, stress-at-break and modulus.

4.3.10 Rheology and dynamic mechanical thermal analysis (DMTA)

Plasticized PVC blends heat pressed into 25 mm disks were characterized by measuring storage modulus (G′), loss modulus (G″), loss factor (tan δ), and complex viscosity (η*), through dynamic oscillatory tests using an Anton Paar Canada (St-Laurent, Quebec, Canada) MCR 302 strain-controlled rheometer. A parallel plate geometry (25 mm diameter), PP25 configuration and a CTD 450 convection oven (operated under nitrogen to prevent PVC degradation) were used. A strain amplitude of 5% within a linear viscoelastic range was applied over a frequency range of 0.01 to 100 rad/s at 170°C.

Dynamic mechanical thermal analysis (DMTA) was conducted on the plasticized PVC blends that had been heat pressed into bars to evaluate transition points and possible post-processing conditions. The SRF12 configuration was used on the same rheometer with the same oven conditions as described above. The DMTA bars were loaded in tension, and a temperature ramp at a rate of 5°C/min was performed from 25°C to 200°C, with an oscillation strain of 0.1% and a frequency of 1 Hz to obtain G′, G″ and tan δ curves. Anton Paar (Ostfildern, Germany) RheoCompassTM software (Version 1.23, 403-Release) was used for the analysis of all rheological and DMTA results.

4.3.11 Acid value determination

The acid value was determined following a procedure adapted from the American Oil Chemists′ Society (AOCS) Cd3a-63. A plasticizer weight of 2.0 to 2.5 g was weighed out in an Erlenmeyer flask and dissolved with 50 to 70 ml of a 1:1 isopropanol:acetone mixture. The resulting solution was stirred to complete solvation on a magnetic stirrer and then neutralized using a 0.1 N solution of potassium hydroxide (KOH) to the first pink colour end point (i.e., stable for 30 seconds). Phenolphthalein indicator was used as well as a 50 ml burette for the 0.1 N KOH solution. The acid value (AV) expressed as mgKOH/g was calculated using the following equation:

$$AV = \frac{ml\ KOH \times F}{W}, \tag{4.1}$$

where F is the factor for the KOH solution (56.108 g/mol KOH × normality of KOH solution) and W is the weight of the sample in grams

4.4 Results and Discussion

4.4.1 Synthesis of additives for gas check prevention

The benchmark PCL-based additive for gas check prevention is PCL_{540}-Succ-C_7 [5]. This additive was effective at preventing gas check formation (Figure 4.2) at concentrations from 10 to 55 phr [5]. To determine if there was a range of PCL-based additives that could be used, three of these were synthesized at three different molecular weights using a PCL core of 540, 900 and 2000 g/mol. PCL_{2000}-Succ-C_7, resulting in a white waxy solid at room temperature. Due to its physical nature, during blending, the higher molecular weight additive was pre-heated until it became a viscous oil to ensure good mixing.

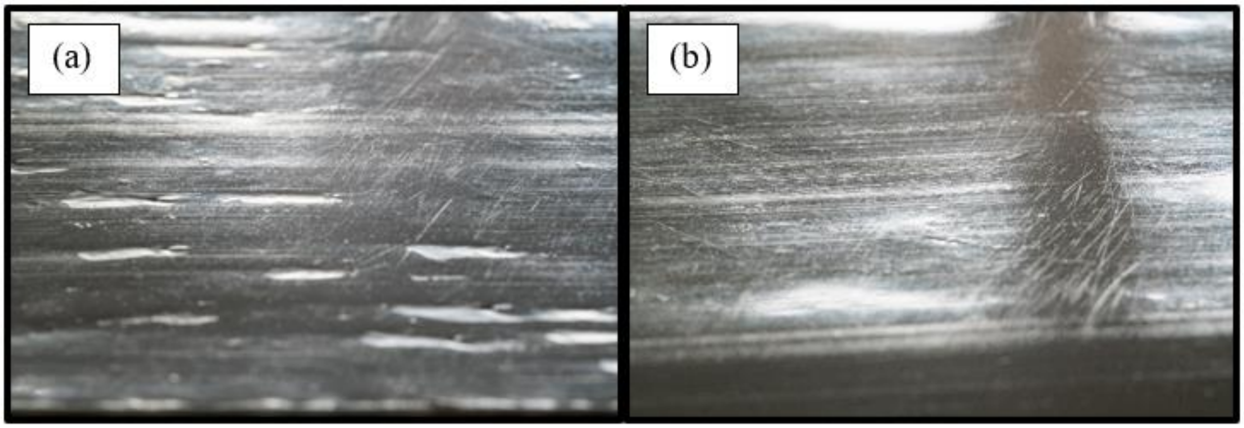

FIGURE 4.1 Calendered PVC films (0.4 mm thickness) (a) without and (b) with PCL_{540}-Succ-C_7 at 10 phr.

PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 have been shown to prevent the formation of gas checks at a concentration of 10 phr [5]. Therefore, 4 calendered films made of PVC, DINP at 55 phr and PCL-based additives at concentrations of 5 phr and 10 phr were produced and the number of gas checks were counted and then averaged per m^2 on each film, as reported in Figure 4.3. Without additive, at the conditions used, 5115 gas checks per m^2 were observed. At 5 phr of additive, the average number of gas checks for PCL_{540}-Succ-C_7, PCL_{900}-Succ-C_7 and PCL_{2000}-Succ-C_7 were approximately 3800, 3300 and 4700 per m^2 of film respectively. At 10 phr, PCL_{2000}-Succ-C_7 did not prevent the formation of gas checks but did reduce the number to 562 per m^2 of film. Even though the higher molecular weight additive did not prevent the formation of gas checks, it performed better compared to films produced with no additives, likely because of mixing and incompatibility issues that can lead to phase separation. Both the PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 were able to completely prevent gas checks when present at 10 phr in the blend.

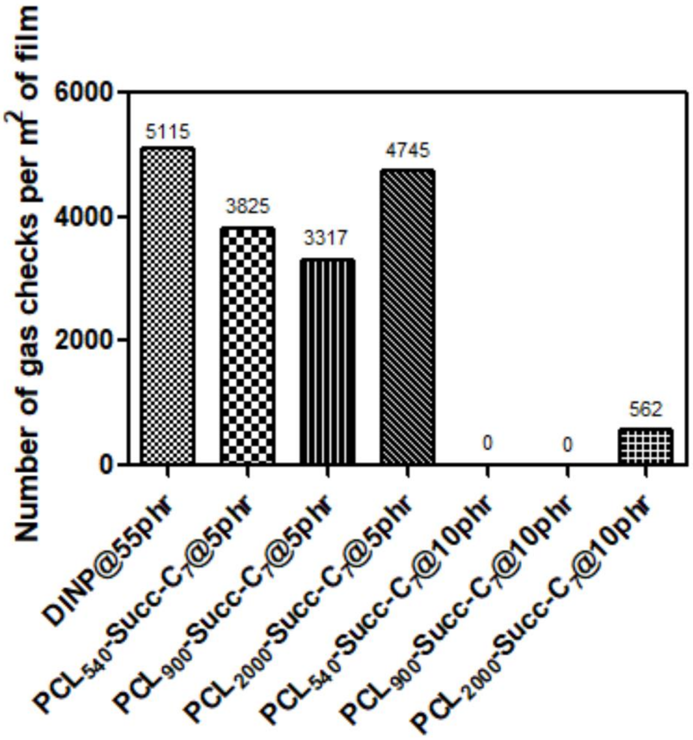

FIGURE 4.2 Number of gas checks per m^2 of films using PCL-based additives at different concentrations in PVC blends.

4.4.2 Thermal properties

The thermal properties of the PCL-based additives as well as their blends with PVC were determined by TGA and DSC analysis. This was important to determine temperature conditions during post-processing operations. The onset degradation temperature of 5% weight loss for all PCL-based additives were in the range of 164°C to 212°C, where the lowest degradation temperature corresponds to the blend with the lowest molecular weight additive and the highest degradation temperature to the blend with the highest molecular weight additive. (see Supporting Information).

The onset degradation temperature (5% weight loss) for neat PVC was determined to be 252°C. PVC blends made with DINP at 55 phr using PCL$_{540}$-Succ-C$_7$ at 10 phr, or PCL$_{900}$-Succ-C$_7$ and PCL$_{2000}$-Succ-C$_7$ at 5 and 10 phr resulted in an onset degradation temperature range from 207 to 214°C. The degradation temperature of all the samples at the three different concentrations are shown in Table 4.2.

TABLE 4.1 Onset degradation temperature of 5% weight loss of PVC + DINP at 55 phr blends with different PCL-based additives at different concentrations.

	Sample	**Onset Degradation temperature of 5% weight loss (°C)**		
		PCL concentration: 0 phr	PCL concentration: 5 phr	PCL concentration: 10 phr
PCL blends	PVC + DINP@55phr	211	-	-
	PVC + DINP@55phr + PCL_{540}-Succ-C_7	-	-	213
	PVC + DINP@55phr + PCL_{900}-Succ-C_7	-	209	207
	PVC + DINP@55phr + PCL_{2000}-Succ-C_7	-	214	209

The onset degradation temperature was not significantly affected by the molecular weight of PCL core or the concentration of gas check additives in PVC blends. All temperatures lie above operating conditions of equipment used in the production of the PVC calendered films, suggesting that degradation of material is not to be expected during calender runs.

The glass transition temperatures (T_g) for the PVC-based additives were in the range from -60.2°C to -72.1°C (See Supporting Information). When PCL-based additives were blended with PVC at 5 and 10 phr, the T_gs range between -63°C and -62°C as indicated in Table 4.3.

TABLE 4.2 Glass transition temperature (T_g) of PVC + DINP at 55 phr blends with different PCL-based additives at different concentrations.

	Sample	**Glass transition temperature (°C)**		
		PCL concentration: 0 phr	PCL concentration: 5 phr	PCL concentration: 10 phr
PCL blends	PVC + DINP@55phr	-63.0	-	-
	PVC + DINP@55phr + PCL_{540}-Succ-C_7	-	-	-62.9
	PVC + DINP@55phr + PCL_{900}-Succ-C_7	-	-63.2	-62.7
	PVC + DINP@55phr + PCL_{2000}-Succ-C_7	-	-62.9	-63.0

Similar to what was observed with the degradation temperature, the T_g is not affected by the addition of the different PCL-based additives at concentrations of 5 and 10 phr, likely due to the fact that DINP is present in the blends at a higher concentration of 55 phr. Thus, the T_g would mostly be influenced by the DINP in the PVC blended films.

4.4.3 Mechanical properties

As shown in Figure 4.4, tensile strength and elongation at break were measured and compared to the films using only DINP at a concentration of 55 phr and the films with DINP at 55 phr and with the three PCL-based additives at concentrations of 5 and 10 phr.

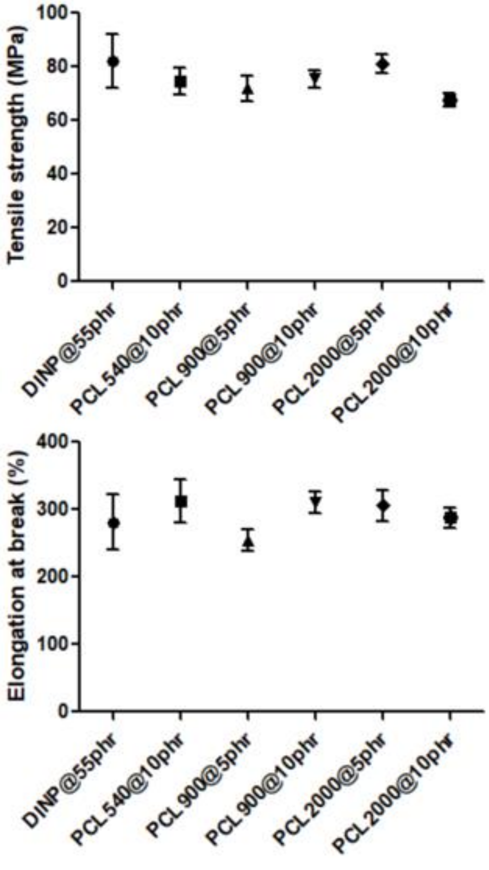

FIGURE 4.3 Tensile strength and strain expressed as percentage (%) elongation at break of PVC blends made with DINP at 55 phr, PCL_{540}-Succ-C_7, PCL_{900}-Succ-C_7 and PCL_{2000}-Succ-C_7 at 5 and 10 phr.

As can be seen from Figure 4.4, tensile strength and elongation at break did vary with the addition of PCL-based additives. Thus, a one-way ANOVA test was conducted with a confidence interval of 95% (α=0.05) along with a Tukey test to compare individually all the results between the standard sample using DINP at 55 phr blend and all the blends with any of the PCL-based additives at concentrations of 5 phr and 10 phr. The results show that the means are not significantly different. Therefore, it is concluded that the mechanical properties of the films are not affected by the presence of PCL-based additives at the concentrations used.

4.4.4 Rheological properties

Because it was hypothesized that viscosity might play a role in gas check prevention, the complex viscosity of plasticized PVC blends was measured. In previous work, an effective PCL-based additive, PCL$_{540}$-Succ-C$_7$, was observed to produce a higher complex viscosity (η*) in plasticized PVC blends compared to blends without the gas check additive [5]. Therefore, a high η* is considered an important property for gas check removal. The η* of PVC blends made with DINP at 55 phr and the different PCL-base additives at concentrations of 5 and 10 phr are shown in Figure 4.5 below.

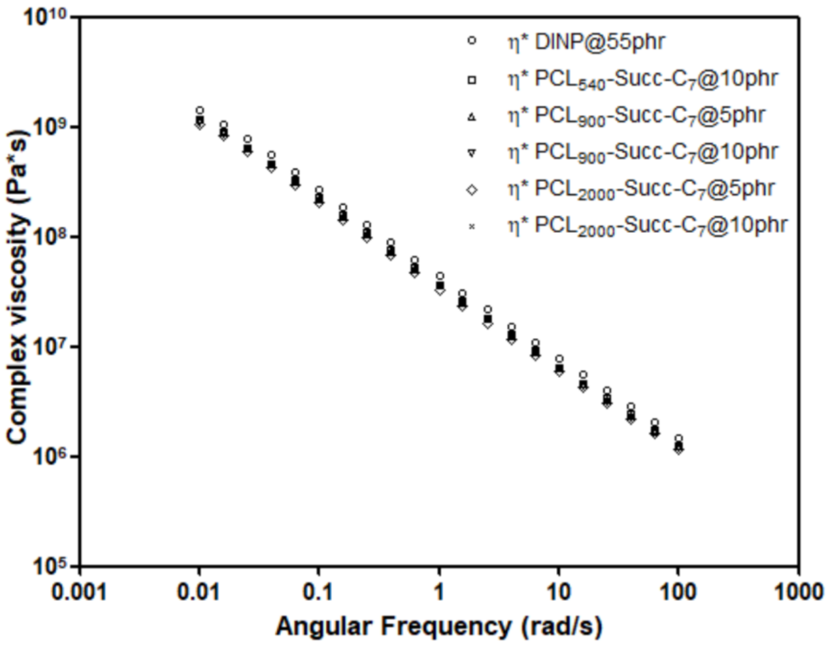

FIGURE 4.4 Complex viscosity as a function of angular frequency of PVC blends made with DINP at 55 phr and PCL-based additives at 5 and 10 phr.

The highest η*obtained was using DINP at 55 phr without any PCL-based additives but is not significantly higher compared to all the samples using PCL-based additives. It can be seen from

Figure 4.5 that the η*of all the samples using PCL-based additives regardless of the concentration are very similar, and the individual series overlap. These results suggest that η* is not affected by the addition of PCL-based additives, and therefore, the rheological properties are not affected.

Additionally, storage modulus (G′) and loss modulus (G′′) were measured, with the results shown in Figure 4.6. The results show that for all the samples regardless of the angular frequency and the concentration of the PCL-based additives, the elastic forces (G′) are dominating over the viscous effects (G′′) suggesting that visco-elastic forces are present in all the samples. However, all samples behave more like an elastic solid instead of a viscous flowing material. Similarly to what was observed with η*, the highest values correspond to plasticized PVC films using only DINP at 55 phr; nevertheless, the results are very similar to the films using PCL-based additives at concentrations of 5 and 10 phr, suggesting that these additives do not affect the viscoelastic properties of the blends.

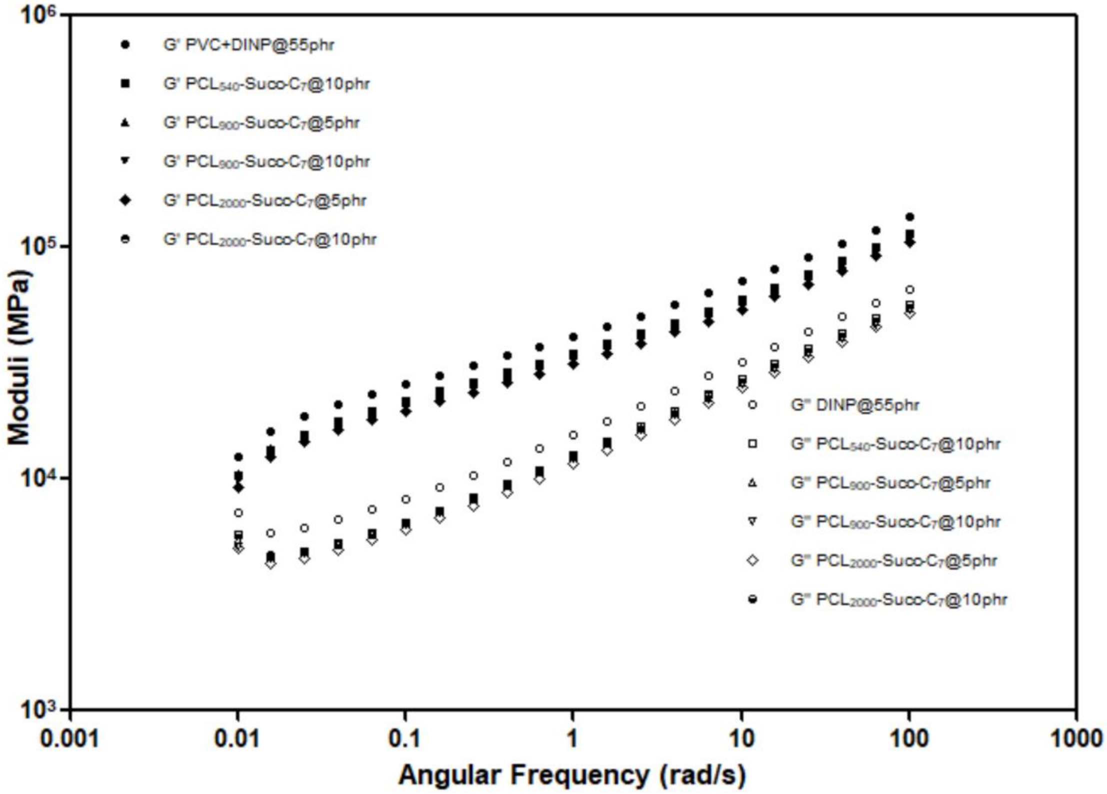

FIGURE 4.5 Storage and loss modulus as a function of angular frequency of PVC blends made with DINP at 55 phr and PCL-based additives at 5 and 10 phr.

DMTA was also performed for the same samples, indicating that regardless of the additive concentration a crossover between G′ and G″ occurs (see Supporting Information). The crossover temperatures are summarized in Table 4.4, with the highest crossover temperature referring to the sample with only 55 phr DINP. Cross-over temperature further decreases as the concentration of the additive and its molecular weight increase. This temperature indicates the samples no longer behave like an elastic solid, with viscous effects beginning to dominate. Viscous effects appear at lower temperatures as the molecular weight increases, because the viscosity increases more as well, therefore, the higher the molecular weight of the additive, the lower the cross-over temperature.

TABLE 4.3 Crossover temperature of the plasticized PVC films, as obtained from DMTA test.

Crossover temperature (˚C)					
DINP @55phr	**PCL540 @10phr**	**PCL900 @5phr**	**PCL900 @10phr**	**PCL2000 @5phr**	**PCL2000 @10phr**
182	175	172	170	164	162

4.4.5 Chemical properties

We proposed earlier that the nature of the additive alters the surface tension of the surrounding polymer with the entrained air. For example, PCL alone (the triol or diol) did not remove the gas checks. However, capping the PCL with the heptyl succinate groups resulted in a molecule that when added into the formulations enabled gas check removal.

The synthesized additives in this study were also titrated at concentrations of 5 phr and 10 phr resulting in acid values between 23 and 35 mgKOH/g. Samples having acid values >30 mgKOH at concentrations of 10 phr completely prevent the formation of gas checks, unlike the sample having acid values <30 mgKOH, which significantly reduced the formation of gas checks, but was not able to completely prevent them (see Figure 4.7).

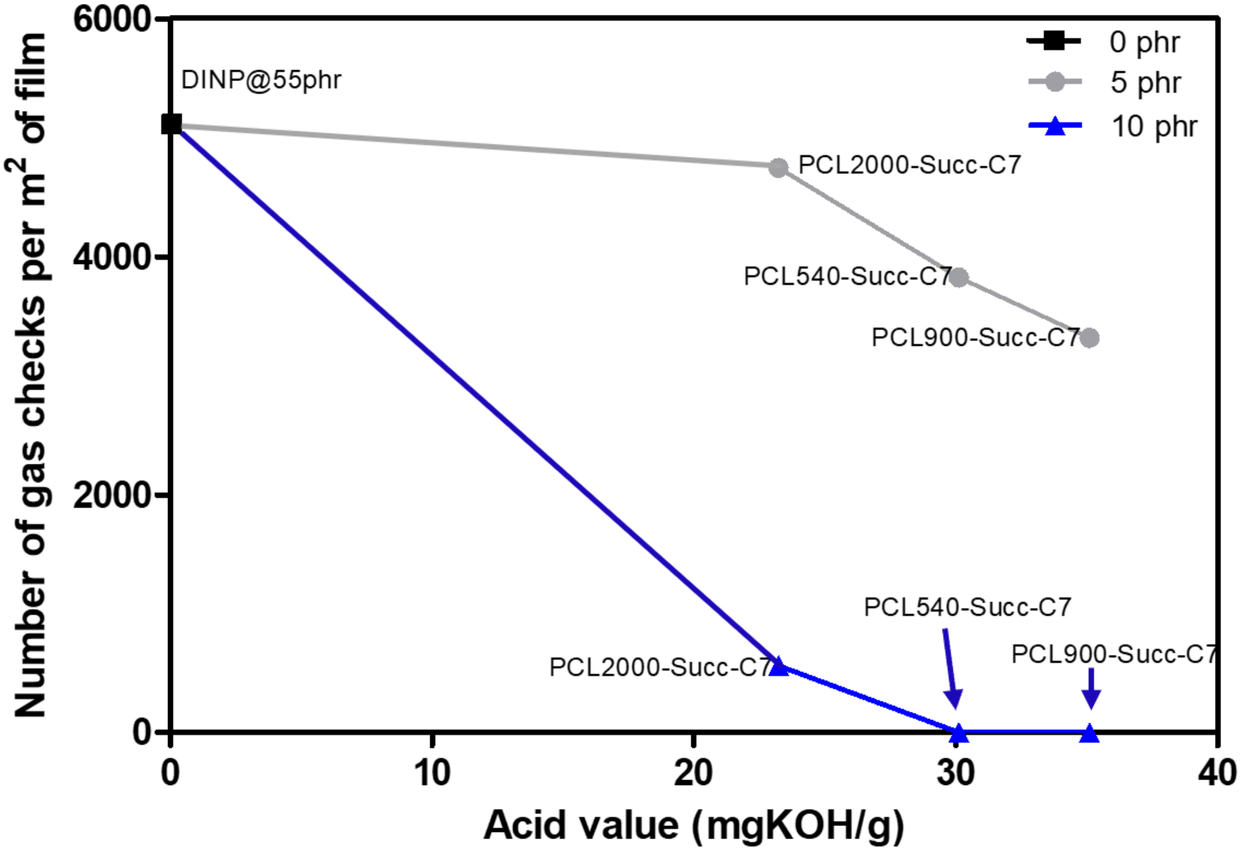

FIGURE 4.6 Number of gas checks vs acid values of synthesized PCL-based additives.

Figure 4.7 clearly shows a relationship between acid value and the number of gas checks per m^2 on calendered films; that is, calendered films using PCL-based additives with low acid values result in films with higher number of gas checks, whereas sheets with high acid values result in films with a lower number of gas checks or even no gas checks on the films, showing that capping the molecule with heptyl succinate groups within a certain molecular weight range results in high acid values. Previous studies from our research group [45], showed that using butyl or decyl with oxalate, fumarate or adipates to cap the molecule also worked effectively in preventing gas checks, suggesting high acid values in other capping agents which can perform similar to heptyl succinate groups. All these capping groups are hydrophobic groups and, thus, a wide number of hydrophobic groups could be potentially used to cap the molecule with an expected similar performance. In addition, the synthesized PCL-based additives, were added to calendered films at concentrations of 5 phr and 10 phr, resulting in a high number of gas checks ranging from 3317 to 4745 number of gas checks per m^2 of films at 5 phr. Increasing the concentration to 10 phr PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 completely prevented the formation of gas checks, however, PCL_{2000}-Succ-C_7 could not prevent the defect, which could be related to compatibility of the PCL with the longer core chain size. Nevertheless, it reduced the concentration of gas checks from 4745 at 5 phr to 562 at 10 phr. These results suggest a close relationship between free acids on the PCL-based additive molecules and the prevention of gas checks.

4.5 Conclusion

Three PCL-based additives of differing molecular weight were synthesized to assess the limits to which PCL-based additives are able to prevent gas checks. Different physical and chemical properties of these additives were tested in order to link them with the prevention of gas checks.

Even though high complex viscosity was hypothesized to be an important parameter in the prevention of gas checks, it is not affected by the presence of PCL-based additives at concentrations of 5 phr and 10 phr, suggesting that rheological properties are not a strong driver in preventing gas checks. Further, the mechanical properties were not affected by the addition of the PCL-based additives. The chemical correlation between gas check prevention and the PCL-based additives was evaluated through acid value determination and showed that high acid values are an important feature for an effective gas check preventer. Low molecular weight PCL-based additives (PCL core M_n of 540 and 900 g/mol) proved to be better gas check additives than their higher molecular counterpart (2000 g/mol PCL core). This shows that while PCL-based additives are effective at preventing gas checks there is a limit to how large the PCL core can be. Therefore, the prevention of gas checks using PCL-based additive is only related to the chemical properties, and not to physical properties as was initially hypothesized.

4.6 References

[1] Tadmor, Z.; C. G. Gogos. *Principles of Polymer Processing*, 2nd ed., Rev. ed.; Wiley-Interscience: Hoboken, N.J, 2006.

[2] Saeki, Y.; Emura, T. Technical Progresses for PVC Production. *Progress in Polymer Science* **2002**, *27* (10), 2055–2131.

[3] Baitz, M.; Kreißig, J.; Byrne, E.; Makishi, C.; Kupfer, T.; Frees, N.; Bey, N.; Söes Hansen, M.; Hansen, A.; Bosch, T. Life Cycle Assessment of PVC and of Principal Competing Materials. *Commissioned by the European Commission. (July 2004)* **2004**, *24*.

[4] Wanli Ma, Yuting Zhu, Ning Cai, Xianhua Wang, Yingquan Chen, Haiping Yang, Hanping Chen, 2023. Preparation of carbon nanotubes by catalytic pyrolysis of dechlorinated PVC. Waste Management 169 (2023) 62–69.

[5] Jamarani R, Halloran MW, Panchal K. Additives to prevent the formation of surface defects during poly(vinyl chloride) calendering. *Polym Eng Sci*.2021;61:1209–1219.

[6] D. Ventrice, Russo E, De Sarro G, Ventrice P. Phthalates: European regulation, chemistry, pharmacokinetic and related toxicity. *Environ Toxicol Pharmacol*. 2013;36(1):88-96.

[7] Balani, K., Verma, V., Agarwal, A. & Narayan, R. *Biosurfaces: A Materials Science and Engineering Perspective*. (John Wiley & Sons, Inc, 2014). doi:10.1002/9781118950623.

[8] Stark, T. D., Choi, H. & Diebel, P. W. Plasticizer Retention in PVC Geomembranes. in *Waste Containment and Remediation* 1–15 (American Society of Civil Engineers, 2005). doi:10.1061/40789(168)22.

[9] Erythropel, H. C., Maric, M. & Cooper, D. G. Designing green plasticizers: influence of molecular geometry on biodegradation and plasticization properties. *Chemosphere* **86**, 759–766 (2012).

4.7 Supporting information

The following is included as Supporting Information to the manuscript.

S1. Differential Scanning Calorimetry

The DSC results for PVC blended samples with PCL-based additives as secondary plasticizer are presented in Figures 4-S1 to 4-S6.

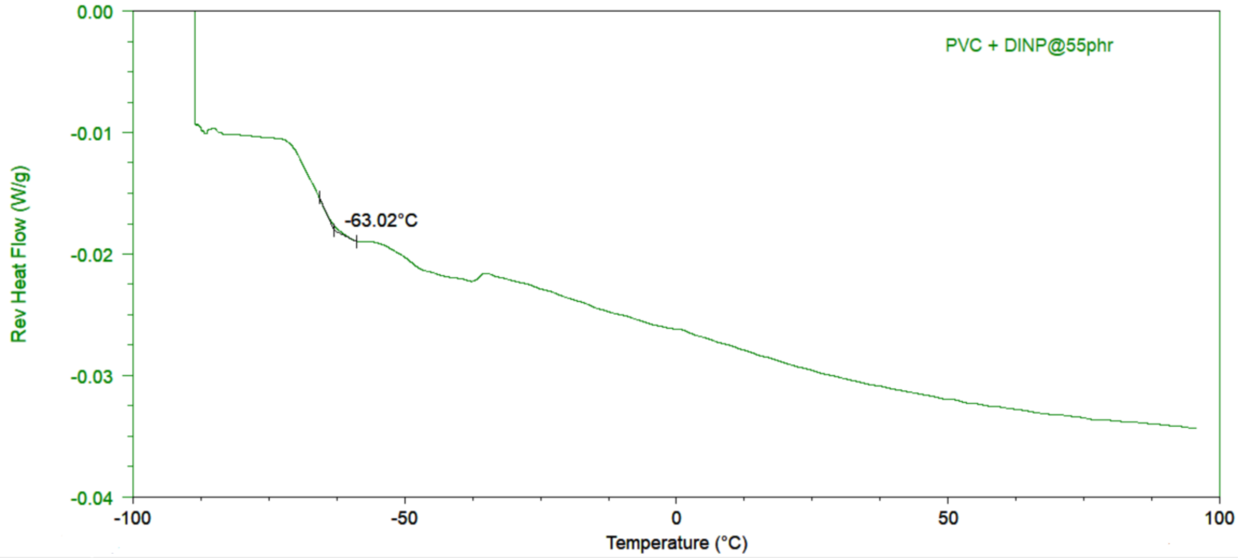

FIGURE 4-S1 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr.

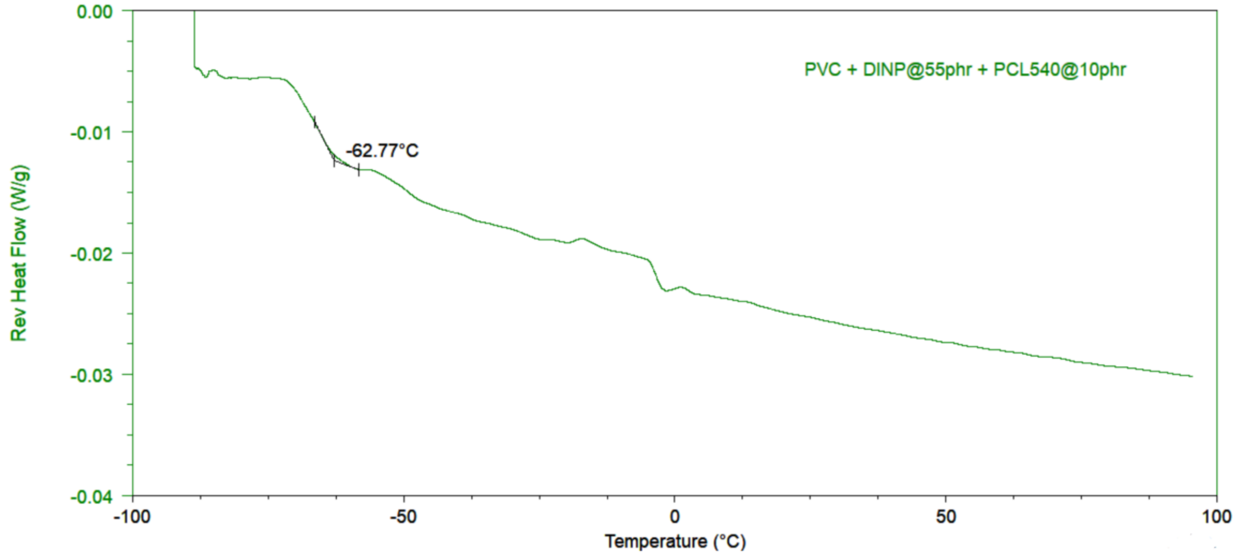

FIGURE 4-S2 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr and PCL_{540}-Succ-C_7 at 10 phr.

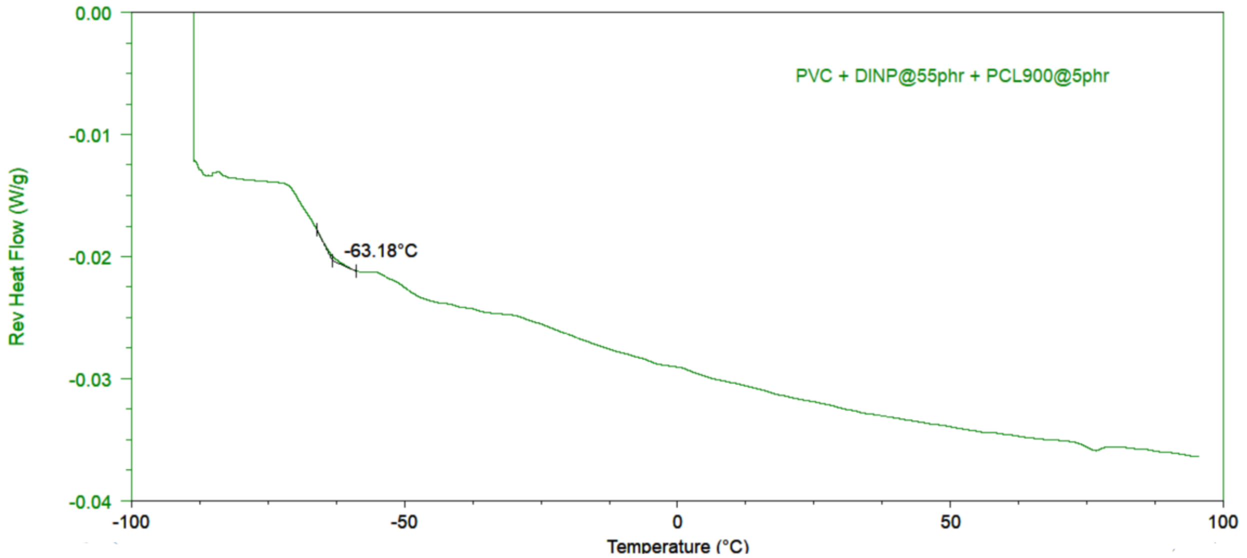

FIGURE 4-S3 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 5 phr.

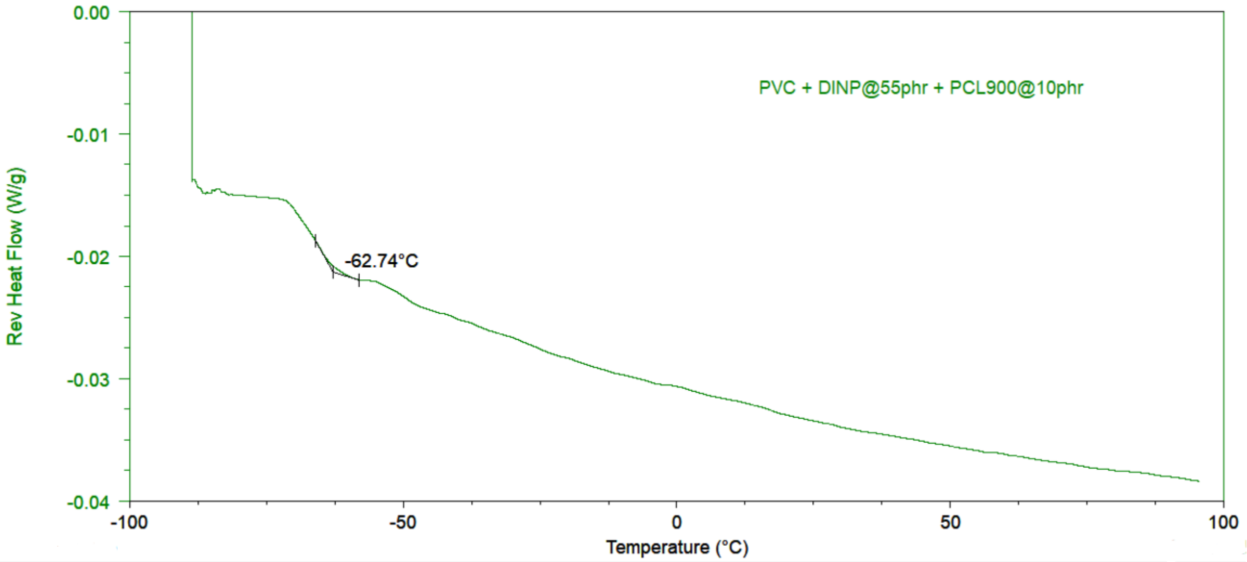

FIGURE 4-S4 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 10 phr.

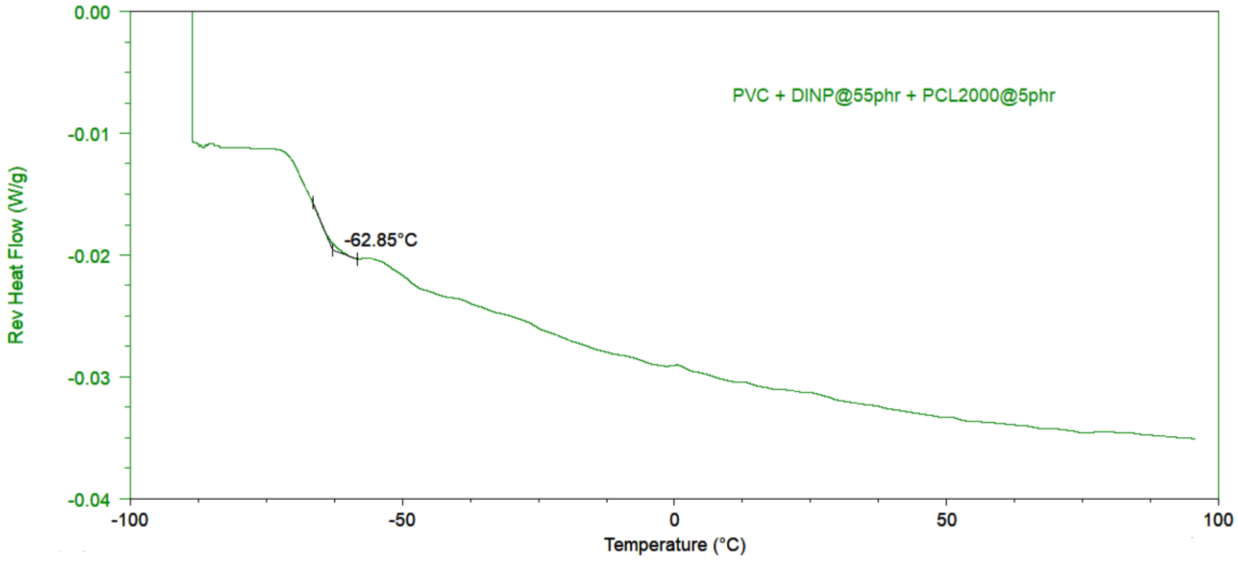

FIGURE 4-S5 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr and PCL$_{2000}$-Succ-C$_7$ at 5 phr.

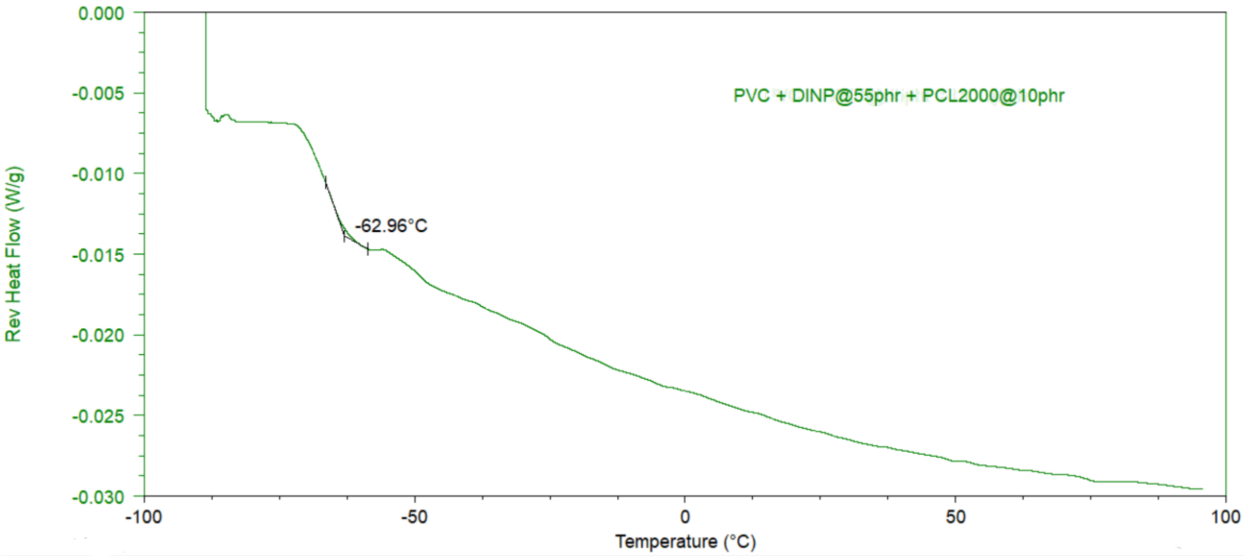

FIGURE 4-S6 DSC thermograms and glass transition temperature for PVC calendering films with DINP at 55 phr and PCL$_{2000}$-Succ-C$_7$ at 5 phr.

S2. Thermal Gravimetric Analysis

The TGA results for PVC blended samples with PCL-based additives as secondary plasticizer are presented in Figures 4-S7 to 4-S12.

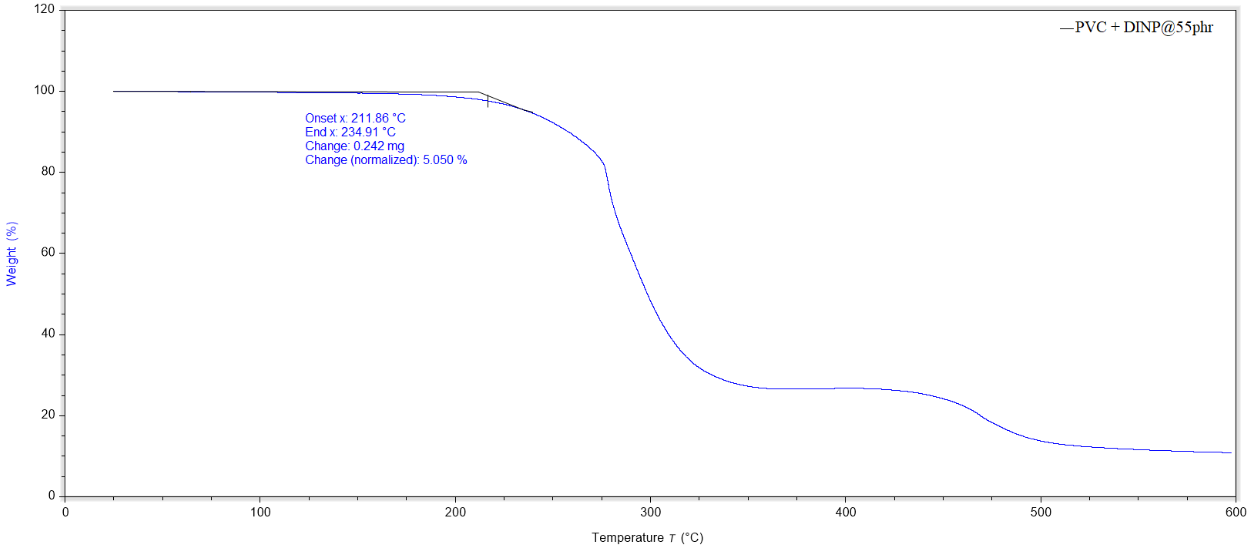

FIGURE 4-S7 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr.

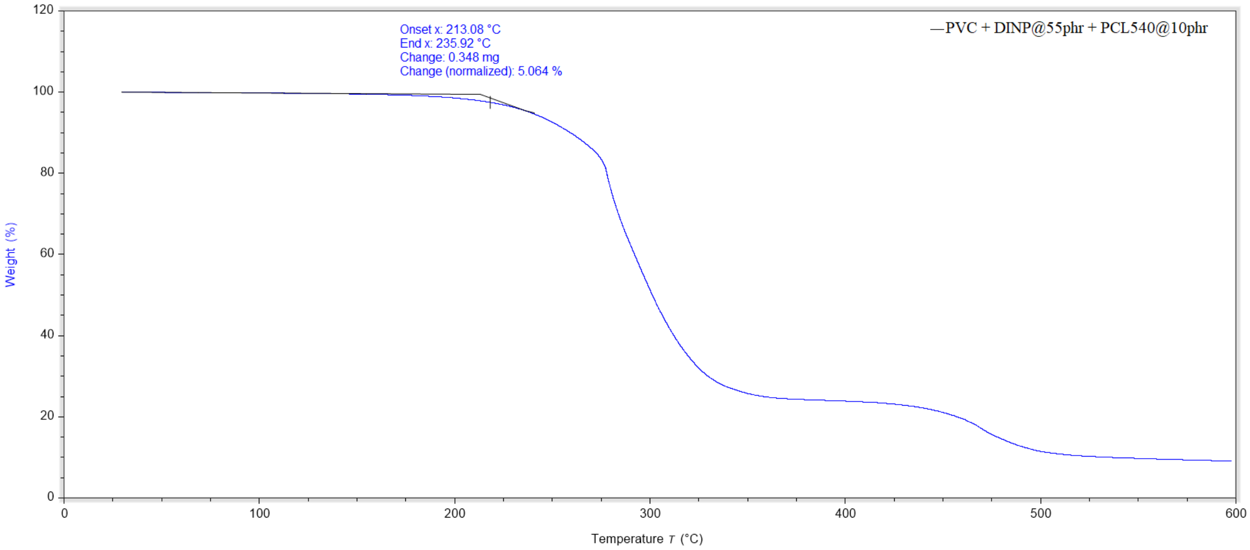

FIGURE 4-S8 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr and PCL$_{540}$-Succ-C$_7$ at 10 phr.

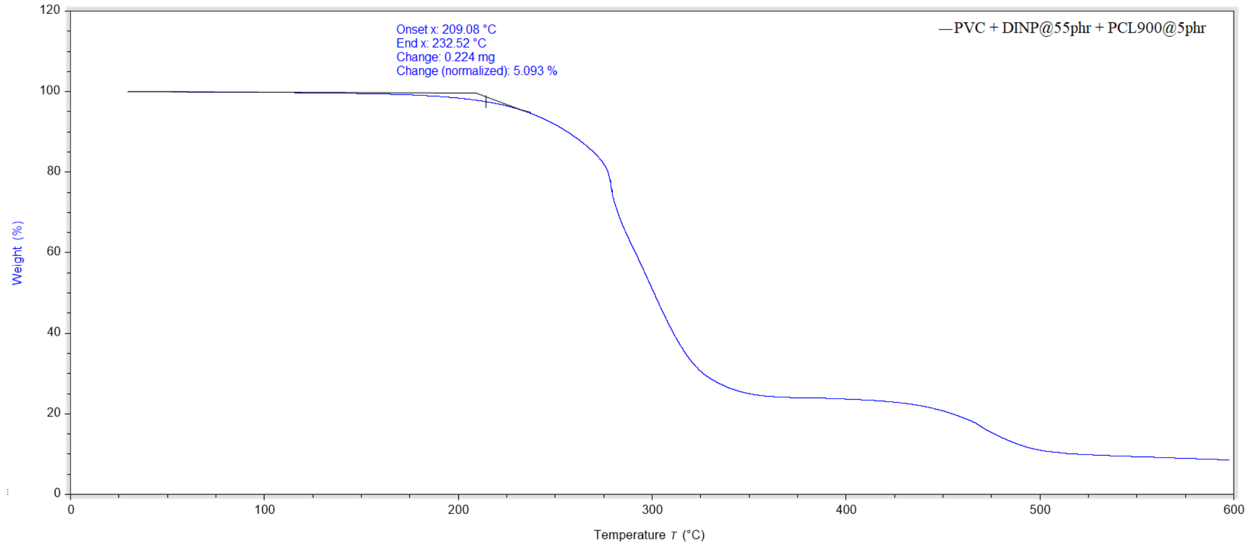

FIGURE 4-S9 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 5 phr.

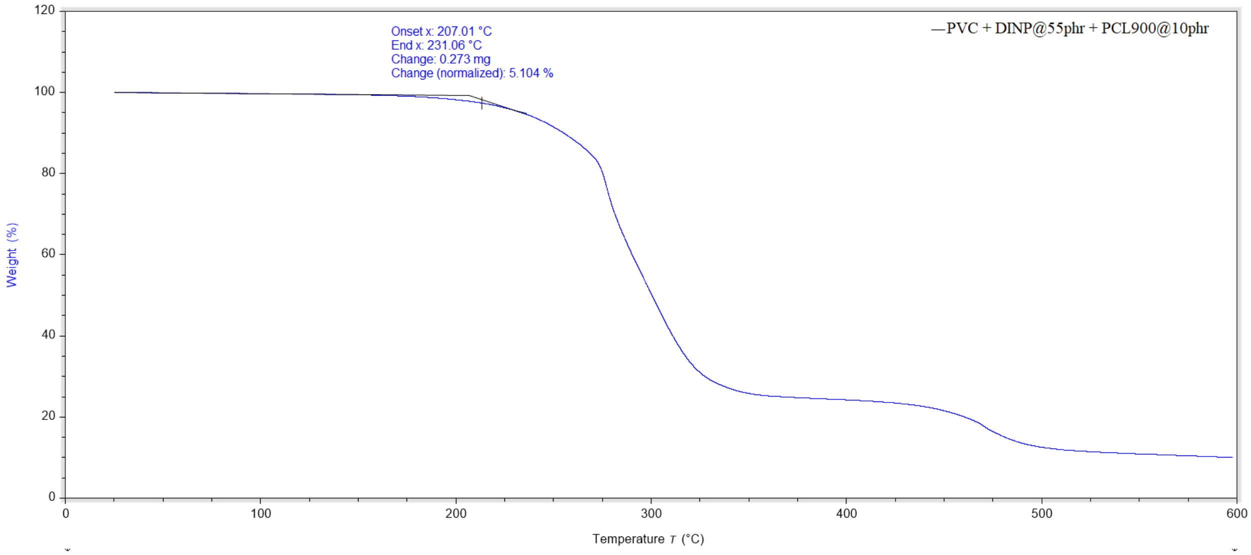

FIGURE 4-S10 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 10 phr.

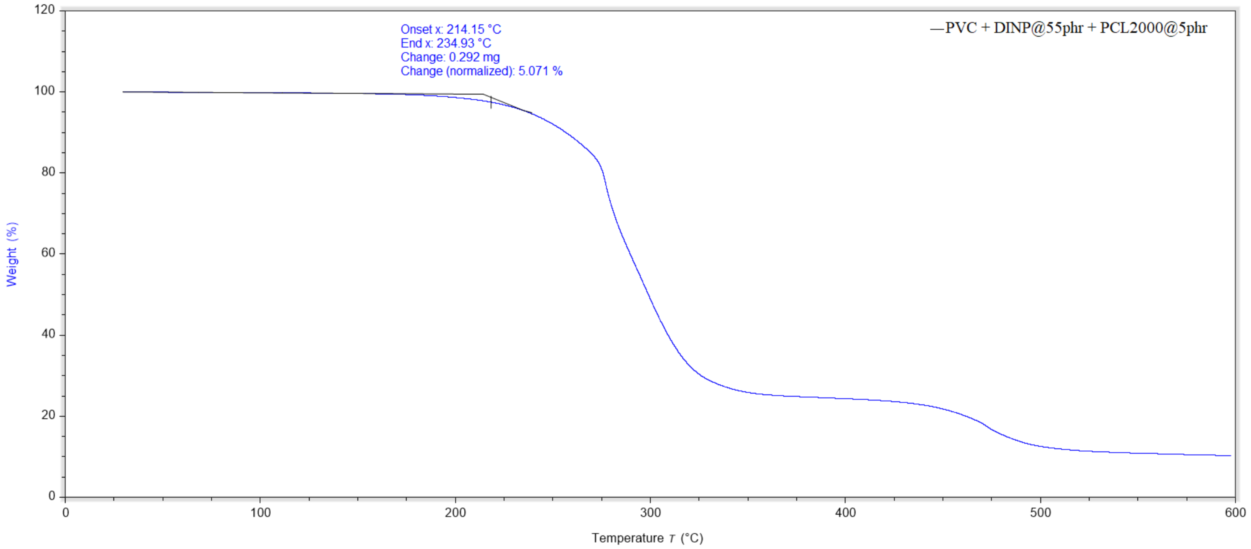

FIGURE 4-S11 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr and PCL_{2000}-Succ-C_7 at 5 phr.

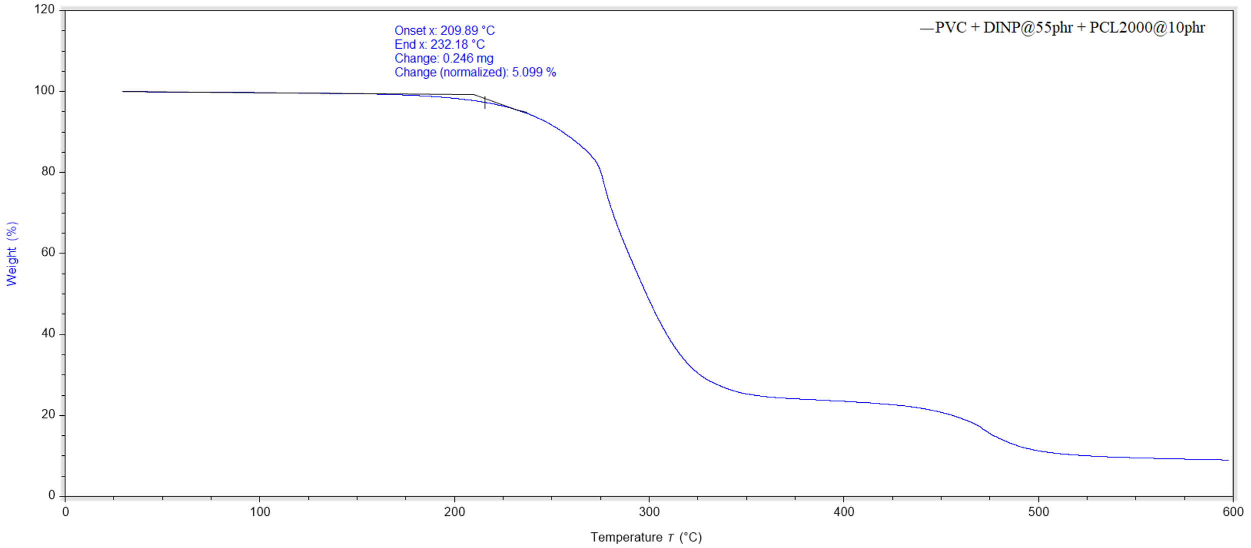

FIGURE 4-S12 TGA thermograms and onset degradation temperature of 5% weight loss for PVC calendering films with DINP at 55 phr and PCL_{2000}-Succ-C_7 at 10 phr.

S3. Dynamic Mechanical Thermal Analysis

The DMTA results for PVC blended samples with PCL-based additives as secondary plasticizer are presented in Figures 4-S13 to 4-S18.

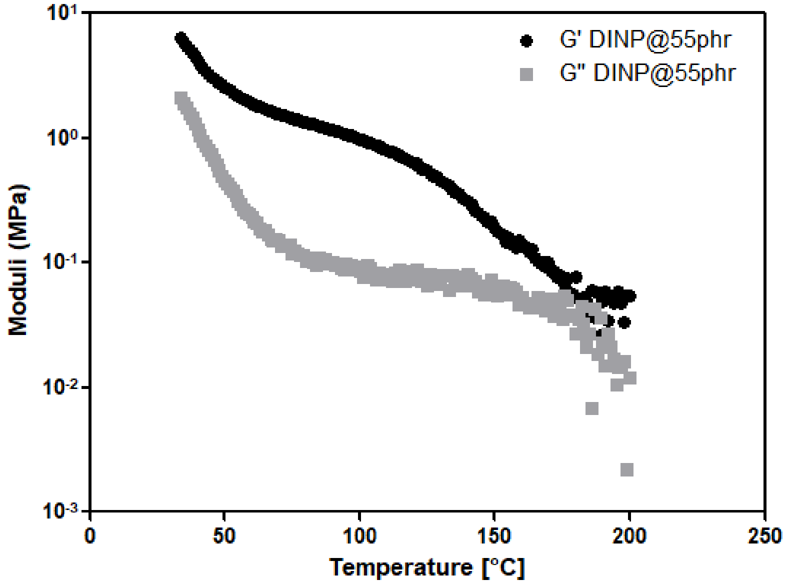

FIGURE 4-S13 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr.

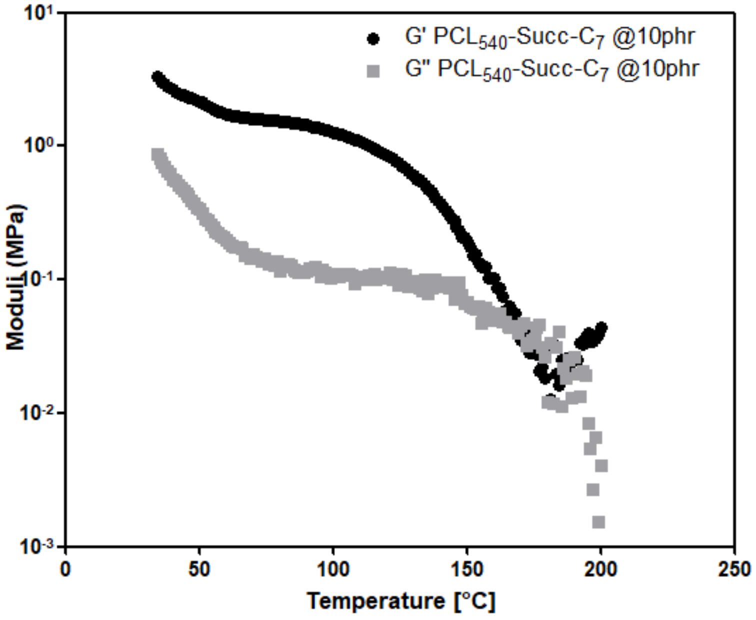

FIGURE 4-S14 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr and PCL$_{540}$-Succ-C$_7$ at 10 phr.

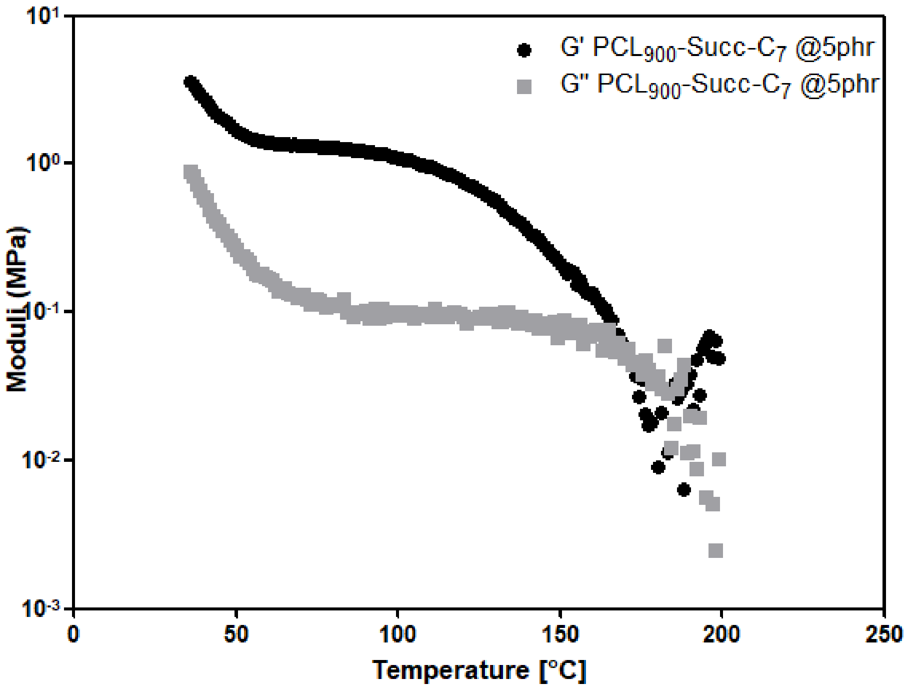

FIGURE 4-S15 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 5 phr.

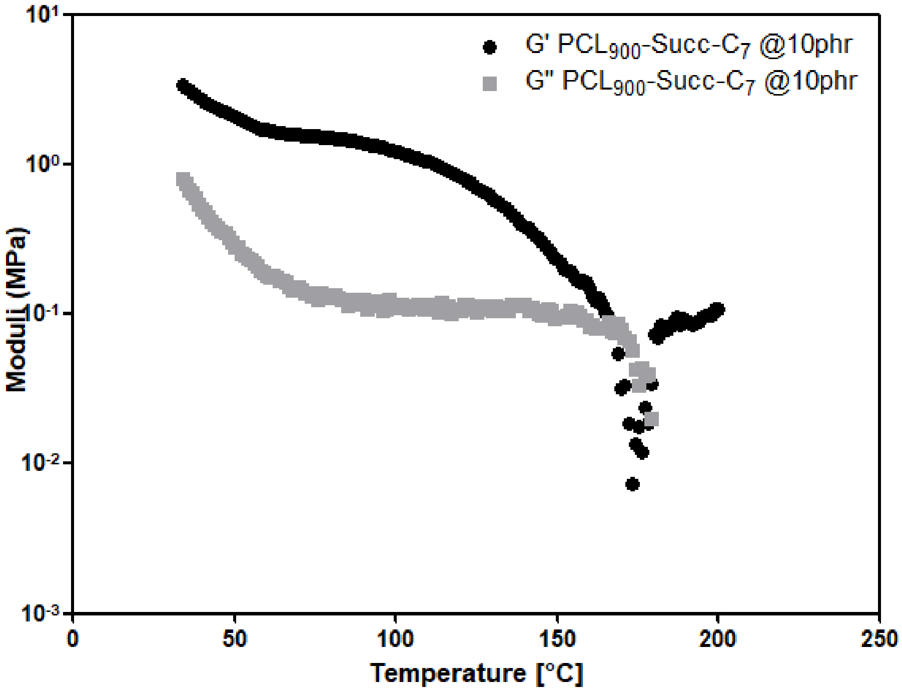

FIGURE 4-S16 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr and PCL_{900}-Succ-C_7 at 10 phr.

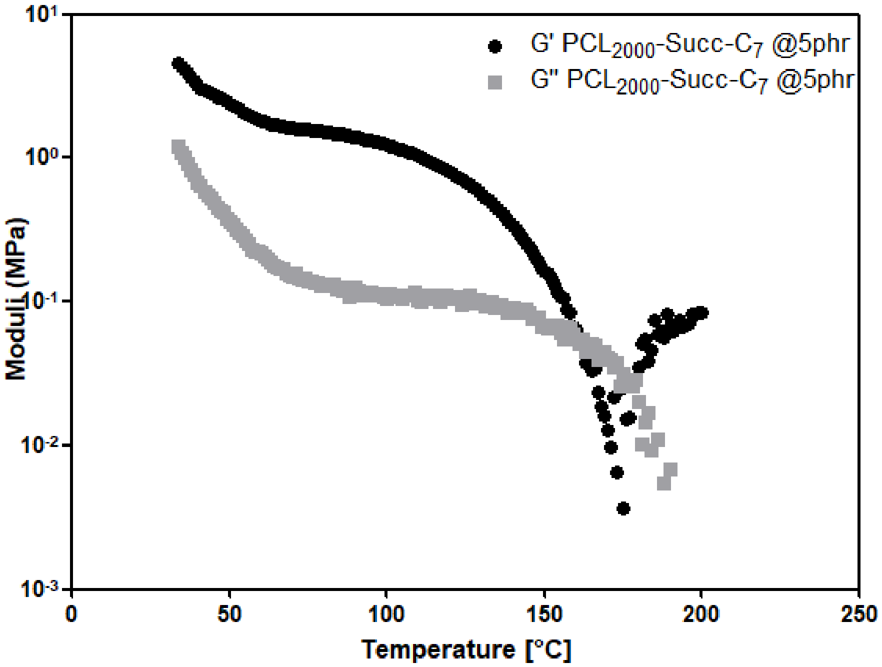

FIGURE 4-S17 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr and PCL_{2000}-Succ-C_7 at 5 phr.

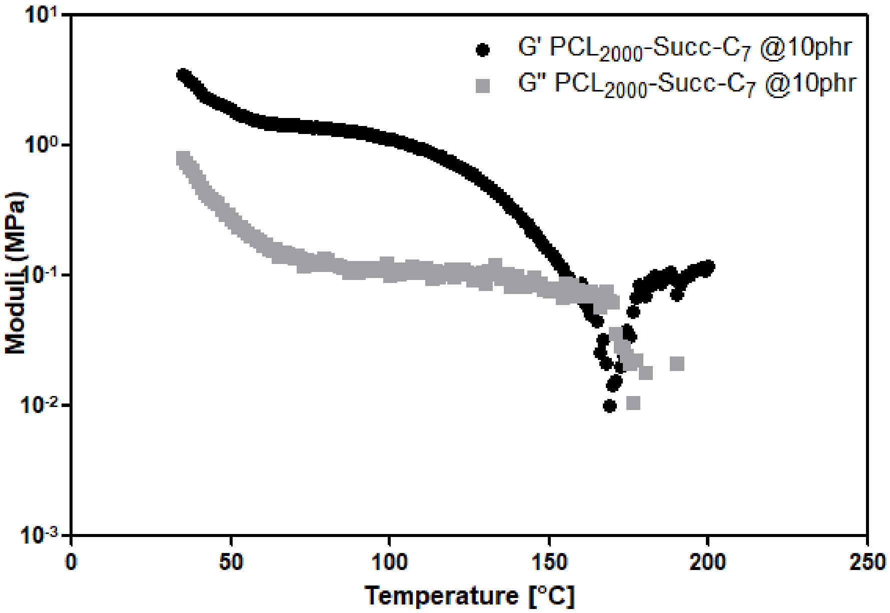

FIGURE 4-S18 Storage and loss modulus as a function of temperature of PVC calendering films with DINP at 55 phr and PCL_{2000}-Succ-C_7 at 10 phr.

S4. Mechanical properties

The result of tensile for PVC blended samples with PCL-based additives as secondary plasticizer are summarized in Table 4-S1

TABLE 4-S1 Mechanical properties of PVC calendering films with DINP at 55 phr and PCL-based additives. Means and standard deviations are reported.

Sample	**Tensile strength (MPa)**	**Elongation at break (%)**
PVC + DINP@55phr	82.1 ± 9.9	281.1 ± 41.0
PVC + DINP@55phr + PCL$_{540}$-Succ-C$_7$@5phr	74.6 ± 5.1	312.6 ± 31.4
PVC + DINP@55phr + PCL$_{900}$-Succ-C$_7$@10phr	75.0 ± 4.7	254.7 ± 16.6
PVC + DINP@55phr + PCL$_{900}$-Succ-C$_7$@10phr	75.5 ± 3.2	309.6 ± 15.7
PVC + DINP@55phr + PCL$_{2000}$-Succ-C$_7$@5phr	81.3 ± 3.5	305.7 ± 23.4
PVC + DINP@55phr + PCL$_{2000}$-Succ-C$_7$@10phr	67.5 ± 2.5	287.5 ± 15.3

5. Investigation of Extruded Poly(vinyl chloride) Blends with Poly(caprolactone)-based Additives as Primary Plasticizer

5.1 Preface

This chapter focuses on evaluating the mechanical, thermal, and rheological properties of PVC blended samples utilizing the PCL-based additives as the primary plasticizer. The synthetic method and characteristics of PCL-based additives remain consistent with those detailed in preceding sections, obviating the need for separate TGA and DSC testing for neat PCL-based additives. The tests were conducted across concentrations of 20, 40, and 60 phr. To comprehend the impact of varying PCL-based additive concentrations on the properties of the blends, the results were compared with PVC blended samples containing DINP at 55 phr. This comparative analysis aimed to elucidate how alterations in the concentration of PCL-based additives influence the overall characteristics of the blends.

5.2 Introduction

Various researchers have attempted to create bio-degradable and sustainable plasticizers as substitutes for phthalate-based counterparts, aiming to mitigate the adverse environmental and health impacts posed by them. The incorporation of PCL-based additives as the primary plasticizer in PVC calendered films represent a progressive step in the evolution and substitution of conventional plasticizers, as long as it demonstrates comparable plasticization performance without substantially altering the physical properties of the calendered films. The aim of this series of experiments is to determine the feasibility of utilizing PCL-based additives as either primary or secondary plasticizers.

5.2 Thermal properties

The thermal properties of PVC extruded samples were determined by TGA and DSC analysis. PVC blends made with PCL_{540}-Succ-C_7, PCL_{900}-Succ-C_7 and PCL_{2000}-Succ-C_7 at 20, 40 and 60 phr resulted in an onset degradation temperature range from 210 to 241°C, and the degradation temperatures are shown in Table 5.1.

TABLE 5.1 Onset degradation temperature of 5% weight loss of PVC blends with different PCL-based additives at different concentrations.

	Sample	**Onset Degradation temperature of 5% weight loss (°C)**			
		PCL concentration: 0 phr	PCL concentration: 20 phr	PCL concentration: 40 phr	PCL concentration: 60 phr
PCL blends	PVC + DINP@55phr	211	-	-	-
	PVC + PCL_{540}-Succ-C_7	-	223	216	210
	PVC + PCL_{900}-Succ-C_7	-	233	230	226
	PVC + PCL_{2000}-Succ-C_7	-	241	231	241

The onset degradation temperature remains largely unaffected by both the molecular weight of the PCL core and the concentration of PCL-based additives in PVC blends, as observed in the study. Importantly, all recorded temperatures surpass the operating conditions of the equipment utilized in the production of PVC calendered films. This observation leads to the conclusion that material degradation is not anticipated during production runs. The study also suggests the PVC blends have robust thermal stability in range of the investigated variations in molecular weight and additive concentrations, affirming their suitability for the intended production processes.

When blending PCL-based additives with PVC at concentrations of 20, 40, and 60 parts per hundred of resin (phr), it was observed that the T_gs were significantly lower than that of pure PVC (T_g = 78.1°C). This outcome aligns with theoretical expectations, as the addition of plasticizers is known to reduce the Tg of PVC [21]. The T_gs were systematically measured for PVC blended samples incorporating the three different PCL-based additives at the mentioned concentrations. Detailed results can be found in Table 5.2.

TABLE 5.2 T_g of PVC blends with different PCL-based additives at different concentrations.

	Sample	**Glass transition temperature (°C)**			
		PCL concentration: 0 phr	PCL concentration: 20 phr	PCL concentration: 40 phr	PCL concentration: 60 phr
PCL blends	PVC + DINP@55phr	-65.0	-	-	-
	PVC + PCL_{540}-Succ-C_7	-	25.3	-10.6	-20.5
	PVC + PCL_{900}-Succ-C_7	-	28.8	-1.8	-13.7
	PVC + PCL_{2000}-Succ-C_7	-	33.2	6.7	-9.3

With increasing molecular weight of the PCL-based additives, agreement with the Flory-Fox equation (see equation (5.1)) was observed, showing that the T_g increases when increasing molecular weight [67].

$$T_g = T_{g,\infty} - \frac{K}{M_n}, \tag{5.1}$$

Here, T_g is the glass transition temperature of the polymer sample, $T_{g,\infty}$ is the maximum glass transition temperature that can be achieved at a theoretical infinite molecular weight, K is an empirical parameter related to the free volume present in the polymer sample and M_n is the molecular weight of the polymer sample.

The precision of the Flory-Fox equation is evident in accurately determining the T_g of homopolymers, such as the PCL-based additives. However, in the context of polymer blends incorporating plasticizers, the more applicable Fox equation [67] is employed (see equation (5.2)). Analogous to the Flory-Fox equation [67], an increase in the molecular weight of any component in the blend corresponds to an elevated T_g. Conversely, an increase in the concentration of the plasticizer (since it has lower T_g than most matrix polymers) leads to a reduction in the T_g of the blend. This observation aligns with the findings presented in Table 5.2, demonstrating a consistent agreement between the Fox equation and the experimental results.

$$\frac{1}{T_{g,blend}} = \frac{x_A}{T_{g,A}} + \frac{(1 - x_A)}{T_{g,B}} \tag{5.2}$$

Here, $T_{g,blend}$ is the glass transition temperature of the blend, x_A is the weight fraction of component A, $T_{g,A}$ is the glass transition temperature of the component A and $T_{g,B}$ is the glass transition temperature of the component B.

5.3 Mechanical properties

From tensile testing, tensile strength and elongation at break were measured for the three PCL-based additives in the polymer matrix at concentrations of 20, 40 and 60 phr (Figure 5.1).

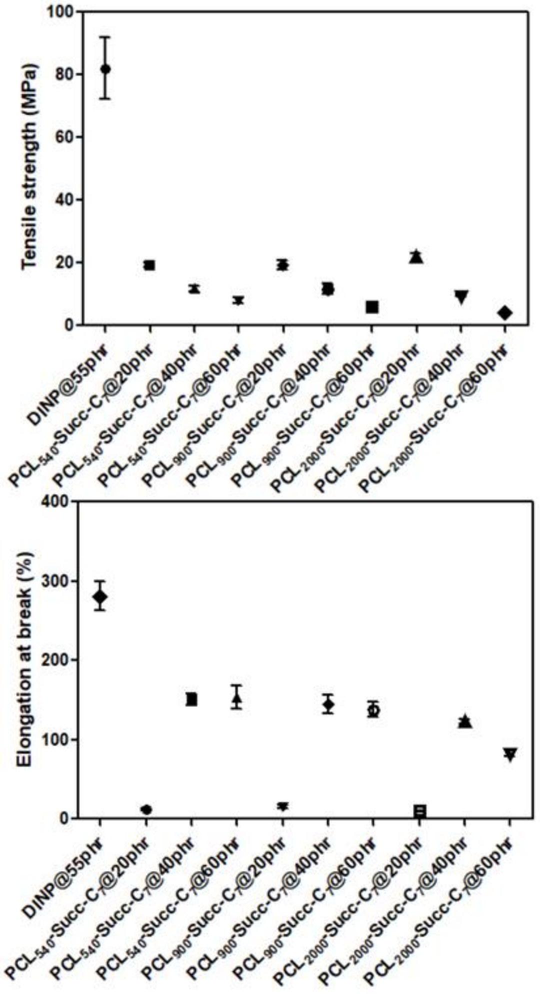

FIGURE 5.1 Tensile strength and strain in % elongation at break of PVC blends made with PCL540-Succ-C7, PCL900-Succ-C7 and PCL2000-Succ-C7 at 20, 40 and 60 phr.

Figure 5.1 illustrates a notable difference between PVC blended samples with DINP at 55 phr and those incorporating PCL-based plasticizers. To statistically assess and compare the tensile strength and elongation at break of PCL-based plasticizer samples at the same concentration and with the same molecular weight, a one-way ANOVA test with a 95% confidence interval ($\alpha = 0.05$) was conducted. Additionally, a Tukey test was employed for individual comparisons.

Regarding tensile strength, all PVC blended samples with PCL-based additives have a significantly lower tensile strength than DINP samples. However, no significant difference was observed among PVC blended samples at the same concentration of PCL-based additives, regardless of molecular weight. However, for PVC blended samples with the same molecular weight at different concentrations, specifically PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7, no significant difference was found between concentrations of 20 and 40 phr, and between concentrations of 40 and 60 phr. Notably, there was a significant difference between blend tensile strength at concentrations of 20 and 60 phr. In contrast, PVC blended samples with PLC_{2000}-Succ-C_7 exhibited a significant difference among all samples at different concentrations, as indicated by the one-way ANOVA test. This analysis simply states that the tensile strength changes rather gradually for a blend with a given PCL-based additive.

Similarly, a one-way ANOVA was employed to analyze elongation at break, all PVC blended samples with PCL-based additives have a significant lower elongation at break than DINP samples. However, for all PVC blended samples with PCL-based additives, there is no significant difference at concentrations of 20 and 40 phr, irrespective of the molecular weight of the additive. However, at 60 phr, while no significant difference was observed between PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7, there is a notable difference between these two additives compared to PCL_{2000}-Succ-C_7.

When examining PVC blended samples with the same molecular weight of PCL additives, a significant difference was identified at 20 phr compared to samples at 40 phr and 60 phr. Interestingly, there was no significant difference between concentrations of 40 and 60 phr for any of the samples within the same molecular weight category. This means that beyond a certain cut-off concentration, in this case 20 phr, there is a little change in the blend tensile properties.

5.4 Rheological properties

The η* of PVC blends made with the different PCL-base additives at concentrations of 20, 40 and 60 is shown in Figure 5.2 below.

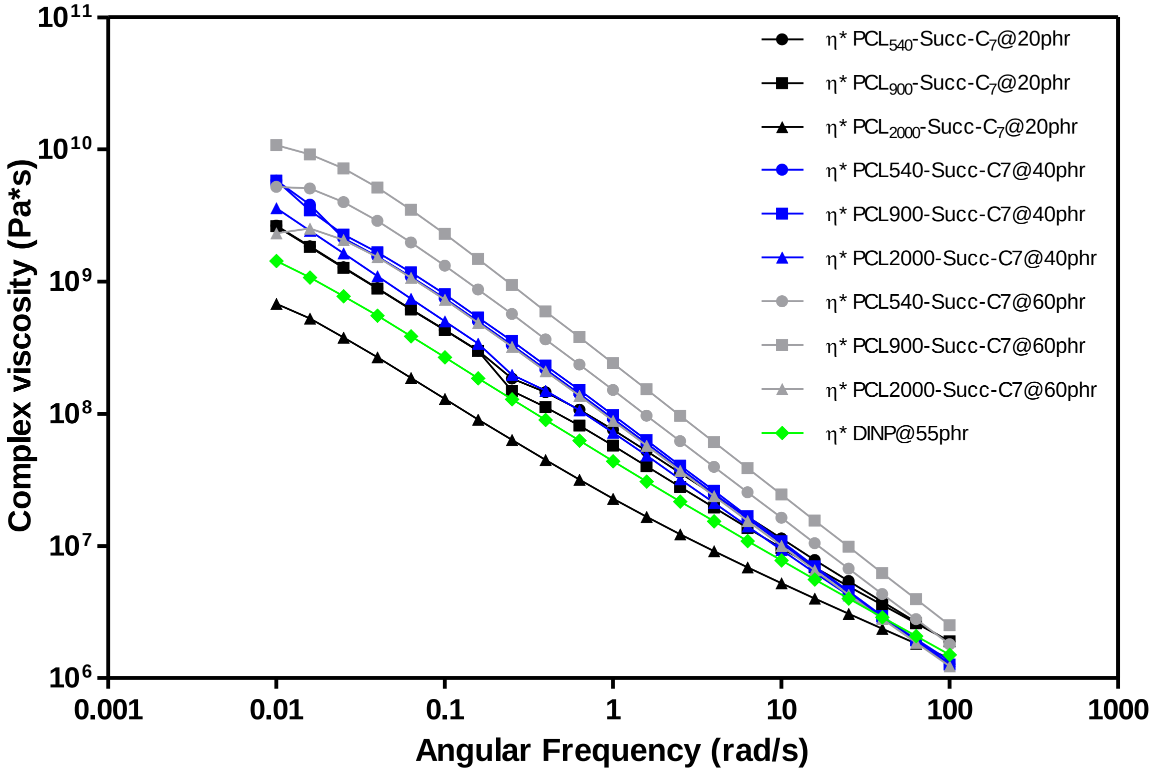

FIGURE 5.2 Complex viscosity as a function of angular frequency of PVC blends made with PCL-based additives at 20, 40 and 60 phr.

The η* follow an expected trend, with the highest values observed in the PVC blended samples containing PCL-based additives at concentrations of 60 phr. The η* of PVC blended samples with PCL-based additives are significantly higher than PVC blended samples with DINP, and this outcome aligns with expectations, given that the viscosity of neat DINP is lower (ranging from 50 to 180 mPa·s), showing a higher difference in viscosity as the concentration of PCL-based additives increases. When comparing all PVC blended samples based on molecular weight, the highest η* was observed with PCL_{900}-Succ-C_7, followed by PCL_{540}-Succ-C_7, and finally PCL_{2000}-Succ-C_7. It is expected that η* increases as the M_n of the samples increases as evidenced in PCL_{540}-

Succ-C_7 and PCL_{900}-Succ-C_7. However, the deviation observed in PCL_{2000}-Succ-C_7 suggests a potential mixing issue when blended with PVC.

In addition to η*, measurements of G' and G" were conducted, and the results are presented in Figure 5.3. The findings reveal that, across all samples and regardless of angular frequency and the concentration of PCL-based additives, the elastic forces (G') consistently dominate over viscous effects (G"). Similar to the η* results, the highest values of G' and G" are observed for plasticized samples at 60 phr, while the lowest values are recorded for PVC blends at 20 phr. Furthermore, the lowest values correspond to blended samples plasticized with PCL_{2000}-Succ-C_7. This suggests the blends are becoming more flexible with additive concentration (i.e., dominance of elastic behavior in the PVC blends) and is influenced by both concentration and the specific PCL-based additive used. Furthermore, the lowest moduli for the blends when the PCL with the highest molecular weight core (PCL_{2000}-Succ-C_7) is used is showing to be an exception. This may suggest ineffective mixing or phase separation compared to the other blends.

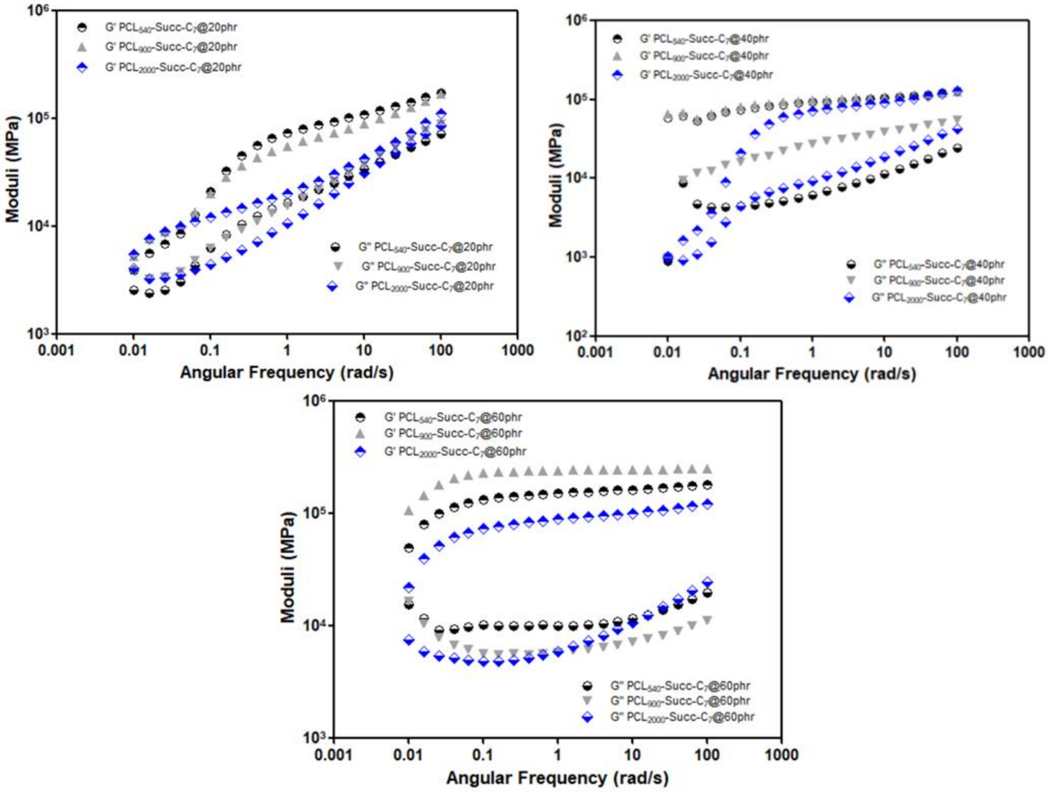

FIGURE 5.3 Storage and loss modulus as a function of angular frequency of PVC extruded samples with PCL-based additives at 20, 40 and 60 phr.

A DMTA test was conducted for the same PVC blended samples, revealing that, for all samples at a concentration of 20 phr, a crossover phenomenon occurs, as illustrated in Figure 5.4. The temperatures at which these crossovers take place are summarized in Table 5.3. It is noteworthy that for the remaining samples plasticized at concentrations of 40 and 60 phr, such crossovers did not occur (refer to Supporting Information). This suggests that within a temperature range spanning from 30°C to 200°C, the elongation forces consistently dominate over viscous effects in these samples. Consequently, these materials exhibit behavior akin to an elastic solid, emphasizing their solid-like characteristics within this specified temperature range.

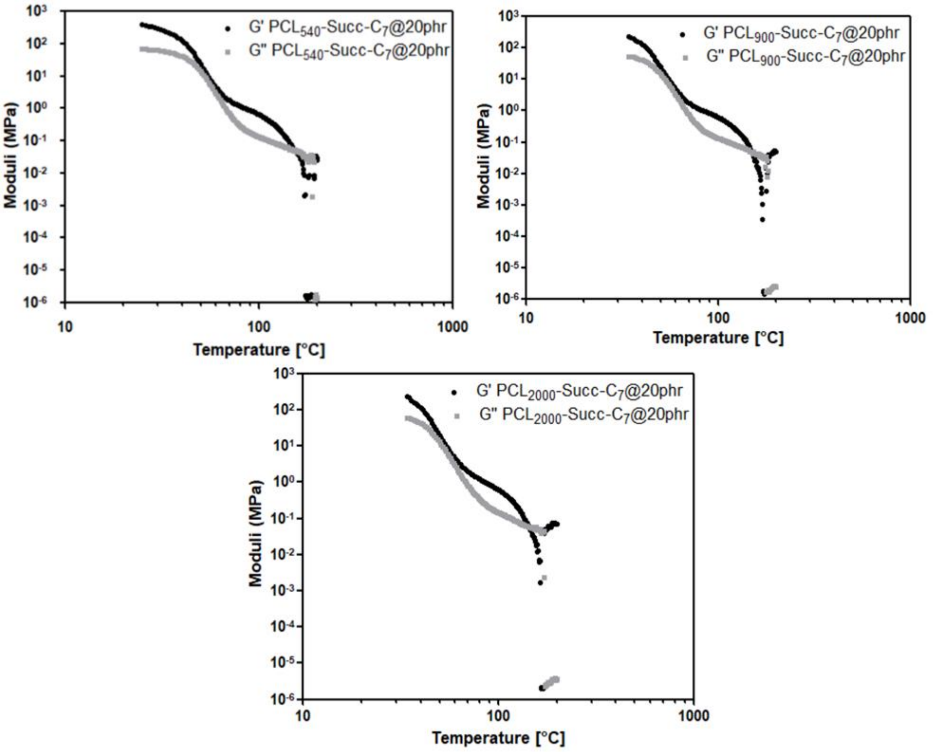

FIGURE 5.4 Storage and loss modulus as a function of temperature of PVC blends made with PCL-based additives at 20, 40 and 60 phr.

TABLE 5.3 Crossover temperature of the extrudate plasticized PVC films, as obtained from DMTA test.

Crossover temperature (˚C)		
PVC + PCL_{540}-Succ-C_7 @ 20 phr	**PVC + PCL_{900}-Succ-C_7 @ 40 phr**	**PVC + PCL_{2000}-Succ-C_7 @ 60 phr**
157	151	145

5.5 Conclusion

The utilization of PVC blended samples with PCL-based additives as a primary plasticizer demonstrated functional properties, albeit with a notable inferiority in mechanical performance when compared to PVC calender films employing DINP. The rheological properties were significantly impacted by using PCL-based additives as a primary plasticizer, resulting in significantly higher η^* compared to DINP samples. Furthermore, distinct rheological behavior was observed in PCL_{2000}-Succ-C compared to PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7, indicating potential challenges such as mixing issues and phase separation from the PVC polymer matrix.

While the thermal properties were influenced by the concentration and M_n of the PCL-based additives, aligning with the predictions of the Flory-Fox equation for homopolymers and the Fox equation for PVC blended samples, these thermal variations do not pose a risk. The onset degradation temperature remains above the operational conditions of equipment used in the production of PVC calendered films.

Therefore, PCL-based additives as primary plasticizers prove effective in plasticizing PVC. However, the observed poor mechanical performance, especially with PCL_{2000}-Succ-C_7, as indicated by rheological results, raises concerns about the viability of these additives as primary plasticizers. The recommendation is to avoid their use in this capacity, particularly PCL_{2000}-Succ-C_7, due to potential mixing issues and indications of phase separation in the blends.

6. General Discussion and Future Work

The demand for bio-based plasticizers in polymer products is on the rise. Despite the numerous proposed bio-based plasticizers, only a few have gained commercial significance, primarily finding use in specialized applications. This thesis aimed to assess a series of modified PCL-based plasticizers as additives to calendered PVC films. Remarkably, this family of compounds demonstrated outstanding performance in mitigating or preventing gas checks at concentrations as low as 10 parts per hundred of resin (phr). Importantly, this was achieved without compromising the mechanical properties of the PVC blended films, where DINP served as the primary plasticizer at a concentration of 55 phr. As primary plasticizer the PCL-based additive was functional but showed poor performance in tensile properties when compared to DINP. This research underscores the potential of these modified PCL-based plasticizers as effective and sustainable alternatives in PVC formulations, showcasing their ability to address specific challenges without sacrificing overall material performance.

The introduction of PCL-based additives as a secondary plasticizer in PVC calendered films has proven effective in reducing or eliminating gas checks without necessitating alterations to the process conditions. Concentrations of 5 and 10 parts per hundred of resin (phr) of PCL-based additives were examined to assess their performance in preventing gas checks. A minimal reduction was observed at 5 phr compared to calendering films without PCL-based additives. However, increasing the concentration to 10 phr resulted in the complete prevention of gas checks with PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7, and a significant reduction from 5115 gas checks per square meter of film without PCL-based additives to 562 gas checks per square meter of film with PCL_{2000}-Succ-C_7.

Representative tests were carried out to delve into the physical and chemical properties responsible for enabling PCL-based additives to limit gas checks. Additionally, PVC blends were extruded with PCL-based additives as the primary plasticizer at concentrations of 20, 40, and 60 phr. These blends underscored the issues with using an excessively high molecular weight PCL additive. Instead of increasing the viscosity as expected, the PCL with a M_n = 2000 g/mol core resulted in lower viscosities (and moduli). This suggests some issues with applying a higher molecular weight PCL, perhaps related to immiscibility.

The thermal properties of PVC blended samples with PCL-based additives, used as secondary plasticizers, were evaluated through TGA and DSC. Notably, these samples did not exhibit a significant difference in the onset degradation temperature, falling within the range of 207 to 214 °C. Given that the process temperature lies below this range, there appears to be no risk of degradation during calendering. Similarly, the glass transition temperature (T_g) measured by DSC did not show a significant difference, ranging from -63 to -62 °C. This provides evidence that this series of PCL-based additives can be incorporated in existing industrial processes without compromising the thermal and mechanical properties of the product, while eliminating unwanted gas checks.

Further, when used as primary plasticizer, PVC extruded samples displayed a wider onset degradation temperature range of 210 to 241 °C. The lowest degradation temperature corresponded to PCL_{540}-Succ-C_7 at 60 phr, while the highest was observed with PCL_{2000}-Succ-C_7 at both 20 and 60 phr. This suggests that a higher molecular weight contributes to improved thermal stability, likely due to the entanglement of the plasticizer within the polymer matrix. The T_g values also exhibited a significant difference, ranging from 33 to -20 °C. The highest T_g correlated with the higher molecular weight plasticizer, aligning with the Flory-Fox equation, which establishes that higher molecular weight leads to a higher blend T_g.

The application of PCL-based additives in calendering PVC films did not significantly impact the mechanical properties, as revealed by the statistical analysis conducted through one-way ANOVA ($\alpha = 0.05$) and the Tukey test. In contrast, the extruded PVC blends using PCL-based additives as the primary plasticizer showed poorer tensile performance compared to PVC blended samples with DINP. In addition, the PVC blended samples exhibited a significant difference between blends at concentrations of 20 phr versus 40 phr, as well as 20 phr versus 60 phr. These results were anticipated, as the tensile testing bars at 20 phr were not sufficiently flexible, resulting in elongations at break ranging from 9 to 20%. In contrast, samples at concentrations of 40 phr and 60 phr were significantly more flexible, with elongations at break approximately ranging from 120 to 170%, with the lowest values observed for PCL_{2000}-Succ-C_7. PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 exhibited similar values (see Appendix). This trend was similarly observed for tensile strength.

Moreover, a significant difference was noted between PVC blends plasticized with DINP compared to those using PCL-based additives as the primary plasticizer. Both elongation at break and tensile strength were significantly higher for DINP plasticized samples. This suggests that although PCL-based additives as a primary plasticizer can indeed affect the mechanical properties of calendering films, they cannot be swapped out for DINP as primary plasticizer by our industrial collaborator. However, as secondary plasticizers at concentrations of 5 and 10 phr, PCL-based additives did not significantly modify the mechanical properties of the PVC blended films. This nuanced understanding of the mechanical impact of PCL-based additives in different roles within PVC formulations is critical towards applying them efficiently.

The rheological properties were assessed through dynamic oscillatory tests, measuring η*, G', and G''. There was insufficient support for the hypothesis that viscosity plays a significant role in preventing gas checks. The extruded PVC blends plasticized with PCL-based additives as the primary plasticizer seemed to support this hypothesis, as η* was significantly lower for samples plasticized with DINP as the primary plasticizer. This difference in η* increased with the concentration of PCL-based additives, reaching up to one order of magnitude with PCL_{900}-Succ-C_7 at 60 phr.

However, calendering PVC blends plasticized with DINP without PCL-based additives resulted in slightly higher η* compared to samples plasticized with DINP and PCL-based additives as secondary plasticizer at concentrations of 5 and 10 phr. The observed difference in η* is deemed insignificant, indicating that PCL-based additives as secondary plasticizers do not impact η* at concentrations of 5 and 10 phr. This finding suggests that the prevention of gas checks and viscosity might not be correlated. It implies that other factors or mechanisms, aside from viscosity, may contribute to the prevention of gas checks in the calendering process. Further exploration and analysis may be necessary to elucidate the underlying mechanisms at play in preventing gas checks during calendering in PVC blends with PCL-based additives.

DMTA revealed a cross-over temperature in PVC films plasticized with DINP and PCL-based additives, marking a transition from the material response from one that is mostly elastic to one that is more like a viscous liquid. The cross-over temperature decreased with increasing molecular weight of PCL-based additives, indicating greater viscosity for higher molecular weight additives. Despite this influence of molecular weight on rheological properties, there was no correlation observed between cross-over temperatures and the prevention of gas checks during calendering. This underscores the previous observations that it is more likely that gas checks prevention is derived from physico-chemical interactions rather than rheology.

The chemical properties were examined by titrating the end-groups of the PCL-based additives to determine the acid value of the synthesized samples. The results indicated a correlation between the acid values and the prevention of gas checks. The lowest acid value was observed for PCL_{2000}-Succ-C_7 (23.25 mgKOH/g). When this additive was used at 10 phr, gas checks were significantly reduced from 5115, observed when using only DINP, to 562 gas checks per square meter of film. In contrast, PCL_{540}-Succ-C_7 (30.12 mgKOH/g) and PCL_{900}-Succ-C_7 (35.10 mgKOH/g) completely prevented the formation of gas checks at 10 phr. The hypothesis is that high acid values, corresponding to the hydrophobic capped n-heptanol groups, decrease the surface tension in the films, preventing air from getting entrapped.

While PCL-based additives have demonstrated functionality as primary plasticizers when blended with PVC, their optimal application appears to be as secondary plasticizers. This inclination arises from the sustained significance of phthalate-based plasticizers, which remain a vital category in industry due to their impressive performance and cost-effectiveness [68]. The utilization of PCL-based additives as primary plasticizers, albeit effective, raises production costs, subsequently elevating the final product's overall cost. This factor compromises the market competitiveness of manufacturers. Phthalate-based plasticizers have maintained their dominance in the industry for decades, owed to their superior performance [69]. Notably, PCL-based additives exhibit sub-optimal mechanical properties when employed as primary plasticizers. However, as secondary plasticizers, particularly with PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 at 10 phr, they showed outstanding performance in preventing gas checks without compromising the mechanical properties of the films. Moreover, these formulations demonstrate no significant deviation in η^* compared to PVC calendered films without PCL-based additives. Enhancements in the production of calendered films not only reduce material wastage and energy consumption but also mitigate production delays attributed to the occurrence of poor-quality films with gas checks. While the pursuit of fully sustainable materials requires further investigation, the ongoing improvement of existing plastics remains a valuable step toward sustainability.

Additional work is required to perform a life cycle assessment (LCA) for evaluating the environmental impacts associated with PCL-based additives in PVC calendering films. For example, the PCL is petro-based, despite it being biodegradable. This is likely to significantly impact the LCA analysis. Further, the implications of incorporating PCL in terms of recyclability have not been addressed, presenting a challenge in recycling a blend of PVC with PCL. Additionally, exploring options to improve the durability of the blend could lead to an extended usable lifetime. Moreover, an in-depth analysis will be undertaken with the objective of substituting the core molecule PCL in the additives with a more environmentally sustainable alternative. Oligo(lactide) esters have been reported recently as effective plasticizers for high molecular weight PLA, with bio-content > 80% and excellent miscibility [70]. We can apply the same ring-opening polymerization (ROP) to lactide (LA), but the enantiomeric nature of the LA monomer can affect the plasticized PLA physical and mechanical properties [71]. Other reports employed levulinic acid (LeA),[72] a top 12 green platform chemical [73] that is claimed to have lower global warming potential than succinic acid (SA) [74] which was tailored with other bio-based components like isosorbide, 1,4 butanediol and lactide units to make PLA plasticizers to balance low migration, good miscibility and mechanical properties. The focus will be on capping the plasticizer with hydrophobic groups to retain a high acid value, ensuring the prevention of gas checks while enhancing the overall environmental sustainability of the formulation.

7. Conclusions

The objectives of this study were to evaluate the efficacy of PCL-based additives as secondary plasticizers at concentrations of 5 and 10 phr, establish a connection to the reduction of gas checks in PVC calendering films, and observe the impact of physical and chemical properties in calendered PVC blends plasticized with PCL-based additives.

All three synthesized PCL-based additives proved effective in reducing gas checks in PVC calendering films. At 10 phr, PCL_{2000}-Succ-C_7 significantly reduced gas checks from 5115 (using DINP as the primary plasticizer without PCL-based additives) to 562 gas checks per square meter of film. PCL_{540}-Succ-C_7 and PCL_{900}-Succ-C_7 at 10 phr completely prevented gas checks. The mechanical properties remained unaffected when PCL-based additives were used as secondary plasticizers at 5 and 10 phr, unlike rheological and thermal properties.

DMTA revealed varying cross-over temperatures between G' and G" based on the molecular weight of the additives, indicating alterations in rheological and thermal properties. However, no clear relationship was found between these properties and the prevention of gas checks.

Chemical properties, assessed through the titration of end-groups, were found to correlate with the occurrence of gas checks in PVC calendering films. Higher acid values of PCL-based additives proved more effective in preventing the formation of gas checks. The hypothesis suggests that hydrophobic end-groups, such as n-heptanol, may decrease the surface tension in the films, consequently preventing the entrapment of air. This indicates that the prevention of gas checks when using PCL-based additives as secondary plasticizers in PVC calendering films is more closely related to chemical properties than rheological properties.

8. References

[1] Wanli Ma, Yuting Zhu, Ning Cai, Xianhua Wang, Yingquan Chen, Haiping Yang, Hanping Chen, 2023. Preparation of carbon nanotubes by catalytic pyrolysis of dechlorinated PVC. Waste Management 169 (2023) 62–69.

[2] Plastics – the Facts 2022, PlasticsEurope, https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/, October, 2022 (accessed 1 November 2022)

[3] K. Kothai Subramanian, L. Senthil Vadivu, M.D. Subramaniyam, Kumar, Ind Crop Prod. 182 (2022), https://doi.org/10.1016/j.indcrop.2022.114933.

[4] Plastics – the Facts 2022, PlasticsEurope, https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/, October 2022 (accessed 1 November 2022).

[5] Elena-Diana, Ungureanu-Comanita & Ghinea, Cristina & Ca, Mihaela & Simion, Isabela & Petraru, Madalina & Gavrilescu, Maria. (2020). Environmental Impacts of Polyvinyl Chloride (PVC) Production Process.

[6] Yu Han, Caili Zhang, Yang Yang, Yunxuan Weng, Piming Ma, Pengwu Xu. Epoxidized isosorbide-based esters with long alkyl chains as efficient and enhanced thermal stability and migration resistance PVC plasticizers. 2023. Polymer Testing 123 (2023) 108048.

[7] Minjia Lu, Pingping Jiang, Pingbo Zhang, Shan Feng, Zhixuan Cui, Qingkui Song, Yong Zhao, Jingxian Shen, Yiyi Fan, Huixian Lu, A multifunctional lactic acid-based plasticizer used for plasticizing PVC and PLA: Endowing PLA elastic restore capability, Journal of Industrial and Engineering Chemistry, Volume 128, 2023, Pages 245-257, ISSN 1226-086X, https://doi.org/10.1016/j.jiec.2023.07.054.

[8] C.E. Wilkes, J.W. Summers, C.A. Daniels, M.T. Berard, PVC Handbook, Hanser, Munich, Cincinnati, 2005.

[9] E. Linde, U.W. Gedde, Plasticizer migration from PVC cable insulation - The challenges of extrapolation methods, Polym. Degrad. Stab. 101 (2014) 24–31.

[10] T. Mekonnen, P. Mussone, H. Khalil, D. Bressler, Progress in bio-based plastics and plasticizing modifications, J. Mater. Chem. A. 1 (2013) 13379–13398.

[11] X.-F. Wei, K.J. Kallio, S. Bruder, M. Bellander, M.S. Hedenqvist, Plasticizer loss in a complex system (polyamide 12): Kinetics, prediction and its effects on mechanical properties, Polym. Degrad. Stab. 169 (2019) 108985.

[12] John Wiley & Sons, Encyclopedia of Polymer Science and Technology (2011).

[13] Allen D. Godwin, Leonard G. Krauskopf Handbook of vinyl chloride, 2nd edition (2008). Wiley series on plastics engineering and technology Chapter 7 Monomeric plasticizers. P. 173 - 221

[14] W. V. Titow. PVC plastics: properties, processing and applications. Elsevier Applied Science Publishers, London and New York, 1990.

[15] Grand View Research, Bio-Plasticizers Market – Market Estimates & Trend Analysis, (2017) 1–44.

[16] R. Wolf, B.L. Kaul, Plastics, Additves, Ullmann's Encycl. Ind. Chem. (2012) 619–671. https://doi.org/10.1002/14356007.a20.

[17] Jia, P.; Xia, H.; Tang, K.; Zhou, Y. Plasticizers Derived from Biomass Resources: A Short Review. Polym. 2018, Vol. 10, Page 13032018,10(12), 1303

[18] Mitsoulis E (2008), 'Numerical simulation of calendering viscoplastic fluids',
J Non-Newtonian Fluid Mech, 154, 77–88.

[19] J. L. Bourgeois & J. F. Agassant (1977) Calendering of PVC: Defects in calendered PVC films and sheets, Journal of Macromolecular Science, Part B: Physics, 14:3, 367-385, DOI: 10.1080/00222347708212907.

[20] Jamarani R, Halloran MW, Panchal K, et al. Additives to prevent the formation of surface defects during poly(vinyl chloride) calendering. Polym Eng Sci. 2021;61:1209–1219.

[21] R. Jamarani, M. W. Halloran, K. Panchal, J. A. Nicell, R. L. Leask, M. Maric, J. Vinyl Addit. Technol. 2021, Poly(ε-caprolactone)-based additives: Plasticization efficacy and migration resistance 27(4), 821.

[22] Titow, W. V., PVC Technology, 4th edn. Elsevier Applied Science Publishers, London and New York, 1984.

[23] W. Forest et al., (Ed.) Ullmans Encyclopiidie der Technischen Chemie, Vol. 14, p. 201 and Vol. 18, p. 87. Urban & Schwarzenberg, Munich and Berlin, 1963.

[24] Charles E. Wilkes, Charles A. Daniels, James W. Summers. 2005, PVC Handbook, Hanser Publications, p. 315

[25] Saeki, Y. & Emura, T. (2002). Technical progresses for PVC production. Progress in Polymer Science - PROG POLYM SCI. 27. 2055-2131. 10.1016/S0079-6700(02)00039-4.

[26] Jorg Oehlmann, Ulrike Schulte-Oehlmann, Werner Kloas, Oana Jagnytsch, Ilka Lutz, Kresten O. Kusk, Leah Wollenberger, Eduarda M. Santos, Gregory C. Paull, Katrien J. W. Van Look, Charles R. Tyler. A critical analysis of the biological impacts of plasticizers on wildlife. Phil. Trans. R. Soc. B (2009) 364, 2047–2062.

[27] Accoyer B (2011) Proposition de loi adoptée par l'Assemblée Nationale, visant à interdire l'utilisation des phtalates, des parabènes et des alkylphénols. Session ordinaire No. 486 de 2010–2011, Paris

[28] Royaux, Adeline & Francke, Isabelle & Balcar, Nathalie & Barabant, Gilles & Bollard, Clémentine & Lavédrine, Bertrand & Cantin, Sophie. (2017). Aging of plasticized polyvinyl chloride in heritage collections: The impact of conditioning and cleaning treatments. Polymer Degradation and Stability. 137. 10.1016/j.polymdegradstab.2017.01.011.

[29] Wei, XF., Linde, E. & Hedenqvist, M.S. Plasticiser loss from plastic or rubber products through diffusion and evaporation. npj Mater Degrad 3, 18 (2019). https://doi.org/10.1038/s41529-019-0080-7

[30] Paulo César Narvaéz Rincón and Oscar Yesid Suárez Palacios Departamento de Ingeniería Química y Ambiental, Universidad Nacional de Colombia, Bogotá, Colombia. Springer-Verlag Berlin Heidelberg 2015 S. Palsule (ed), Encyclopedia of Polymers and Composites, DOI 10.1007/978-3-642-37179-0_73-1

[31] A.D. Godwin, Plasticizer selection for specific applications, Basic Chem. Intermed. Technol. (1933) 175157–75.

[32] Kirkpatrick A (1940) Some relations between molecular structure and plasticizing effect. J Appl Phys 11:255–261

[33] B.P. Shtarkman, I.N. Razinskaya, Plasticization mechanism and structure of polymers, Acta Polym. 34 (1983) 514–520.

[34] Doolittle A (1944) Mechanism of solvent action. Ind Eng Chem 36:239–244

[35] Doolittle A (1946) Influence of molecular size and shape on temperature dependence of solvent ability. Ind Eng Chem 38:535–540

[36] Wypych G (2012) The handbook of plasticizers, 2nd edn. William Andrew Publishing, Boston

[37] Fox T, Flory P (1950) Second-order transition temperatures and related properties of polystyrene I: influence of molecular weight. J Appl Phys 21:581–591

[38] Richard F. Grossman, Handbook of Vinyl Formulating, Second Edition, Wiley Series on Plastics Engineering and Technology (2008).

[39] Godwin, A. D. Plasticizers. InAppl. Plast. Eng. Handb., 2nd ed.,2017, 533−553.DOI: 10.1016/B978-0-323-39040-8/00025-0.

[40] Mankidy, R.; Wiseman, S.; Ma, H.; Giesy, J. P. Biological Impact ofPhthalates.Toxicol. Lett.2013,217(1), 50−58

[41] Rasmussen, L. M.; Sen, N.; Vera, J. C.; Liu, X.; Craig, Z. R. Effectsof in Vitro Exposure to Dibutyl Phthalate, Mono-Butyl Phthalate, andAcetyl Tributyl Citrate on Ovarian Antral Follicle Growth and Viability.Biol. Reprod.2017,96(5), 1105−1117.

[42] Sheikh, I. A.; Beg, M. A. Structural Characterization of PotentialEndocrine Disrupting Activity of Alternate Plasticizers Di-(2-Ethyl-hexyl) Adipate (DEHA), Acetyl Tributyl Citrate (ATBC) and 2,2,4-Trimethyl 1,3-Pentanediol Diisobutyrate (TPIB) with Human SexHormone-Binding Globu.Reprod. Toxicol.2019,83,46−53.

[43] Vasconcelos, A. L.; Silva, M. J.; Louro, H. In Vitro Exposure tothe Next-Generation Plasticizer Diisononyl Cyclohexane-1,2-Dicarbox-ylate (DINCH): Cytotoxicity and Genotoxicity Assessment in HumanCells.J. Toxicol. Environ. Heal. - Part A Curr. Issues2019,82(9), 526−536.

[44] Saad, N.; Bereketoglu, C.; Pradhan, A. Di(Isononyl) Cyclo-hexane-1,2-Dicarboxylate (DINCH) Alters Transcriptional Profiles,Lipid Metabolism and Behavior in Zebrafish Larvae.Heliyon2021,7(9), No. e07951

[45] D.S. Achilias, C. Roupakias, P. Megalokonomos, A.A. Lappas, E.V. Antonakou, Chemical recycling of plastic wastes made from polyethylene (LDPE andHDPE) and polypropylene (PP), J. Hazard. Mater. 149 (2007) 536–542.

[46] Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J Hazard Mater. 2018 Feb 15;344:179-199. doi: 10.1016/j.jhazmat.2017.10.014. Epub 2017 Oct 9. PMID: 29035713.

[47] Plastics Europe, Compelling facts about plastics. An analysis of European plastics production, demand and recovery for 2008. Brussles: Plastics Europe. 2009.

[48] T. Mekonnen, P. Mussone, H. Khalil, D. Bressler, Progress in bio-based plastics and plasticizing modifications, J. Mater. Chem. 1 (43) (2013) 13379–13398.

[49] Rudolph J. Jaeger, Robert J. Rubin, Plasticizers from Plastic Devices: Extraction, Metabolism, and Accumulation by Biological Systems. Science 170, 460-462 (1970). DOI:10.1126/science.170.3956.460

[50] Jaeger RJ, Rubin RJ. Migration of a phthalate ester plasticizer from polyvinyl chloride blood bags into stored human blood and its localization in human tissues. N Engl J Med. 1972 Nov 30;287(22):1114-8. doi: 10.1056/NEJM197211302872203. PMID: 5082191.

[51] Saabome S. Muobom, Abdul-Malik S. Umar, Yoon Soongseok, Adu-Poku Brolin. A review on Plasticizers and Eco-Friendly Bioplasticizers: Biomass Source and Market. International Journal of Engineering Research & Technology (IJERT) ISSN: 2278-0181, Vol 9 1138-1144.

[52] A. H. Tullo, *Chem. Eng. News*, 2000, 78, 21–31

[53] T. Mekonnen, P. Mussone, H. Khalil and D. Bressler Journal of Materials Chemistry A 2013 Vol. 1 Issue 43 Pages 13379-13398 DOI: 10.1039/C3TA12555F http://dx.doi.org/10.1039/C3TA12555F

[54] Paul H. Daniels. A Brief Overview of Theories of PVC Plasticization and Methods Used to Evaluate PVC-Plasticizer Interaction. JOURNAL OF VINYL & ADDITIVE TECHNOLOGY——2009

[55] Evan Mitsoulis, Nickolas D. Polychronopoulos, Savvas G. Hatzikiriakos. Calendering of thermoplastics: models and computations. Int. Polym. Proc. 2022; 37(4): 341–356.

[56] Capelle, Gerd. (2018). Calendering Technology. 10.1201/9780203740378-4.

[57] Ardichvili G (1938), 'Versuch der Rationalen Bestimmung der Bombierung von Kalanderwalzen', Kautschuk, 14, 23–25, 41–45.

[58] Finston M (1951), 'Thermal effects in calendering of viscous fluids', J Appl Mech, 18, 12–17.

[59] Paslay P R (1957), 'Calendering of a viscoelastic material', J Appl Mech, 24, 602–605.

[60] Bekin N G, Litvinov V V and Petrushanskiy V Yu (1976), 'Method of calculation of the energy and hydrodynamic characteristics of the calendering of polymeric materials', Intern Polym Sci Tech, 3, T55–T67.

[61] Tseng A A and Sun P F (1990), 'A finite difference study of roll design in calendering processing', Intern Polym Proc, 5, 292–299.

[62] Luther S and Mewes D (2004), 'Three-dimensional polymer flow in the calender bank', Polym Eng Sci, 44, 1642–1647.

[63] Agassant J-F (1980), Le calandrage des matières thermoplastiques, Doctoral thesis, Paris 6, Université Pierre et Marie Curie.

[64] Luther, S. & Mewes, Dieter. (2004). Three-dimensional polymer flow in the calender bank. Polymer Engineering and Science - POLYM ENG SCI. 44. 1642-1647. 10.1002/pen.20162.

[65] Tadmor, Z.; C. G. Gogos. Principles of Polymer Processing, 2nd ed., Rev. ed.; Wiley-Interscience: Hoboken, N.J, 2006.

[66] Erythropel, H. C., Maric, M. & Cooper, D. G. Designing green plasticizers: influence of molecular geometry on biodegradation and plasticization properties. Chemosphere 86, 759–766 (2012).

[67] C. Hagiopol, Georgia-Pacific Resins, Inc., Decatur, GA, USA (2005). Encyclopedia of Condensed Matter Physics, p.239.

[68] Godwin, A. D. 28 - Plasticizers. In *Applied Plastics Engineering Handbook*; Kutz, M., Ed.; Plastics Design Library; William Andrew Publishing: Oxford, 2011; pp 487–501. https://doi.org/10.1016/B978-1-4377-3514-7.10028-5

[69] Ma, Y.; Liao, S.; Li, Q.; Guan, Q.; Jia, P.; Zhou, Y. Physical and Chemical Modifications of Poly(Vinyl Chloride) Materials to Prevent Plasticizer Migration - Still on the Run. React. Funct. Polym. 2020, 147, 104458. https://doi.org/10.1016/j.reactfunctpolym.2019.104458.

[70] Jeong, H.; Yuk, J. S.; Lee, H.; Kang, S.; Park, H.; Park, S. H.; Shin, J. Green Chem. 2021, 23, 7549-7565.

[71] López-Rodríguez, N.; Sarasua, J. R. Polym. Eng. Sci. 2013, 53, 2073−2080.

[72] Xuan, W.; Odelius, K.; Hakkarainen, M. ACS Omega 2022, 7, 14305-14316.

[73] Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass: Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas; National Renewable Energy Lab.: Golden, CO (United States), 2004.

[74] Hafyan, R. H.; Bhullar, L.; Putra, Z. A.; Bilad, M. R.; Wirzal, M. D. H.; Nordin, N. A. H. M. IOP Conf. Ser. Mater. Sci. Eng. 2020, 778, 012140.

Appendix

A1. Differential Scanning Calorimetry

The DSC results for PVC blended samples with PCL-based additives as primary plasticizer are presented in Figures A.1 to A.4.

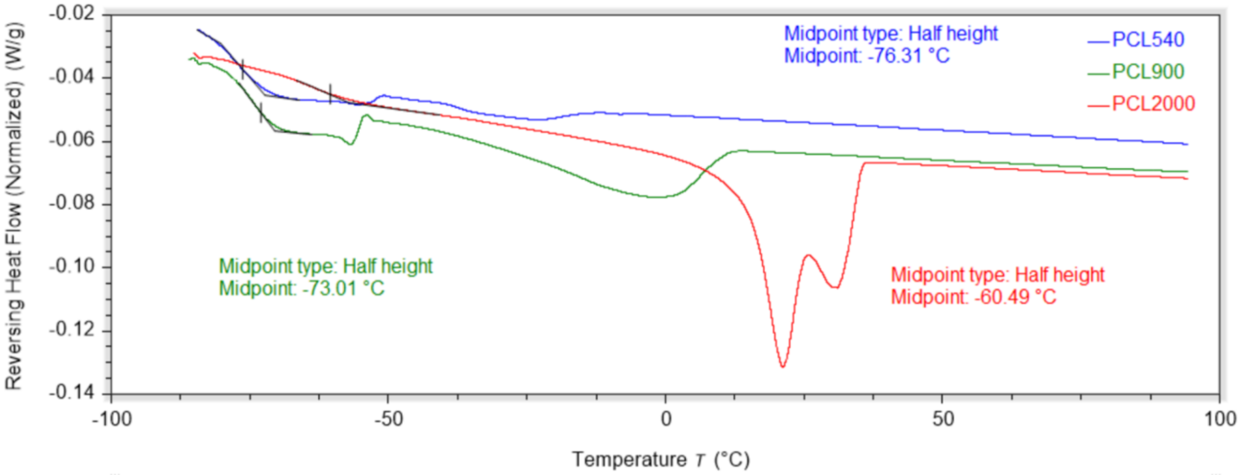

FIGURE A.1 DSC thermograms and glass transition temperature for PCL-based additives.

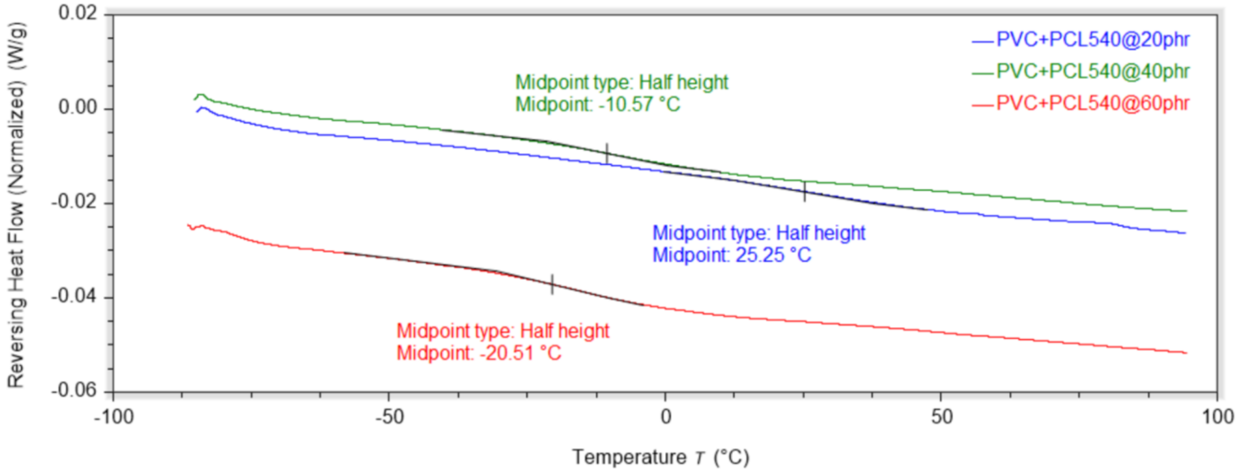

FIGURE A.2 DSC thermograms and glass transition temperature for PVC extruded samples with PCL_{540}-Succ-C_7 at 20, 40 and 60 phr.

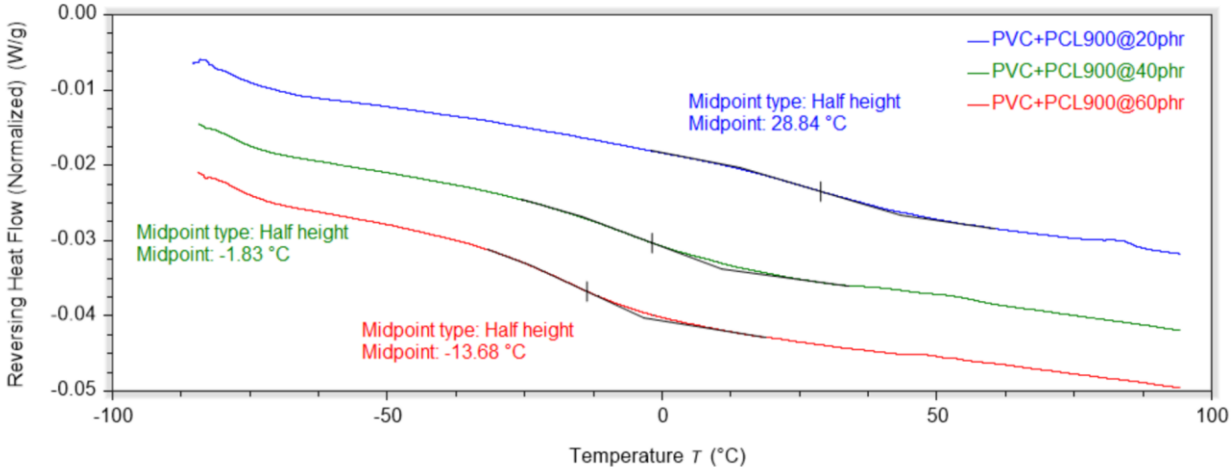

FIGURE A.3 DSC thermograms and glass transition temperature for PVC extruded samples with PCL$_{900}$-Succ-C$_7$ at 20, 40 and 60 phr.

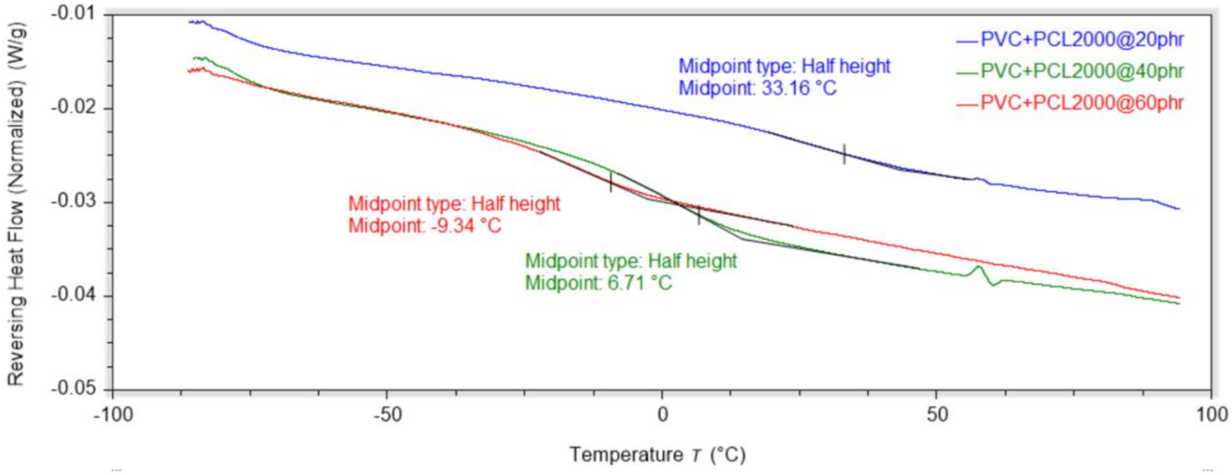

FIGURE A.4 DSC thermograms and glass transition temperature for PVC extruded samples with PCL$_{2000}$-Succ-C$_7$ at 20, 40 and 60 phr.

A2. Thermal Gravimetric Analysis

The TGA results for PVC blended samples with PCL-based additives as primary plasticizer are presented in Figures A.5 to A.8

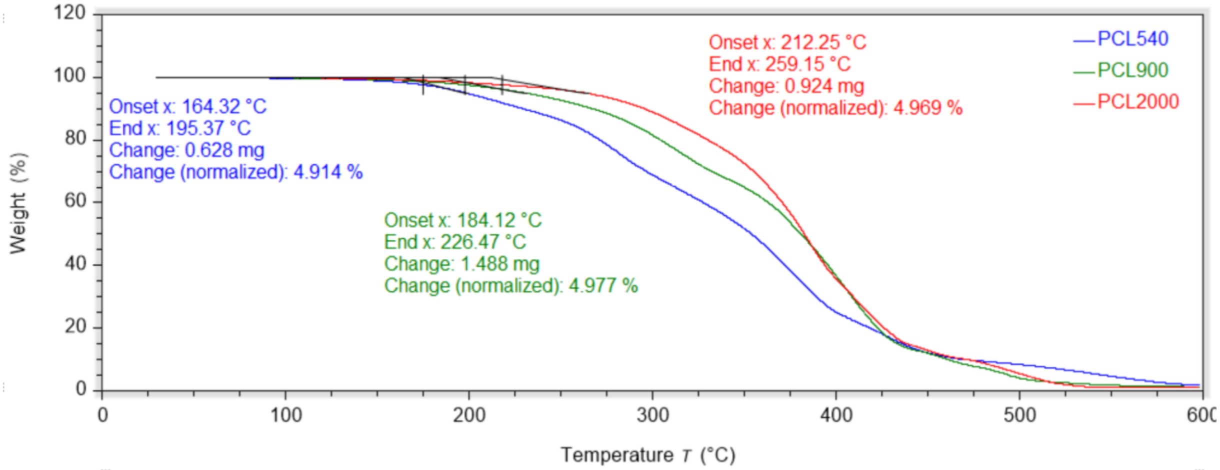

FIGURE A.5 TGA thermograms and glass transition temperature for PCL-based additives.

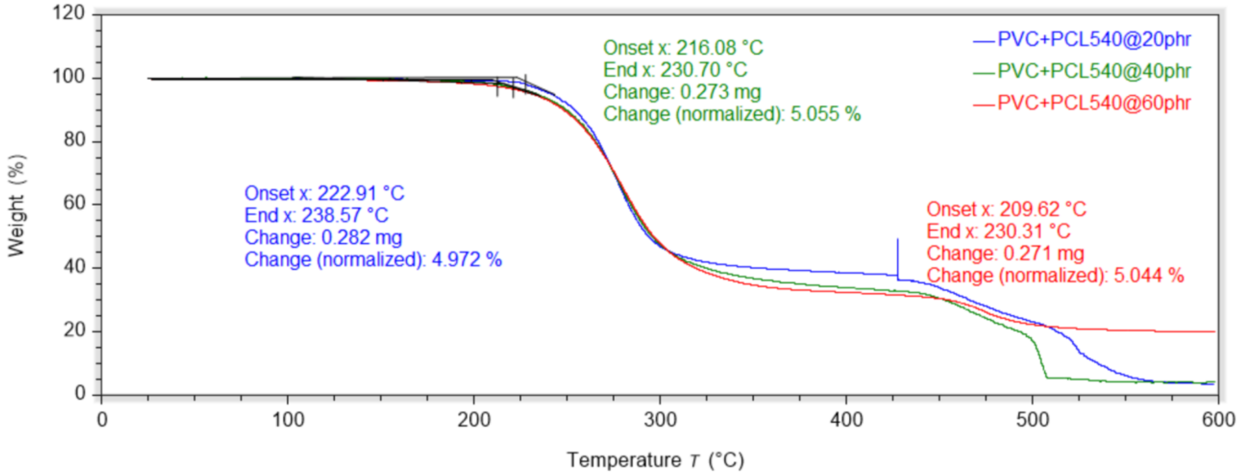

FIGURE A.6 TGA thermograms and glass transition temperature for PVC extruded samples with PCL_{540}-Succ-C_7 at 20, 40 and 60 phr.

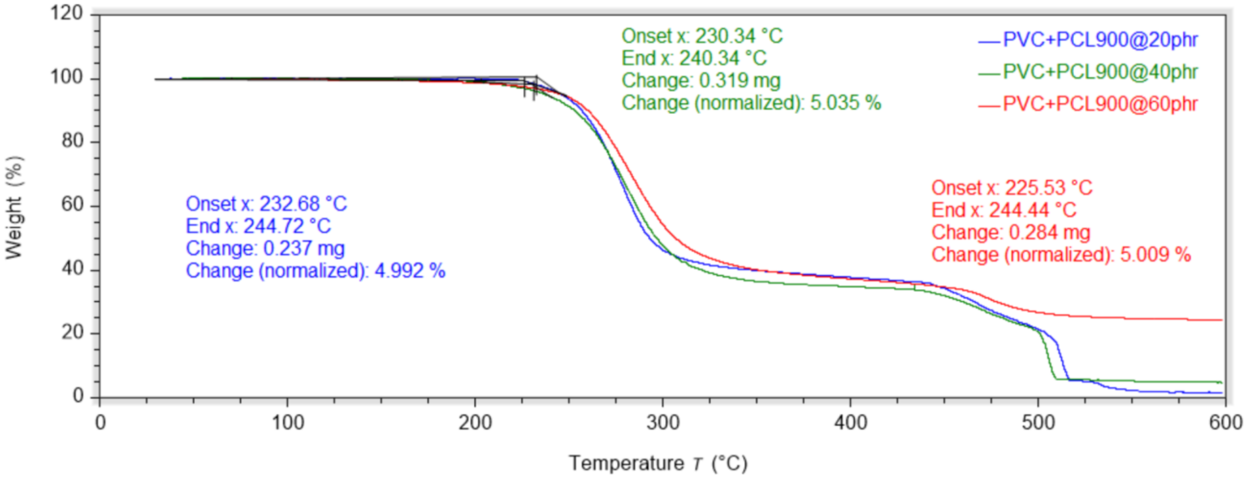

FIGURE A.7 TGA thermograms and glass transition temperature for PVC extruded samples with PCL_{900}-Succ-C_7 at 20, 40 and 60 phr.

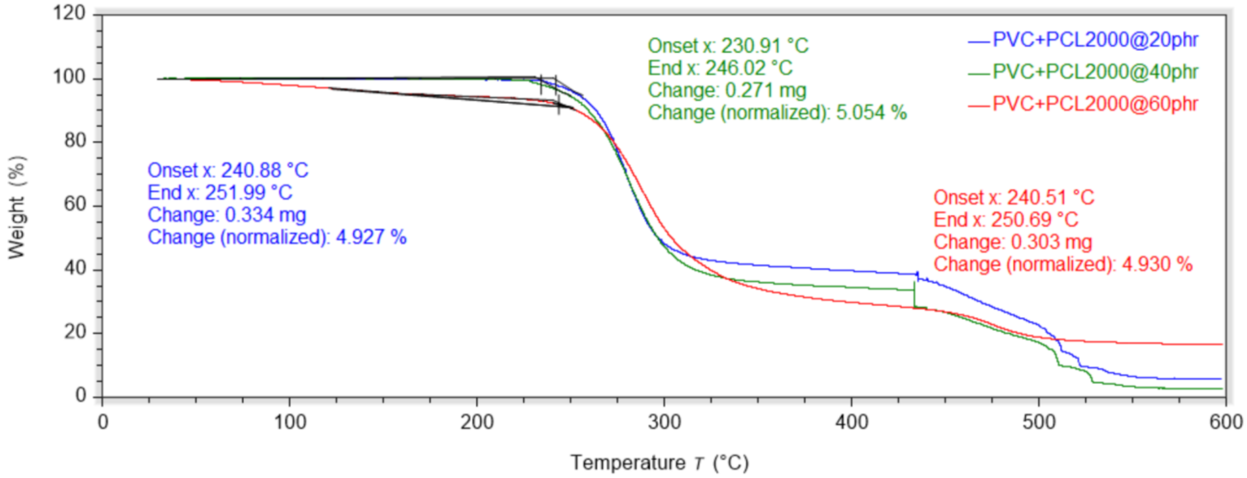

FIGURE A.8 TGA thermograms and glass transition temperature for PVC extruded samples with PCL_{2000}-Succ-C_7 at 20, 40 and 60 phr.

A3. Dynamic Mechanical Thermal Analysis

The DMTA results for PVC blended samples with PCL-based additives as primary plasticizer are presented in Figures A.9 to A14.

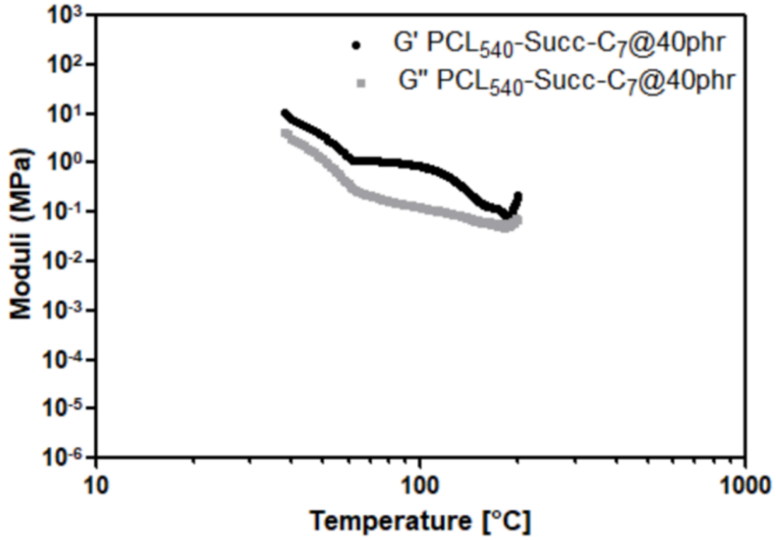

FIGURE A.9 Storage and loss modulus as a function of temperature of PVC extruded samples PCL$_{540}$-Succ-C$_7$ at 40 phr.

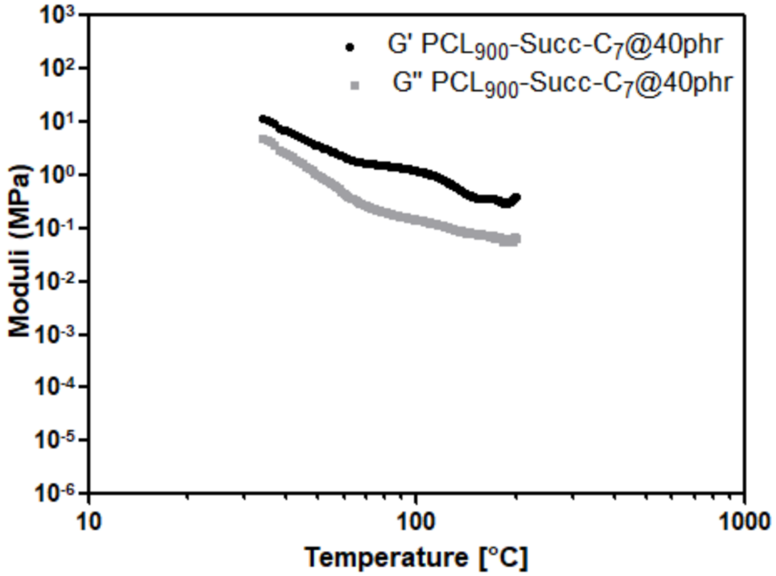

FIGURE A.10 Storage and loss modulus as a function of temperature of PVC extruded samples PCL$_{900}$-Succ-C$_7$ at 40 phr.

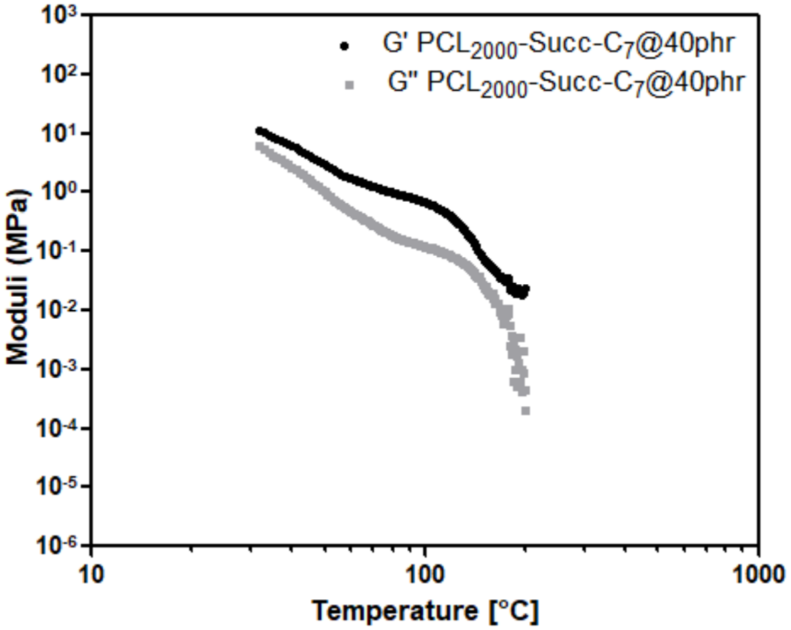

FIGURE A.11 Storage and loss modulus as a function of temperature of PVC extruded samples PCL_{2000}-Succ-C_7 at 40 phr.

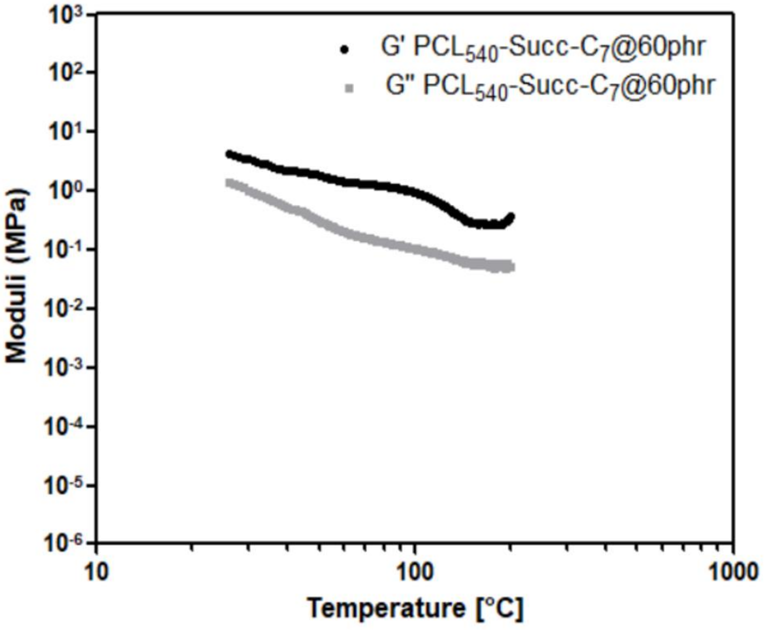

FIGURE A.12 Storage and loss modulus as a function of temperature of PVC extruded samples PCL_{540}-Succ-C_7 at 60 phr.

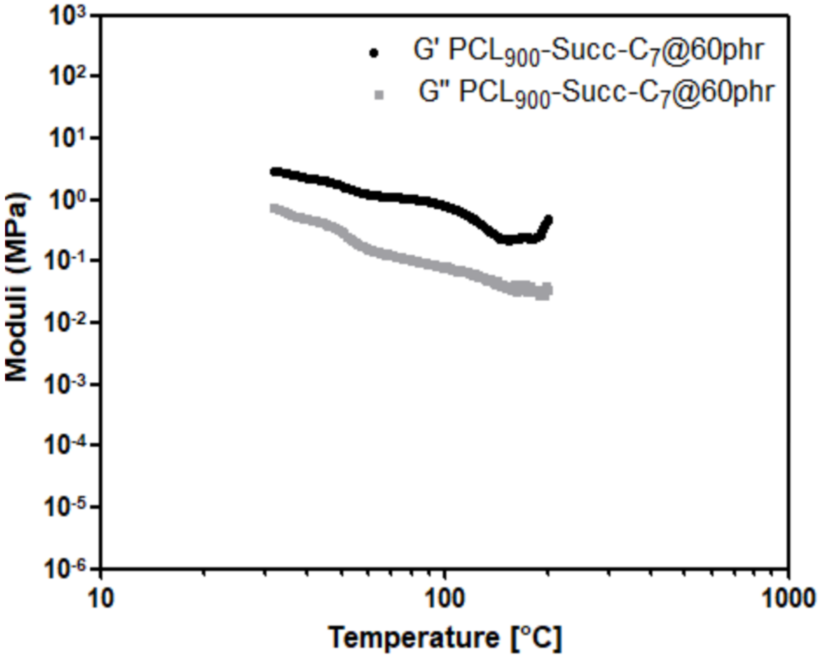

FIGURE A.13 Storage and loss modulus as a function of temperature of PVC extruded samples PCL_{900}-Succ-C_7 at 60 phr.

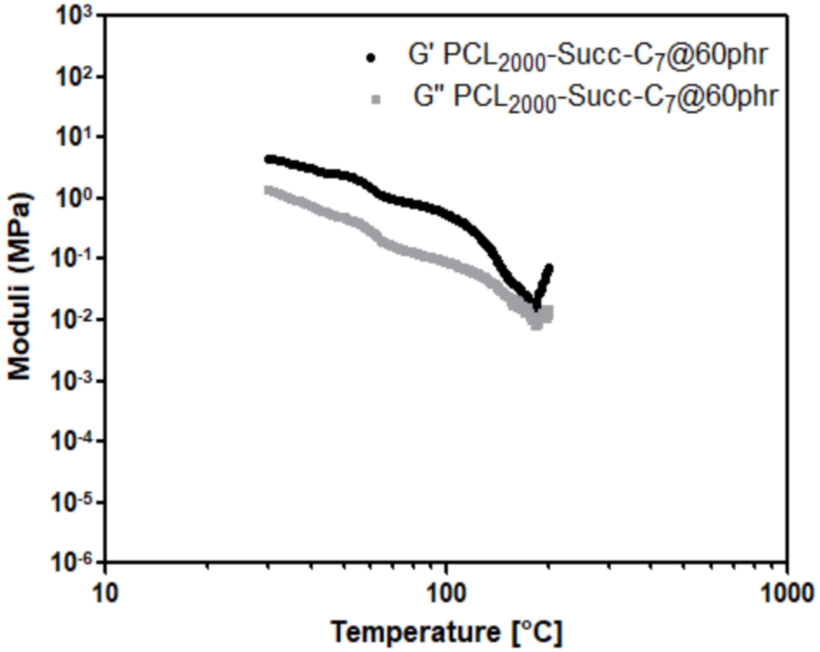

FIGURE A.14 Storage and loss modulus as a function of temperature of PVC extruded samples PCL_{2000}-Succ-C_7 at 60 phr.

A4. Mechanical properties

The result of tensile for PVC blended samples with PCL-based additives as primary plasticizer are summarized in Table A.1

TABLE A.1 Mechanical properties of PVC extruded samples with PCL-based additives. Means and standard deviations are reported.

Sample	Tensile strength (MPa)	Elongation at break (%)
PVC + PCL$_{540}$-Succ-C$_7$ @20 phr	19.2 ± 0.7	11.9 ± 2.2
PVC + PCL$_{540}$-Succ-C$_7$ @40 phr	11.8 ± 1.0	150.2 ± 16.5
PVC + PCL$_{540}$-Succ-C$_7$ @60 phr	7.9 ± 0.9	153.2 ± 25.2
PVC + PCL$_{900}$-Succ-C$_7$ @20 phr	19.2 ± 1.5	15.4 ± 4.7
PVC + PCL$_{900}$-Succ-C$_7$ @40 phr	11.6 ± 1.7	145.0 ± 25.1
PVC + PCL$_{900}$-Succ-C$_7$ @60 phr	5.9 ± 0.6	138.2 ± 15.3
PVC + PCL$_{2000}$-Succ-C$_7$ @20 phr	21.8 ± 1.4	10.14 ± 1.0
PVC + PCL$_{2000}$-Succ-C$_7$ @40 phr	9.5 ± 0.2	122.7 ± 5.9
PVC + PCL$_{2000}$-Succ-C$_7$ @60 phr	4.2 ± 0.3	82.7 ± 6.1

.