Evaluation of an Additive for Gas Check Reduction During PVC Calendering

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Abstract

Poly(vinyl chloride) (PVC) is one of the most important plastic materials produced today, as it is a relatively inexpensive and an extremely versatile polymer. PVC can be processed and formed in a variety of ways, but to produce PVC film and sheets in large quantities, calendering is almost always the preferred production method. Calendering is a technique whereby a heated mass of thermoplastic can be transformed into a film or sheet by pressing it through heated cylindrical rolls.

There is currently an upper limit to the thickness of films which can be calendered without sacrificing quality or consistency of the product formed. This is largely due to surface defects known as "gas checks" that tend to dramatically increase in number as the film gauge increases. Gas checks are surface defects believed to be due to gas (air) trapped in the PVC film. Currently, gas checks are reduced by altering the manufacturing process parameters such as decreasing the distance between the rollers, increasing the speed of the rollers, or increasing the viscosity of the polymer blend being calendered. In order to manufacture thicker sheets, several thinner sheets must be calendered and then pressed or laminated together, potentially leading to weak interfaces in the material.

This thesis demonstrates the ability of a triheptylsuccinate-terminated poly(caprolactone) compound with a PCL triol core (M_n = 540 g/mol) (PCL_{540}-[(succ)-C_7]$_3$) to effectively eliminate gas checks in calendered PVC sheets of up to 0.8 mm thick, a film gauge that is greater than the generally accepted manufacturing limits. It also shows that PCL_{540}-[(succ)-C_7]$_3$ does not greatly affect the properties of PVC blends when used in small quantities (i.e., 10 phr) other than the observed effect on reducing gas checks. The impact of PCL_{540}-[(succ)-C_7]$_3$ loading on processing parameters was documented by the mixing torque profiles and the final blend tensile and thermal properties compared to control mixes. Overall, this shows that PCL$_{540}$-[(succ)-C$_{7}$]$_{3}$ can be added in small quantities to effectively eliminate gas check defects from PVC calendering operations without significantly affecting the required processing or product properties.

Résumé

Le poly(chlorure de vinyle) (PVC) est l'une des matières plastiques les plus importantes produites aujourd'hui, car il s'agit d'un polymère relativement peu coûteux et extrêmement polyvalent. Le PVC peut être traité et formé de diverses manières, mais pour produire des films et des feuilles de PVC en grandes quantités, le calandrage est presque toujours la méthode de production préférée. Le calandrage est une technique par laquelle une masse chauffée de thermoplastique peut être transformée en film ou en feuille en la pressant à travers des rouleaux cylindriques chauffés.

Il existe actuellement une limite supérieure à l'épaisseur des films qui peuvent être calandrés sans sacrifier la qualité ou l'uniformité du produit formé. Cela est dû en grande partie à des défauts de surface connus sous le nom de "contrôles de gaz", dont le nombre tend à augmenter considérablement au fur et à mesure que l'épaisseur du film s'accroît. Les défauts de gaz sont des défauts de surface que l'on pense être dû au gaz (air) piégé dans le film PVC. Actuellement, les défauts de gaz sont réduits en modifiant les paramètres du processus de fabrication, par exemple en diminuant la distance entre les rouleaux, en augmentant la vitesse des rouleaux ou en augmentant la viscosité du mélange de polymères calandré. Pour fabriquer des feuilles plus épaisses, il faut calandrer plusieurs feuilles plus fines, puis les presser ou les laminer ensemble, ce qui risque d'affaiblir les interfaces du matériau.

Cette thèse démontre la capacité d'un composé de poly(caprolactone) à terminaison triheptylsuccinate avec un noyau PCL triol (Mn = 540 g/mol) (PCL540-[(succ)-C7]3) à éliminer efficacement les contrôles de gaz dans les feuilles de PVC calandrées d'une épaisseur allant jusqu'à 0,8 mm, une épaisseur de film qui est supérieur aux limites de fabrication généralement acceptées. Elle montre également que le PCL540-[(succ)-C7]3 n'affecte pas beaucoup les propriétés des mélanges de PVC lorsqu'il est utilisé en petites quantités (c.-à-d. 10 pce), à l'exception de l'effet observé sur la réduction des défauts de gaz. L'impact de la charge de PCL540-[(succ)-C7]3 sur les paramètres de traitement a été documenté par les profils de couple de mélange et les propriétés thermiques et de traction du mélange final par rapport aux mélanges de contrôle. Dans l'ensemble, cela montre que le PCL540-[(succ)-C7]3 peut être ajouté en petites quantités pour éliminer efficacement les défauts de gaz des opérations de calandrage du PVC sans affecter de manière significative les propriétés de traitement ou de produit requises.

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Contribution of Authors

The following manuscript-based thesis contains the following article that has been prepared for submission to the *Journal of Vinyl and Additive Technology*, as follows:

> Rideout, A., Panchal, K., Nicell, J.A., Maric, M., Leask, R.L. (2023). "Gas Check Reduction for Calendered Poly(vinyl chloride) Sheets Containing Succinate-Capped Poly(caprolactone) Star-Shaped Plasticizers"

The author of this thesis, A. Rideout, is the first author on this publication and was responsible for planning and performing experiments, other than the calendering which was carried out by Kushal Panchal at our industry collaborators facility. He interpreted and analyzed the results from the calendering and other experiments. The co-authors, Richard Leask, Jim Nicell, and Milan Maric were responsible for funding acquisition, supervision of the research project, experimental design, and editing of the manuscript. Kushal Panchal contributed to the experimental design and editing of the manuscript.

1 Introduction

Poly(vinyl chloride) (PVC) plastics are a versatile class of polymers that accounts for 10% of the plastics market with approximately 44.3 million metric tonnes of PVC resin produced each year [1-3]. PVC is a relatively inexpensive and an extremely versatile polymer used in a wide range of applications in many different areas such as construction, packaging, medicine, and consumer products [4, 5]. As of March 2023, the cost in USD per pound for volume resin of PVC ranges from 72 to 74¢/lb, which is lower than other major polymers such as poly(ethylene) at 72 to 87¢/lb, poly(propylene) at 76 to 80¢/lb, and poly(styrene) at 99 to 109¢/lb [6].

PVC's versatility is due largely to its compatibility with a wide range of additives [7, 8]. Additives allow manufacturers to alter processing, mechanical properties, and aesthetics to produce PVC products for a variety of applications. PVC accounts for 75% of the usage of the plastics additives market by mass, of which plasticizers make up over 50% of all plastic additives by mass [9, 10]. The latter are used to lower the glass transition temperature of the polymer to make it softer and more flexible [11]. Plasticizers are heavily used in PVC manufacturing, and the most widely used plasticizers are phthalate acid esters (PAE) [12]. PAEs are an external plasticizer, meaning they are not chemically bound to the PVC matrix and can leach out over time resulting in their widespread presence in the natural environment [13, 14]. PAEs have been under heavy scrutiny recently, due to growing concern over their effects on human health and the environment [15-17]. Because of this, many countries have restricted or banned PAEs for a number of applications, such as food packaging, medical devices, and children's toys [18, 19].

In previous work focussed on the development of potential alternative plasticizers to PAE's, a novel effect of succinate-capped polycaprolactone triols (PCL_{540}-[(succ)-C_7]$_3$) was observed. That is, at low concentrations, these compounds are able to effectively reduce surface defects, commonly known as “gas checks,” in calendered PVC sheets [20]. Gas checks are a common defect in PVC calendering, seen as a visual defect consisting of small egg-shaped inclusions on the film’s surface (see Figure 1.1) but can also negatively affect the film properties, such as reduced tensile strength and increased permeability at the site of the defect [21]. The current method for reducing gas checks is through alterations in the calendering process, such as decreasing the calendering speed or decreasing the distance between the rollers (i.e., the nip roll width) [21]. This can complicate and slow the calendering process, as well as limit the functionality and thickness of the end product, as process parameters must remain within a set limit to avoid surface defects. Currently, the manufacturing range for calendered PVC sheets is between 0.05 to 0.5 mm, as it is difficult to maintain consistency and quality at thicker gauges [21-23].

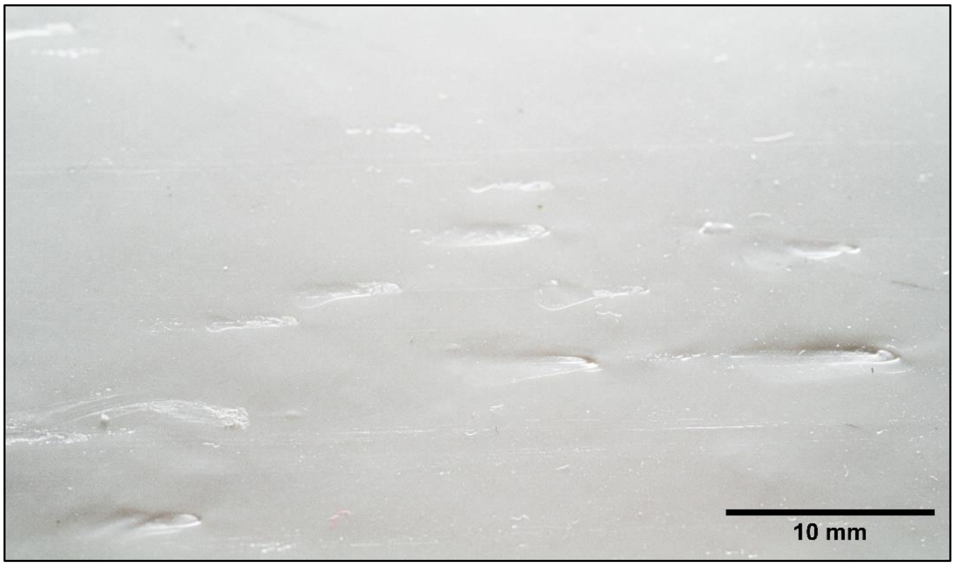

Figure 1.1: Gas check defects on a PVC film.

Using PCL_{540}-[(succ)-C_7]$_3$ as a processing aid has the potential to reduce the operational complexity of PVC calendering, as well as expand the operating range for calendered PVC sheets. This would also have the additional benefit of reducing energy cost and waste for calendered PVC sheets.

Therefore, the primary objective of this work is to evaluate whether PCL_{540}-[(succ)-C_7]$_3$ can be added to a typical PVC calendering formulation without significantly altering the processing parameters or final properties of the calendered PVC other than the observed effect on reducing gas checks. The investigated effects of PCL_{540}-[(succ)-C_7]$_3$ on PVC blends include testing of tensile, rheological, and thermal properties. This work also investigates the expansion of calendering operating parameters using PCL_{540}-[(succ)-C_7]$_3$ as a processing aid, which includes demonstrating that PCL_{540}-[(succ)-C_7]$_3$ can effectively reduce gas checks in calendered PVC films at thicker gauges without resorting to post-calendering lamination. This work also explores the potential economic and environmental benefits to using PCL_{540}-[(succ)-C_7]$_3$ in a PVC calendering operation.

The objectives of this study were the following:

1. Measure the effect of PCL_{540}-[(succ)-C_7]$_3$ on the processing, mechanical, and thermal properties of PVC blends.
2. Evaluate the effectiveness of PCL_{540}-[(succ)-C_7]$_3$ at reducing gas checks in calendered PVC sheets at thicker film gauges.
3. Conduct a preliminary life cycle assessment to determine the comparative environmental impact of producing 1 kg of calendered PVC at varying thicknesses with and without PCL_{540}-[(succ)-C_7]$_3$.

2 Literature Review

2.1 PVC and Plasticizers

Vinyl chloride was first synthesized in 1835 by Liebig and has since had a major impact on polymer chemistry and the world. PVC is used in a wide variety of industries [3, 24] with an estimated 44.3 million metric tonnes of PVC resin produced each year, making it the second most produced thermoplastic resin by volume. Construction is the largest market for PVC products, accounting for 70% of PVC consumption in North America, but PVC is also widely used in medical applications, packaging, and consumer products [4, 25].

On its own, PVC is an extremely heat- and light-sensitive polymer with low thermal stability. However, through the use of additives, PVC can achieve a high level of versatility for a wide range of applications [26-28]. PVC accounts for the greatest volume of plastics additives and is responsible for 75% of additives by weight and 60% by value [9]. Plasticizers make up the largest segment of the plastics additives market, as more than 50% of all plastic additives are plasticizers, of which 80% are used in PVC manufacturing [10]. Heat stabilizers and processing aids are the next two largest segments of the PVC additives market, together accounting for two thirds of the remaining fraction of PVC additives used globally [29].

One of the most critical tasks for the PVC industry is to develop less toxic and more environmentally friendly additives for PVC. Phthalate acid esters (PAEs) are the most widely used family of plasticizers in PVC manufacturing, accounting for 70% of the plasticizer market and include di(2-ethylhexyl) phthalate (DEHP) which makes up 37% of the total plasticizer market and diisononyl phthalate (DINP) which makes up 17% of the total plasticizer market [12]. The molecular structures for DEHP and DINP are shown in Figure 2.1.

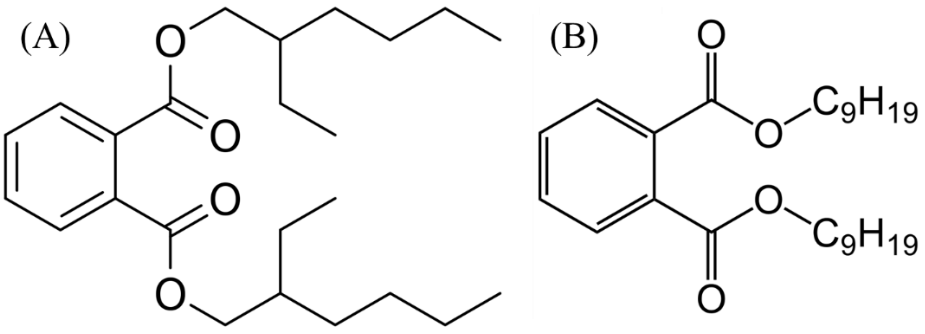

Figure 2.1: Molecular structures of the most commonly used phthalate acid esters: (A) di-(2-ethylhexyl) phthalate (DEHP) and (B) diisononyl phthalate (DINP).

Due to health and environmental concerns associated with PAEs that have arisen in recent years, a growing number of countries are placing restrictions on the manufacturing and usage of DEHP and other PAEs [18, 19, 30]. In particular, DEHP has been shown to have carcinogenic effects on mice and rats and has been classified as "possibly carcinogenic" by the International Agency for Research on Cancer (IARC) [31]. Animal studies have also shown DEHP to exhibit reproductive toxicity and negative effects on endocrine activity [31, 32]. Not surprisingly, due to these health concerns, restrictions have been placed on the use of DEHP in specific applications where exposure is more likely such as, for instance, the banning of DEHP for use in children's toys in China, the United States, and the EU [15-17]. In addition, the World Health Organization has placed recommended limits on DEHP concentrations in drinking water at 8 μg/L,

Phthalates are also a major pollutant, with DEHP being ubiquitous in the environment [17]. DEHP is easily biodegraded under some aerobic conditions, however DEHP readily adsorbs onto organic matter which decreases its bioavailability for degradation significantly [17]. Additionally, under anaerobic conditions or in temperatures between 4-10°C, the biodegradation of DEHP becomes virtually negligible [17]. Metabolites of phthalates (mPAE) such as mono (2-ethylhexyl) phthalate (mEHP) are also toxic themselves, mPAEs are readily produced both *in vivo* and *in vitro*, and can have negative effects on reproductive and cellular development [33, 34].

Due to the health and environmental issues with DEHP and other phthalates along with the tightening restrictions on the manufacturing and usage of phthalates there is an incentive to develop plasticizers with a less harmful effect on humans and the environment. There are many alternative plasticizers in use today, the largest group being terephthalates which currently represent 7% of the plasticizer market [35]. In comparison, other segments of the PVC additives market have had better success phasing out harmful chemicals, such as with lead-based heat stabilizers which were once one of the most commonly used PVC stabilizers [36]. These compounds were successfully phased out in the European Union by 2015 following the 2010 VinylPlus® commitment [37-40].

2.2 Poly(vinyl chloride) Calendering

Calendering is a process by which a heated mass of thermoplastic is converted to a film or sheet by pressing it through heated cylindrical rolls [22, 41, 42], as pictured in Figure 2.2 [43]. PVC is the most commonly calendered thermoplastic, although some rubbers, poly(urethane) compositions, and poly(propylene) compounds are also fashioned into sheets through calendering [41, 44]. Calendering is best suited to high-volume production runs, as calenders are capable of higher production speeds than extruders, which are the other most common way of producing PVC sheets [22, 45]. Other than the economic benefits associated with high production volumes, calenders can also produce uniform films and sheets to a higher tolerance than extruders [46]. Advancements made in the efficiency of calendering processes have largely been accomplished through empirical tests, as the process of calendering is still not fully understood and continues to be studied [22, 41].

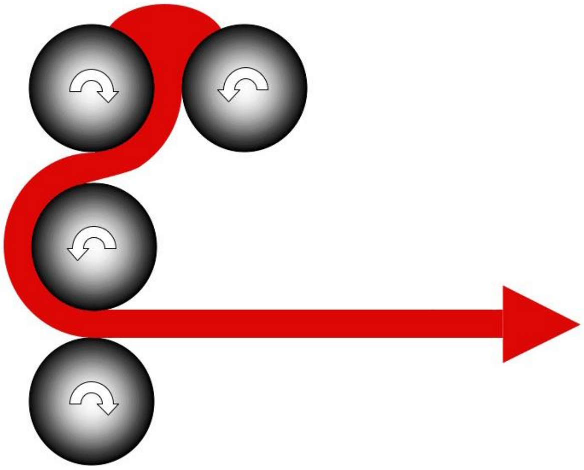

Figure 2.2: Simplified diagram of the calendering process [43] (Creative Commons).

2.2.1 Calendering Defects

The most common defects in PVC calendering are [21, 23, 44, 47]:

1. Dimensional non-uniformities that are seen as variations in thickness parallel to the calender roll due to the rolls tendency to bow under large forces and which can be addressed by using crowned rolls that have a bigger diameter in the center of the roll.
2. Structural anomalies experienced as particulate and crystalline structure changes in the PVC caused by elevated temperature and stress.
3. Mattness, which represents a loss of surface gloss on the portion of the surface that is not in contact with the roll after the sheet leaves the calender gap and which tend to occurs at wall shear stresses above 0.5MPa [23].
4. V-shapes in which surface thickness irregularities of up to 3 μm are experienced in the form of open Vs with vertices near the center of the sheet.

5. Air bubbles (gas checks) which become entrained in the polymer melt in the recirculating melt bank, and then pass through the calender nip and result in elongated egg-shaped inclusions oriented along the direction of the calender flow.

Of all these defects, gas checks are the primary reason for the upper limit to film thickness of 20 to 25 mils (0.5 to 0.64 mm) [48]. Currently, to produce sheets and films of a thicker gauge without an abundance of gas checks forming, several thinner sheets must be produced and then pressed or laminated together. If gas checks could be avoided when using a thicker film gauge, it could reduce or eliminate the need for these additional process steps. Calendering defects are typically eliminated or reduced through changes being made manually to the processing parameters such as temperature, nip-roll distance, and calender speed [21, 47, 49]. Safe operating ranges for producing consistent and uniform sheets without defects have been developed empirically, however defects can still occur and calender processes require careful monitoring by operators [21, 47]. Gas checks are less prevalent at lower nip distances, higher calender speeds, and with higher apparent viscosity of the calendered polymer [21]. All of these relate to a higher pressure in the calender bank, and lower hydrostatic pressures are correlated with increased contamination of air in the calendered sheet [48]. Additives to reduce or eliminate gas checks could reduce the operational complexity and increase the consistency of the calendering process.

2.2.2 Models of the Calendering Process

As the calendering process is not completely understood, the reason for the occurrence of surface defects is also not known. A simplified diagram of the calender bank and nip region can be seen below in Figure 2.3. The reason for gas entrapment in the polymer sheet is thought to be due to the following mechanism. Air bubbles enter the polymer flow where the sheet enters into the bank, where they then reach a stagnation point, reverse direction, and travel backwards into the bank, before reversing again in a closed inner vortex [48]. With increasing nip distance, the stagnation point recedes quickly from the nip region. As the air bubbles have a much lower viscosity than the polymer melt, when the hydrostatic pressure in the nip is sufficiently high, they are preferentially rejected from the calender sheet so long as they are: (a) not too close to the roll surfaces, and (b) at or behind the stagnation point. As the nip distance increases however, the hydrostatic pressure in the nip drops off sharply, and the stagnation point moves away rapidly, leading to increased air entrainment [48]. This aligns with the observations of Bourgeois and Agassant [21], who found that air entrapment was reduced with lower nip distances and higher viscosity polymers, however it still remains to be proven as to the mechanism by which gas checks are formed.

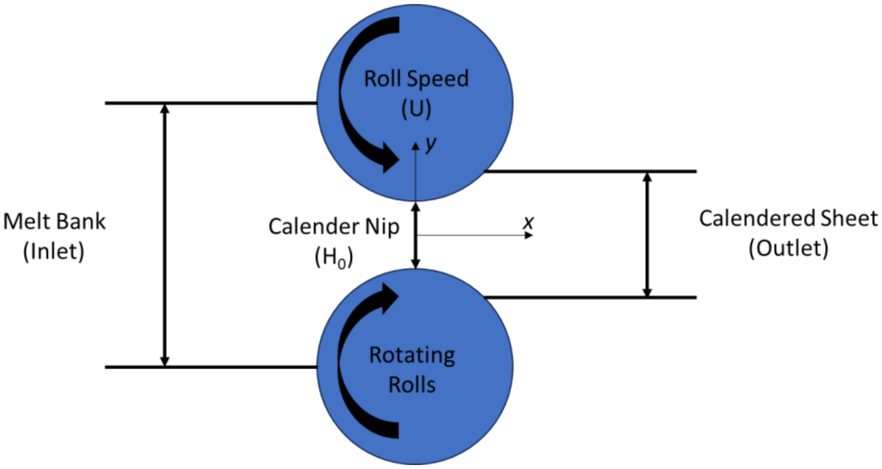

Figure 2.3: Simplified diagram of calender nip region and melt bank.

There have been several attempts at creating analytical and numerical models to describe the calendering process for polymetric materials, dating back to the 1950s with R. E. Gaskell’s work which helped provide a foundation for future models [50, 51]. Gaskell approximated the flow between the rolls as one-dimensional, as the gap between the calender rolls was small when compared to the diameter of the calender rolls. His model attempted to predict the pressure drop along the machine direction, considering the polymer melt as both a Newtonian fluid and a Bingham plastic. This was later expanded to power-law fluids by McKelvey [52] and Middleman [53]. Alston and Astill [51] created a one-dimensional model for non-Newtonian fluids using a hyperbolic tangent viscosity model, where the pseudoplastic material exhibits Newtonian behaviour at both high and low shear rates, and a shear-thinning effect at intermediate shear rates. Vlachopoulos and Hrymak [54] studied the calendering of rigid PVC both theoretically and experimentally using a non-isothermal power-law model based on the lubrication approximation theory.

Numerical approaches describing the calendering process have been attempted more recently, aided greatly by improvements in computational speed. Agassant and Avenas [47] and Bourgeois [21] used experimental data to develop an empirical model to predict the torque, force and polymer heating as a function of calendering parameters to better inform calender industrial operators. They also observed a large recirculation zone along with smaller vortices developing prior to the calender rolls. Kiparissides and Vlachopoulos [55] used a finite difference procedure with the lubrication approximation to study the temperature profile of the calender bank, and identified localized regions of excessive heating which can be detrimental to temperature sensitive materials such as PVC. Sofou and Mitsoulis [56-58] used numerical methods to develop a two-dimensional model of the calender bank, with and without the lubrication approximation, to help describe the vortex patterns upstream from the calender rolls, temperature, and pressure distributions.

In Mitsoulis's work [57] on the calendering of viscoplastic fluids, they note a relationship between the calender speed, nip distance, and viscoelastic properties of the calendered polymer, and the size and distribution of yielded/unyielded regions within the calender bank. The dimensionless

Bingham number (Bn) is defined by Equation 2.1 [57] where τ_y is the yield stress, K is the consistency index, n is the power-law index, H_0 is the nip distance, and U is the roll speed. They found that as Bn increases, the vorticity before the calender bank decreases in size and intensity, disappearing completely for Bn ≥ 1 [57]. The size of unyielded regions within the polymer melt and the maximum pressure within the calender bank also increased with Bn [57]. They also found that the vorticity within the calender bank became smaller as the shear-thinning characteristics of the fluid increased [57]. As previously stated, gas entrapment is thought to occur within the recirculation zone in the calender bank; reduced vorticity, higher pressures, and regions of unyielded viscoplastic fluids may prevent air from entering the polymer melt and forming gas check defects [21, 48, 57].

$$Bn = \frac{\tau_y}{K}\left(\frac{H_0}{U}\right)^n \tag{2.1}$$

Early three-dimensional experimental observations of the calendering process revealed three principal conclusions: (1) the calendered sheet spreads transversely to flow direction; (2) three vortices form in and near the melt bank; and (3) the material is conveyed from the melt bank to the sides through a spiralling flow pattern [58, 59]. With the aid of three-dimensional computer models of calender processes, a better understanding of the vortex patterns in the calender bank was developed, in addition to predictions of the detachment points of the sheet from the calender rolls [58, 60].

Even with the recent progress in furthering our understanding of the calender process, the development of an analytical solution remains a prevailing problem in calendering [58]. The reduction of defects must therefore be done through empirical observations, which leads to a potentially narrower range of operations than is necessary or optimal.

2.2.3 Reduction of Calender Defects through Additives

In previous work [61, 62], it was shown that succinate-capped poly(caprolactone) (PCL) based additives were able to effectively reduce gas checks in calendered PVC films. This appeared to be the first instance reported of additives being used for this specific purpose. In concentrations as low as 8 parts per hundred rubber (phr), it was observed that several PCL-based additives were able to significantly reduce or completely eliminate gas checks in calendered films in bench scale tests [62]. The reasons for why these additives are so effective is not well understood, although there was an observed relationship where blends that reduced gas checks had higher complex viscosities than those that did not. Surface tension did not seem to be a significant factor in gas check elimination, as blends which removed gas checks had a similar surface tension to those that did not remove gas checks; i.e., 33 dynes/cm in blends which removed gas checks compared to 30 dynes/cm in blends which did not [62]. The effect of surface chemistry on the effectiveness of PCL-based additives on reducing gas checks has not been thoroughly explored yet, however there have been some preliminary findings which have shown that PCL_{540}-[(succ)-C_7]$_3$ is not as effective when synthesized in non-stoichiometric amounts to ensure the succinate end groups are fully capped. PCL_{540}-[(succ)-C_7]$_3$ synthesized with an excess of n-heptanol had a lower acid value than PCL_{540}-[(succ)-C_7]$_3$ produced in stoichiometric amounts and was not as effective at reducing gas checks. Regardless of the mechanism by which PCL_{540}-[(succ)-C_7]$_3$ functions, its important effect on reducing gas checks could have several cost and environmental benefits such as significantly reducing wastage due to substandard product, as well as potentially increasing the operational range for calender processes. It is therefore important to study its processing potential to see if there are any issues arising from its incorporation into a manufacturing process, such as required process changes or negative impacts on the properties of the final product. These potential issues were investigated by measuring the effect of adding PCL_{540}-[(succ)-C_7]$_3$ to commercial PVC blends.

2.3 Measuring Environmental Impact

Life cycle assessments (LCA) are an essential tool to help quantify the “greenness” of new and existing products and help guide technological advancements towards a more sustainable future [63]. There are many computer programs which compile LCA reports from all over the world into a database that can then be used to assess the impact of new products or processes on a host of factors, such as their impact on carbon emissions, human toxicity, and ozone depletion [63, 64].

LCAs are comprised of 4 stages: i.e., goal and scope definition, inventory analysis, impact assessment, and interpretation [63]. Life cycle analysis is an iterative process and, as such, as it progresses previous steps may need to be updated and refined to assess the total environmental or economic cost more accurately[65]. The general framework for an LCA as described by the international organization for standardization (ISO) can be seen in Figure 2.4 [66].

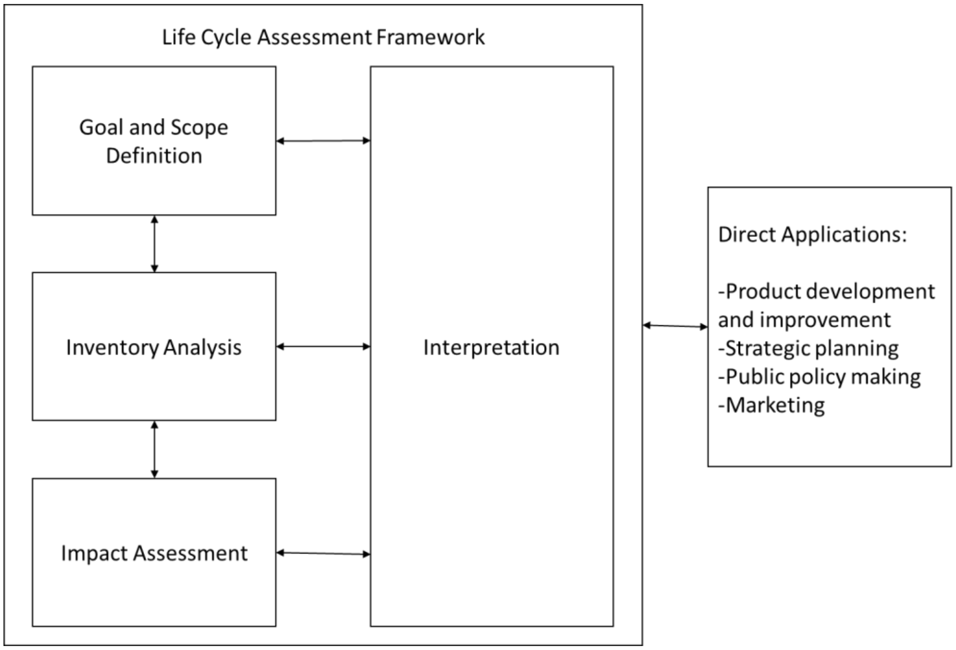

Figure 2.4: The general methodological framework for LCA (ISO 14040).

Goal and scope definition as it pertains to LCA involves defining the functional units for comparison between products or processes, as well as defining the system boundaries for the process [67]. Life cycle inventory analysis (LCI) compiles and quantifies the inputs and outputs of a product into and out of the atmosphere, biosphere, and technosphere [63]. The impact assessment takes the data obtained from the previous step and assesses the magnitude and significance of it to various impact categories, to achieve an overall impact score for the product or process in comparison to other existing or novel alternatives [68]. Interpretation deals with evaluating the consistency, sensitivity, and completeness of the results as well as an uncertainty analysis to determine whether further data is required [63]. Interpretation should also contain the conclusions and recommendations to go along with an assessment [69].

LCA suffers from several major challenges, including gaps in life cycle inventory databases, generalization of impacts across different cultures and ecosystems, and poor standardization of LCA practices. Currently LCI databases contain approximately 500 commonly used chemicals, which is only a fraction of the approximately 85,000 chemicals used in commerce [70]. In order to fill in these gaps, LCA practitioners must estimate the missing chemical LCI data of which the most common approach is to fill in the gaps from available LCI data to “build up” more complicated chemicals from the available datasets using stoichiometric calculations [70]. This approach tends to underestimate the global warming results by approximately 35 to 50%, and of the other 18 LCA impact categories only 4 to 5 categories were within 10% of the actual plant results [70]. There are several challenges to performing the more accurate methods for LCA, such as an unavailability of primary data from chemical plants, a large variety in the unit operations and process configurations used for the production of different chemicals, and the sheer number of chemicals missing from the current LCI database which may be required for any one process [70].

There is also the issue of generalizing LCA studies to regions for which they might have an exaggerated impact such as being in close proximity to humans or delicate ecosystems, which can result in underestimating the environmental or social impact for that region [71]. Nevertheless, even with its challenges and flaws, LCA is still an important tool for evaluating the environmental and social impacts of new products and processes. Importantly, performing an LCA during product development, although imperfect, can help avoid the replacement of existing harmful chemicals with those that may be worse in terms of their environmental impact.

3 Methods

This section provides an expanded methods section for the experiments that are reported in the following manuscript and the life cycle analysis.

3.1 Batch Mixing

Fifty (50) g batches of PVC mix with a total plasticizer content of 54 phr and varying 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$ were prepared and loaded into a Rheocord System 40 double-arm internal batch mixer (Haake Buchler). Batches were mixed at a temperature of 175ºC and a rotational speed of 50 rpm for 15 minutes. After 15 minutes the batch mixer was turned off and the heaters were unplugged from the mixer, the front plate was then removed, and the mixed PVC was scraped off from the twin screws and from inside the middle plate. The mixed PVC was then set aside to be used for other experiments. Torque mixing curves for the samples were used to obtain the maximum torque achieved when mixing, the final average mixing torque, the time to reach the final average torque, as well as the slope of the initial increase in torque.

3.2 Hot Press Molding

Hot press molding was using to produce specimens for tensile and rheological testing of the PVC blends. Specimens were pressed in steel molds placed inside a heated Carver Manual Hydraulic Press (Wabash, IN). The previously mixed PVC blends were cut into small pieces and loaded into steel molds. Three geometries were produced using this method: (1) ASTM D638 type IV test bars for tensile testing; (2) 25-mm diameter disks for rheology testing; and (3) 50 × 10 × 1.5 mm rectangular molds for dynamic mechanical thermal analysis (DMTA). The test bars and disks were pressed in two stages at a temperature of 175ºC and pressures of 5 megatons (MT) for 5 minutes and 10 MT for 10 minutes. The rectangular bars were pressed in three stages at a temperature of 175ºC and pressures of 5 MT for 5 minutes, 10 MT for 10 minutes, and 15 MT for 30 minutes.

3.3 Tensile Testing

Tensile testing was performed using a Shimadzu (Kyoto, Japan) Easy Test instrument at a strain rate of 10 mm per minute. Specimens were pressed into ASTM D638 test bars and measurements of the length, width, and thickness of each test bar was taken with a digital caliper prior to testing. Six specimens were tested for each PVC/ PCL_{540}-[(succ)-C_7]$_3$ blend. The maximum stress and strain for each specimen was determined from the resulting stress/strain curve.

3.4 Rheology

A parallel plate geometry was employed in oscillatory mode for the PVC/ PCL_{540}-[(succ)-C_7]$_3$ blends using an Anton Paar (Graz, Austria) MCR 302 instrument using a PP25 configuration to determine the storage and viscous moduli. Disks (25-mm diameter) were placed between parallel plates with a 1-mm gap at 175ºC under nitrogen in a CTD 450 convection oven. Samples were tested at a shear strain of 1.0% and an angular frequency which was decreased logarithmically from 100 to 0.1 rad/s.

3.5 Dynamic Mechanical Thermal Analysis

DMTA was performed using an Anton Paar (Graz, Austria) MCR 302 instrument with an SRF12 configuration. Rectangular bars (50 × 10 × 1.5 mm) were loaded under tension into a CTD 450 convection oven at room temperature in nitrogen. Measurements of each specimen were taken prior to testing using a digital caliper. Each specimen was secured into the SRF12 and then the upper component was raised until the specimen experienced approximately 0.1 N of tension. The specimens were then applied with a constant oscillatory strain of 0.1% and a frequency of 1 Hz, as the temperature was increased to 175ºC.

3.6 Calendering

Calendered PVC films were produced by an industry partner as reported in previous work [20]. All calendered blends contained 100 phr 70 k PVC suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid. The treatment group contained the same base components while also containing 10 phr of the PCL gas check additive. The pre-mixture was blended using a Harteck two-roll mill HTR-300 (d = 120 mm, T = 160°C, 45 rpm). The mill was pre-heated for a minimum of 1 h after which time the pre-mixture was added to the mill. Mixing was performed for 7 min, starting from the time of film formation on the mill rolls. The milled film was cut into four pieces, each of which was fed separately into the lab-scale calender (d = 180 mm, T = 160-170°C, P = 45 psi, 50 rpm). The calender nip distance was set to achieve film gauges of 0.4 mm and 0.8mm +/−0.05 mm. Each of the four pieces was mixed for 1 min on the calender before being removed. Each blend resulted in 3 or 4 sheets of film.

3.7 Gas Check Counting

Gas checks were counted manually by sectioning off three 7 cm × 7 cm squares on each film. The same areas were sectioned off from each film in the bottom left corner, middle, and top right corner. The gas checks were each marked with a black dot, and then the section was photographed, and the black dots were counted from the photograph. The number of gas checks from each area were then averaged to calculate the average number of gas checks for each film. This average was then normalized per square meter (m^2) of calendered film.

3.8 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed using a TA Instruments (New Castle, USA) 5500 Discovery to determine the thermal stability of the PVC/PCL_{540}-[(succ)-C_7]$_3$ blends. TGA was conducted under nitrogen with a flow rate of 25 mL/min from temperatures of 25-600ºC at a heating rate of 10ºC/min. Platinum high temperature pans were first heated with a blow torch until white hot to remove any impurities, then each pan was tarred on the TA 5500 Discovery. Between 5 and 10 mg of each PVC blend was then loaded into a pan and loaded into the TA 5500 Discovery. The thermal degradation onset temperature was determined according to ASTM standard method E2550 using TA instruments TRIOS software.

3.9 Differential Scanning Calorimetry

The glass transition temperatures (T_g) for each PVC blend were determined through differential scanning calorimetry (DSC) using a TA Instruments DSC2500 (New Castle, USA). DSC was performed over a temperature range of -90 to 100ºC with a heating rate of 10ºC/min. Approximately 8 mg of each PVC sample was loaded into a Tzero aluminum hermetic pan, which was then punctured to create a pin hole to prevent pressure buildup. The pans were then placed into the DSC2500 loading area and tested. The T_g was estimated using the half-height method using the TA instruments TRIOS software. Complete thermographs can be found in the Supplemental Information section.

3.10 Statistics

GraphPad Prism 9 was used for statistical analysis using one-way and two-way ANOVA with Bonferroni post-tests. P-values of less that 0.05 were interpreted as significant.

3.11 Life Cycle Analysis

SimaPro life cycle assessment software was used to perform the lifecycle analysis. The ecoinvent database was used for the inventory analysis and CML-IA methodology was used for the impact assessment. The goal of the life cycle assessment was to determine whether the benefits of using PCL_{540}-[(succ)-C_7]$_3$ in a PVC calendering operation would outweigh the environmental impacts of its synthesis. This was a cradle-to-gate analysis, the scope being defined as from the extraction of natural resources to the synthesis of 1 kg of calendered PVC. Inventory analysis was done using stoichiometric approximations to estimate the data for chemicals not found in the ecoinvent database. The chemical processes were obtained through published papers and patents. Impact assessment was done using the CML-IA baseline V3.07/EU25 methodology to calculate the environmental impact of producing PVC sheets with and without PCL_{540}-[(succ)-C_7]$_3$ of varying thicknesses.

4 Surface Defect Reduction for Thick Calendered Poly(vinyl chloride) Sheets Containing Succinate-Capped Poly(caprolactone) Star-Shaped Plasticizers

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4.1 Preface

This section contains a draft manuscript that is to be submitted for publication to the *Journal of Vinyl and Additive Technology*. The objective of this work is to evaluate the performance of PVC blends containing PCL_{540}-[(succ)-C_7]$_3$, as well as to explore the limits for PCL_{540}-[(succ)-C_7]$_3$ to effectively reduce gas checks in calendered PVC film. It includes an assessment of the properties of PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ during processing, as well as the mechanical and thermal properties of the PVC blends. The article shows the effect of PCL_{540}-[(succ)-C_7]$_3$ loading on standard PVC blends. The tensile properties, rheological properties, torque mixing profiles, and glass transition temperature for PVC blends with various PCL_{540}-[(succ)-C_7]$_3$ loadings are examined. As well, the ability of PCL_{540}-[(succ)-C_7]$_3$ to eliminate gas checks at thick film gauges (0.8 mm) is reported. The gas check reduction effect of PCL_{540}-[(succ)-C_7]$_3$, is highlighted and some theories are presented as to how the additive helps gas check reduction and suggests broader implications of its potential use.

4.2 Abstract

Gas checks are defects that mar the surfaces of flexible poly(vinyl chloride) (PVC) calendered films and are typically reduced through changes in the calender operating parameters, a costly exercise which also limits the sheet thickness and the production rate. It has been previously shown that adding a low concentration of poly(caprolactone) (PCL)-based star-shaped compound can eliminate gas check defects in PVC calendering. This work investigates in further detail the effect of a triheptylsuccinate-terminated poly(caprolactone) compound with a PCL triol core (M_n = 540g/mol) (PCL_{540}-[(succ)-C_7]$_3$) on the material, thermal, and processing properties of PVC blends containing diisononyl phthalate (DINP) as a primary plasticizer and PCL_{540}-[(succ)-C_7]$_3$ in low quantities (i.e., 0, 5, or 10 parts per hundred rubber (phr)) as a secondary plasticizer and processing aid. The most significant differences between PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ and those without were in the rheological properties of the PVC blends at higher temperatures and lower angular frequencies. At these conditions, the PVC blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ had a complex viscosity nearly three times higher than those containing only DINP. PVC/PCL_{540}-[(succ)-C_7]$_3$ blends had comparable tensile properties to those containing only DINP, with no significant change in maximum elongation and a 28% increase in maximum stress. PCL_{540}-[(succ)-C_7]$_3$ was also shown to effectively remove gas check defects from calendered PVC films of twice the thickness of those without the PCL_{540}-[(succ)-C_7]$_3$ additive. In addition to reduced wastage of marred films, the increased calender operating range of PVC films containing PCL_{540}-[(succ)-C_7]$_3$ has the potential to significantly reduce energy costs for the calendering of thick PVC films.

4.3 Introduction

Poly(vinyl chloride) (PVC) is the fifth most produced plastic by weight with 38 million tonnes of PVC processed each year [1]. PVC products use more additives by volume than any other manufactured plastics [2-4] mainly due to the use of large volumes of plasticizers [5]. Plasticizers account for nearly one third of the total plastic additives market [3, 6] and are vital for making PVC processable and malleable [7].

Several methods may be used to compound PVC with plasticizer. One such method, calendering, is an industrial process wherein heated thermoplastics are passed through a system of heated rollers to form a continuous sheet [8]. PVC accounts for the majority of calendered polymers, as relatively few other polymers are processed in this way [8]. There are several common defects when calendering PVC, such as air entrapments (gas checks), chevrons, and mattness [9]. Gas checks are physical defects that are hypothesized to result from air being entrapped in the PVC sheet during calendering and which are generally observed as blemishes varying in size in the direction of calender flow [9, 10]. While they are mainly experienced as a visual defect, they can have localized negative effects on film quality, such as increased permeability in food wrappings and compromised mechanical properties [9]. Current processing methods used to reduce gas checks include alterations in the calendering process, such as decreasing the calendering speed or decreasing the distance between rollers (i.e., nip roll width). This can complicate and slow the calendering process, as can limit the functionality and thickness of the end product, as process parameters must be limited within a set range in order to avoid gas checks [9]. For instance, calendered film thickness is generally limited to the range of 0.05 - 0.5 mm, as it is difficult to maintain consistency and quality at thicker gauges [8, 9, 11, 12].

While developing an alternative to phthalate-based plasticizers for PVC, it was found that a series of poly(caprolactone) (PCL)-based compounds with diester linkers and alkyl chain cappers were effective at reducing or eliminating the formation of gas checks during PVC calendering at concentrations as low as 5 phr [13, 14]. Notably, the use of an additive to avoid gas checks thereby improving product quality, would also allow for the removal of processing steps in the production of thicker films, as the currently used method for the production of thick calendered PVC sheets involves calendering several thin sheets of PVC and pressing or laminating them together [8, 9, 15]. Using additives to prevent gas checks could also improve existing manufacturing processes by reducing waste product and improving operating line efficiency and consistency.

This work investigates the effect on the physical properties of a typical PVC mix when using a triheptylsuccinate-terminated poly(caprolactone) with a PCL triol core (M_n = 540g/mol) compound (PCL_{540}-[(succ)-$C_7]_3$) as a secondary plasticizer in conjunction with diisononyl phthalate. The structures for PCL_{540}-[(succ)-$C_7]_3$ and diisononyl phthalate (DINP) can be seen in Figure 4.1. The goal was to determine whether the addition of PCL_{540}-[(succ)-$C_7]_3$ would significantly affect either the required processing conditions or the properties of the final product, other than the observed effect on gas check reduction. This work also explores whether PCL_{540}-[(succ)-$C_7]_3$ as a gas check reduction additive allows for the expansion of PVC calendering operation range.

4.4 Materials

Dry poly(vinyl chloride) mixes with and without diisononyl phthalate (DINP) were obtained from Canadian General-Tower Ltd. (Cambridge, Ontario). Contents of the standard mixes are outlined below in Table 4.1. Poly(caprolactone) star-shaped plasticizer was synthesized as previously published [13]. The two standard mixes were weighed out and combined with 0/5/10 parts per hundred rubber (phr) PCL_{540}-[(succ)-C_7]$_3$ to create a total plasticizer concentration of 54 phr with DINP.

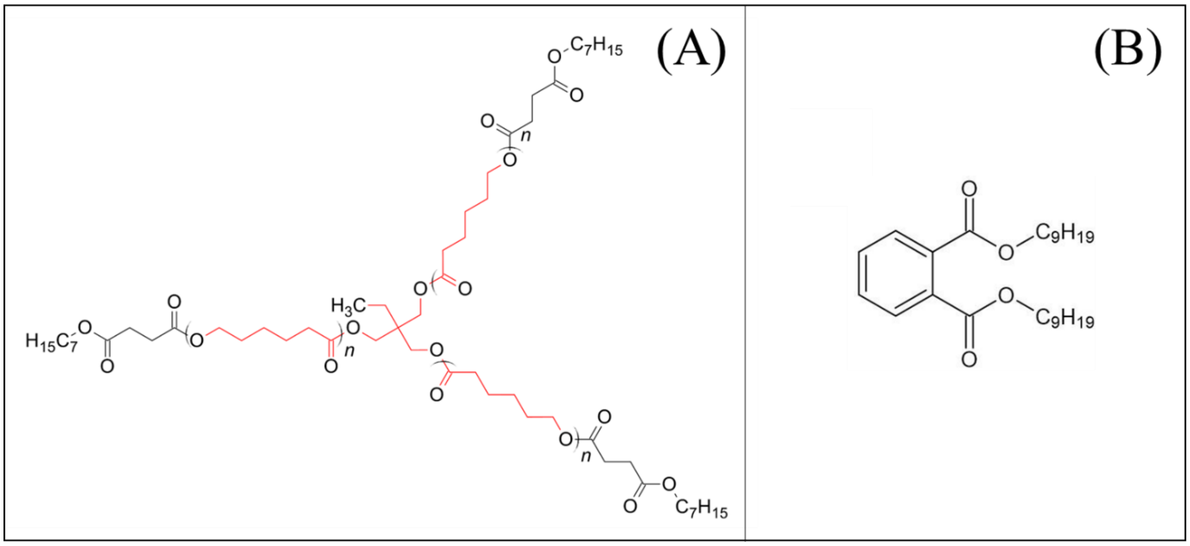

Figure 4.1: Molecular structures of additives in polyvinyl chloride blends: (A) PCL_{540}-[(succ)-C_7]$_3$ and (B) diisononyl phthalate.

Table 4.1: Commercial PVC blends obtained from Canadian General-Tower Ltd. (Ontario, Canada).

Generic Material Name	**Component Quantity (phr)**	
	PVC mix with DINP	PVC mix without DINP
Suspension PVC resin 70K	100	100
Acrylic process aid	1	1
Silica	0.3	0.3
Stearic Acid	0.5	0.5
Antimicrobial Agent	1.25	1.25
DINP Plasticizer	54	0
Ba/Zn Heat stabilizer	2	2
ESO	3	3
Carbon Black Pigment	6	0

4.5 Methods

4.5.1 Batch Mixing

Fifty (50) g batches of PVC mix with a total plasticizer content of 54 phr and varying 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$ was prepared and loaded into a Rheocord System 40 double-arm internal batch mixer (Haake Buchler). Batches were mixed at a temperature of 175ºC and a rotational speed of 50 rpm for 15 minutes. Torque mixing curves for the samples were used to obtain the maximum torque achieved when mixing, the final average mixing torque, the time to reach the final average torque, as well as the slope of the initial increase in torque. Full torque mixing curves can be found in the Supplemental Information section.

4.5.2 Hot Press Molding

Hot press molding was using to produce specimens for tensile and rheological testing of the PVC blends. Specimens were pressed in steel molds placed inside a heated Carver Manual Hydraulic Press (Wabash, IN). The previously mixed PVC blends were cut into small pieces and loaded into steel molds. Three geometries were produced using this method: (1) ASTM D638 type IV test bars for tensile testing; (2) 25-mm diameter disks for rheology testing; and (3) 50 × 10 × 1.5 mm rectangular molds for dynamic mechanical thermal analysis (DMTA). The test bars and disks were pressed in two stages at a temperature of 175ºC and pressures of 5 MT for 5 minutes and 10 MT for 10 minutes. The rectangular bars were pressed in three stages at a temperature of 175ºC and pressures of 5 MT for 5 minutes, 10 MT for 10 minutes, and 15 MT for 30 minutes.

4.5.3 Tensile Testing

Tensile testing was performed using a Shimadzu (Kyoto, Japan) Easy Test instrument at a strain rate of 10 mm per minute. Specimens were pressed into ASTM D638 test bars, and measurements of the length, width, and thickness of each test bar was taken with a digital caliper prior to testing.

Six specimens were tested for each PVC/ PCL_{540}-[(succ)-C_7]$_3$ blend. The maximum stress and strain for each specimen was determined from the resulting stress/strain curve.

4.5.4 Rheology

A parallel plate geometry was employed in oscillatory mode for the PVC/ PCL_{540}-[(succ)-C_7]$_3$ blends using an Anton Paar (Graz, Austria) MCR 302 instrument using a PP25 configuration to determine the storage and viscous moduli. Disks (25-mm diameter) were placed between parallel plates with a 1-mm gap at 175ºC under nitrogen in a CTD 450 convection oven. Samples were tested at a shear strain of 1.0% and an angular frequency which was decreased logarithmically from 100 to 0.1 rad/s.

4.5.5 Dynamic Mechanical Thermal Analysis

DMTA was performed using an Anton Paar (Graz, Austria) MCR 302 instrument with an SRF12 configuration. Rectangular bars (50 × 10 × 1.5 mm) were loaded under tension into a CTD 450 convection oven at room temperature in nitrogen. Measurements of each specimen were taken prior to testing using a digital caliper. The specimens were applied with a constant oscillatory strain of 0.1% and a frequency of 1 Hz, as the temperature was increased to 175ºC.

4.5.6 Calendering

Calendered PVC films were produced by an industry partner, Canadian General-Tower Ltd. (Ontario, Canada) as reported in previous work [13]. All calendered blends contained 100 phr 70 k PVC suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid. The treatment group contained the same base components while also containing 10 phr of the PCL gas check additive. The pre-mixture was blended using a Harteck two-roll mill HTR-300 (d = 120 mm, T = 160°C, 45 rpm). The mill was pre-heated for a minimum of 1 h after which time the pre-mixture was added to the mill. Mixing was performed for 7 min, starting from the time of film formation on the mill rolls. The milled film was cut into four pieces, each of which was fed separately into the lab-scale calender (d = 180 mm, T = 160-170°C, P = 45 psi, 50 rpm). The calender nip distance was set to achieve film gauges of 0.4 mm and 0.8 mm +/−0.05 mm. Each of the four pieces was mixed for 1 min on the calender before being removed. Each blend resulted in three or four sheets of film.

4.5.7 Gas Check Counting

Gas checks were counted manually by sectioning off three 7 cm × 7 cm squares on each film. The same areas were sectioned off from each film in the bottom left corner, middle, and top right corner. The number of gas checks from each area were then averaged to calculate the average number of gas checks for each film. This average was then normalized per square meter (m^2) of calendered film.

4.5.8 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed using a TA Instruments (New Castle, USA) 5500 Discovery to determine the thermal stability of the PVC/PCL_{540}-[(succ)-$C_7]_3$ blends. TGA was conducted under nitrogen with a flow rate of 25 mL/min from temperatures of 25-600ºC at a heating rate of 10ºC/min. The thermal degradation onset temperature was determined according to ASTM standard method E2550 using TA instruments TRIOS software. Complete thermographs can be found in Figure 5.1 in the Supplemental Information section.

4.5.9 Differential Scanning Calorimetry

The glass transition temperatures (T_g) for each PVC blend were found by performing differential scanning calorimetry (DSC) with a TA Instruments DSC2500 (New Castle, USA). DSC was performed over a temperature range of -90 to 100ºC with a heating rate of 10ºC/min. The T_g was estimated using the half-height method using the TA instruments TRIOS software. Complete DSC thermographs can be found in Figure 5.2 in the Supplemental Information section.

4.5.10 Statistics

GraphPad Prism 9 was used for statistical analysis using one-way and two-way ANOVA with Bonferroni post-tests. P-values of less that 0.05 were interpreted as significant.

4.6 Results

4.6.1 Mixing Properties

The results of the batch mixing experiments showing differences in the torque mixing curves for PVC mixes with 0, 5. And 10 phr of PCL_{540}-[(succ)-C_7]$_3$ are presented in Figure 4.2 and summarized in Table 4.2. There was a non-significant ($p > 0.05$, one-way ANOVA) increase in maximum achieved torque with PCL_{540}-[(succ)-C_7]$_3$ loading, with the average maximum achieved torques being 13.4, 14.3, and 14.6 N·m for 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$, respectively. There was also a non-significant increase in final average torque with the average final torques being 7.9, 8.1, and 8.5 N·m for 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$, respectively. The final average torque was taken by averaging the torque values over the range where the torque curve remained flat. The time to reach equilbrium had a non-significant decrease with PCL_{540}-[(succ)-C_7]$_3$ loading, on average being 320, 300, and 280 s for 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$, respectively. Time to reach equilibrium was defined as the time (in seconds) from the maximum achieved torque until the final average torque was reached.

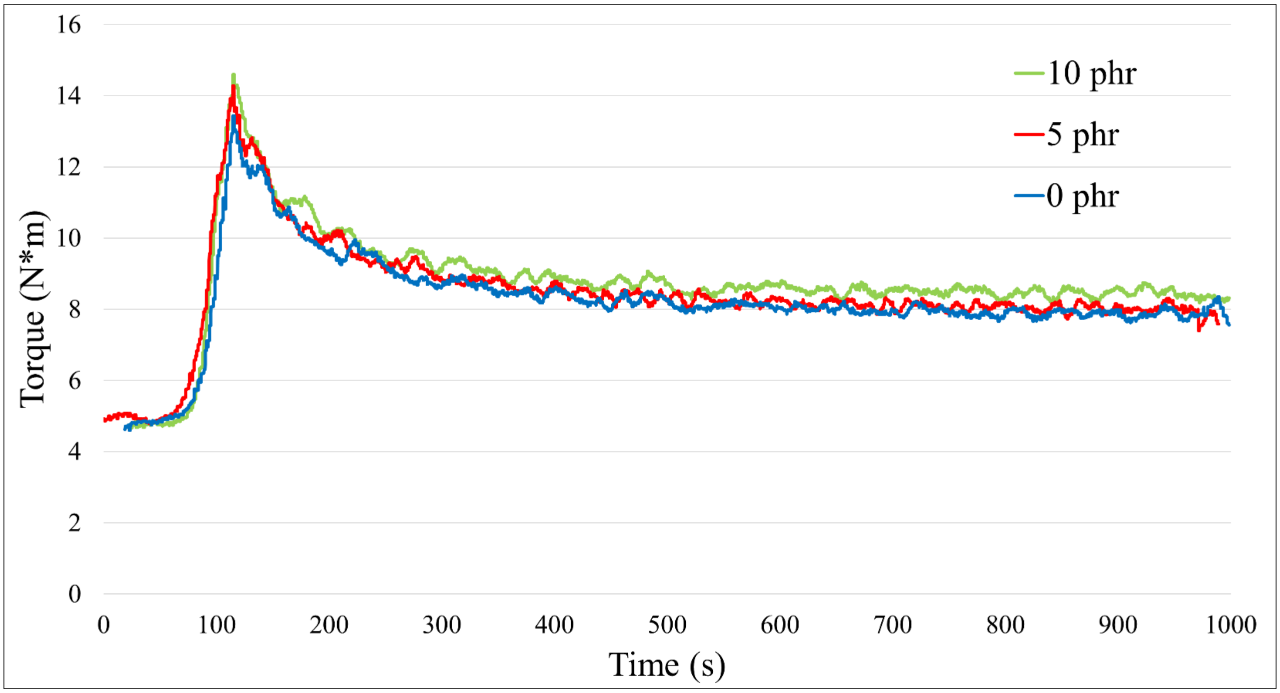

Figure 4.2:Average batch mixing torque curves for PVC blends with 0, 5, and 10 phr of PCL_{540}*-[(succ)-*C_7*]*$_3$*.*

Table 4.2: Properties of PVC blends during mixing with 0, 5, and 10 phr of PCL_{540}*-[(succ)-*C_7*]*$_3$*.*

PCL_{540}-[(succ)-C_7]$_3$ Concentration (phr)	Time from Maximum Torque to Final Average Torque (s)		Maximum Achieved Torque (N·m)		Final Average Torque (N·m)	
	Mean	STD	Mean	STD	Mean	STD
0	320	9.5	13.4	0.28	7.9	0.18
5	300	30	14.3	0.95	8.1	0.33
10	280	39	14.6	0.32	8.5	0.15
p-value	0.27		0.13		0.06	

4.6.2 Thermal Properties

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) revealed comparable thermal stability between all mixes, with an initial degradation onset temperature of T ≈ 265ºC for approximately 70% of total mass and a further degradation at T ≈ 450ºC for a further 13% of total mass. A summary of the TGA data can be seen below in Table 4.3, and the full thermographs can be found in the Supplemental Information section.

Table 4.3: Thermogravimetric analysis data for PVC mixes with 0, 5, and 10 phr of PCL540-[(succ)-C7]3 (n = 1).

PCL_{540}-[(succ)-C_7]$_3$ Concentration (phr)	Onset 1 (°C)	End 1 (°C)	Change 1 (%)	Onset 2 (°C)	End 2 (°C)	Change 2 (%)
0	266	314	73	447	474	14
5	264	321	72	447	491	14
10	266	313	71	450	473	16

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) showed a significant ($p < 0.01$, one-way ANOVA) increase in T_g with increased PCL_{540}-[(succ)-C_7]$_3$ loading (Figure 4.3). The average T_g for each sample was -34, -31, and -28°C for 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$, respectively. This is only a 6.2°C increase in glass transition temperature when replacing 10 phr of DINP with 10 phr of PCL_{540}-[(succ)-C_7]$_3$. This increase in T_g was reflected in a small increase in maximum stress during tensile testing, as seen in Table 4.4. Full thermograms for both DSC and TGA can be found in the Supplemental Information section.

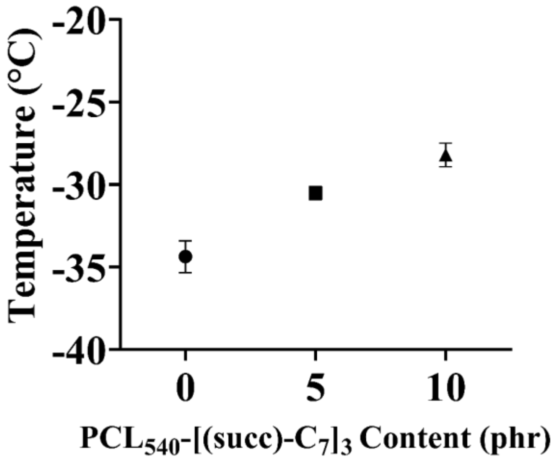

Figure 4.3: Glass transition temperatures (Mean ± SEM) for PVC blends with 0, 5, and 10 phr of PCL_{540}*-[(succ)-*$C_7]_3$ *(n = 3,* $p < 0.01$*).*

4.6.3 Mechanical Properties

Tensile Testing

The average resulting stress-strain curve from tensile testing can be seen in Figure 4.4. The relevant parameters from tensile testing are the maximum stress and the maximum strain, a summary of which can be found in Table 4.4. PCL_{540}-[(succ)-$C_7]_3$ content did not have a significant effect on maximum strain ($p > 0.05$, one-way ANOVA), but it did influence maximum stress ($p < 0.05$, one-way ANOVA). Significant differences in the maximum achieved stress were only apparent at a PCL_{540}-[(succ)-$C_7]_3$ concentration of 10 phr, with the average maximum achieved stresses being 14, 15, and 18 MPa for 0, 5, and 10.phr of PCL_{540}-[(succ)-$C_7]_3$, respectively. Strain not changing significantly while the maximum stress is increasing indicates that the PVC blends with a higher PCL_{540}-[(succ)-$C_7]_3$ content were stiffer than those with lower PCL_{540}-[(succ)-$C_7]_3$ content. This was reflected in the Young's modulus of the blends, which generally increased with PCL_{540}-[(succ)-$C_7]_3$ loading from 0.046 MPa at 0 phr to 0.053 and 0.062 MPa at 5 and 10 phr, respectively [16, 17].

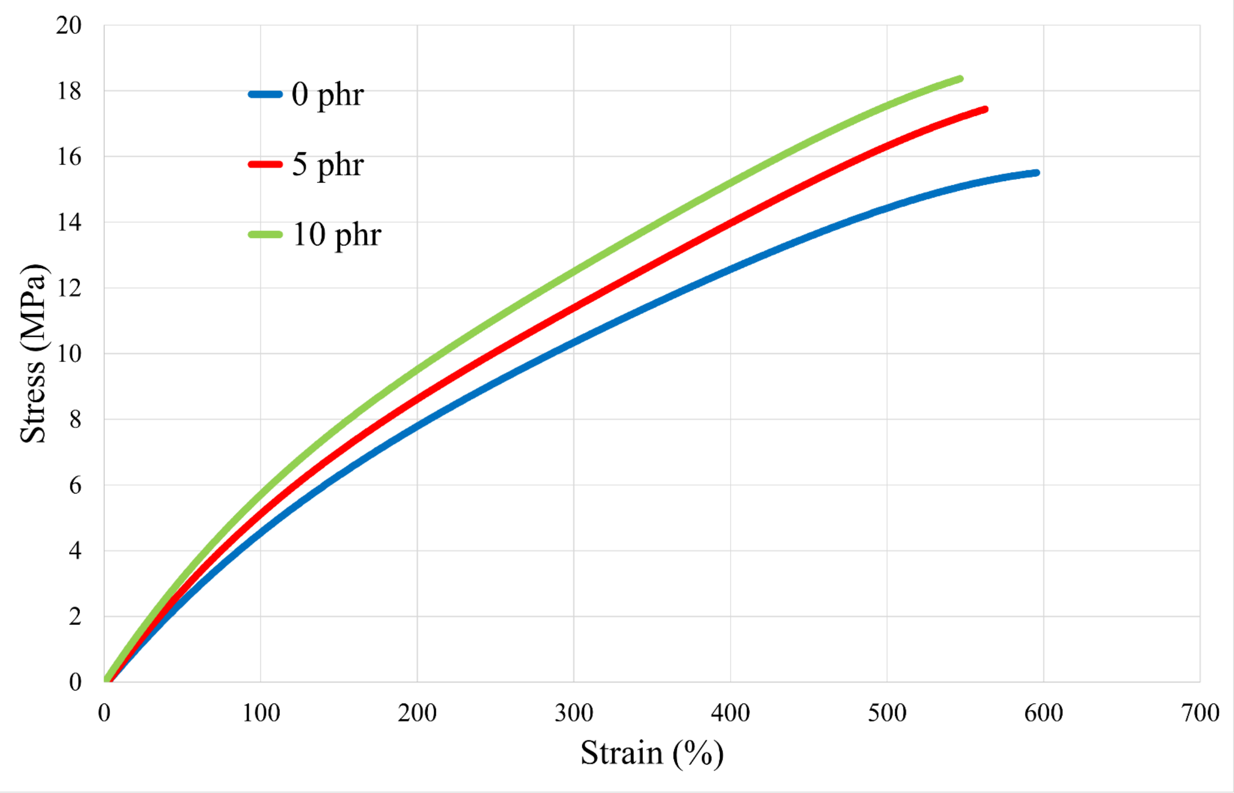

Figure 4.4:Stress-strain curves for PVC blends containing 0, 5, and 10 phr of PCL$_{540}$-[(succ)-C$_{7}$]$_{3}$.

Table 4.4: Tensile properties of PVC blends with 0, 5, and 10 phr of PCL$_{540}$-[(succ)-C$_{7}$]$_{3}$.

PCL540-[(succ)-C7]$_3$ Concentration (phr)	Maximum Strain (%)		Maximum Stress (MPa)	
	Mean	STD	Mean	STD
0	510	110	14	1.8
5	450	77	15	1.6
10	550	32	18	0.90
p-value	0.28		0.01	

Rheology

Parallel plate tests in oscillatory mode showed no significant difference between complex viscosity, loss modulus, or storage modulus between 0 and 5 phr of PCL. However, when analyzing the rheological properties based on PCL$_{540}$-[(succ)-C$_{7}$]$_{3}$ content and angular frequency, there was a very significant ($p < 0.01$, two-way ANOVA) difference in complex viscosity at 10 phr of PCL$_{540}$-[(succ)-C$_{7}$]$_{3}$, particularly at lower frequencies, driven mainly by a relative increase in storage modulus when compared to lower PCL_{540}-[(succ)-C_7]$_3$ loading. The complex viscosities and storage moduli between the 0 and 5 phr mixes was statistically significant ($p<0.05$) from the 10 phr mixes at angular frequencies below 1.58 rad/s, while the loss moduli achieved statistical significance ($p<0.05$) at angular frequencies below 3.98 rad/s. The average complex viscosities, storage moduli, and loss moduli of the PVC blends are shown below in Figure 4.5.

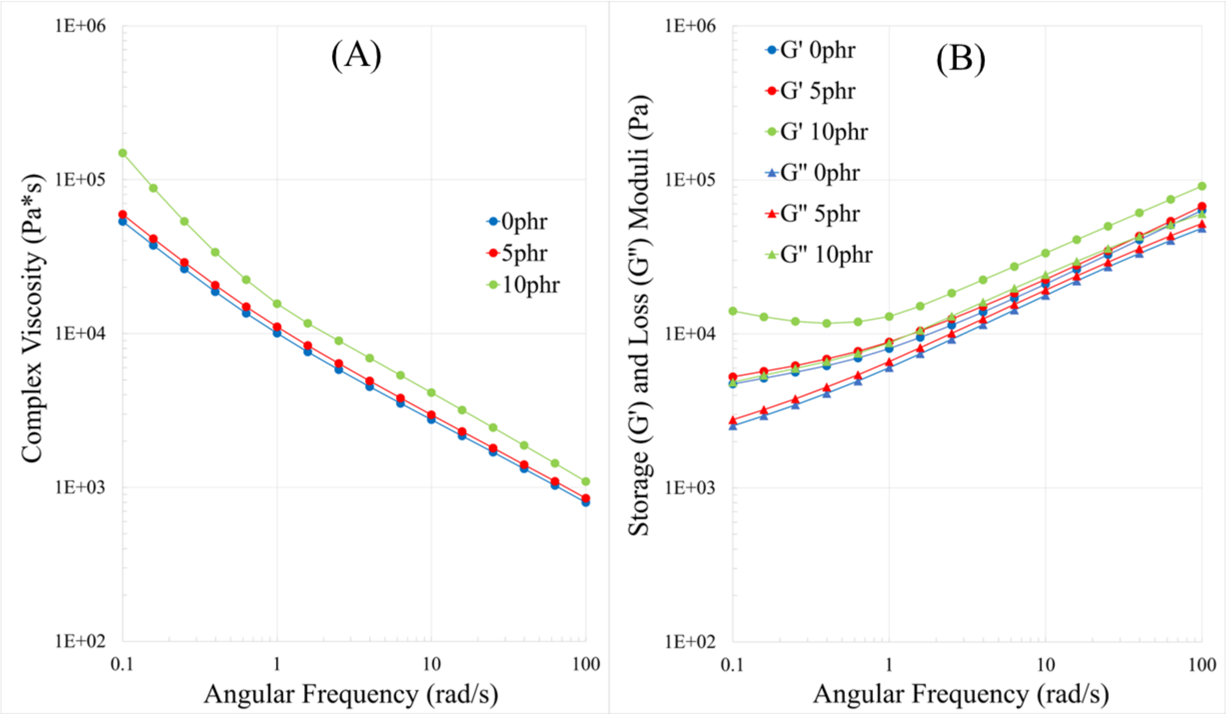

Figure 4.5: (A) Average complex viscosity ($n = 3$, $p < 0.01$) and (B) Storage moduli ($n = 3$, $p = 0.01$) and loss moduli ($n = 3$, $p < 0.01$) measurements for PVC blends with 0, 5, and 10 phr of PCL_{540}-[(succ)-C_7]$_3$ at 175℃.

Dynamic Thermal Mechanical Analysis

Dynamic thermal mechanical analysis (DMTA) was performed to examine the effect of temperature on the PVC blends with varying amounts of PCL, the average measured properties recorded from DMTA can be seen below in Figure 4.6. The different blends exhibited similar storage (G′) and loss (G″) moduli at elevated temperatures up until 100°C, at which point the storage moduli began to decrease at an increasing rate. The point at which the storage modulus (G′) dropped below the loss modulus (G″), corresponds to when the loss factor exceeds unity (tan $\delta > 1$) and is also indicative of the sample beginning to enter the melt flow region [18-20].

4.6.4 Film Properties

Calendered films at three different gauges were produced to measure the ability of PCL_{540}-[(succ)-C_7]$_3$ to reduce gas checks at increasing film thicknesses. As shown in Figure 4.7, with the addition of PCL_{540}-[(succ)-C_7]$_3$, a nearly complete elimination of gas check defects was observed, even at film gauges nearly double the upper limit of the operating range. As seen below in Figure 4.8, PCL_{540}-[(succ)-C_7]$_3$ effectively reduced gas checks at gauges of 0.4, 0.6, and 0.8 mm from an average of 3400, 2200, and 4200 gas checks per square meter (GC/m^2), respectively, without the PCL additive to zero in nearly all cases with the PCL additive. Films at gauges of 0.4, and 0.8 mm were produced in triplicates, while only one replicate at 0.6 mm was performed.

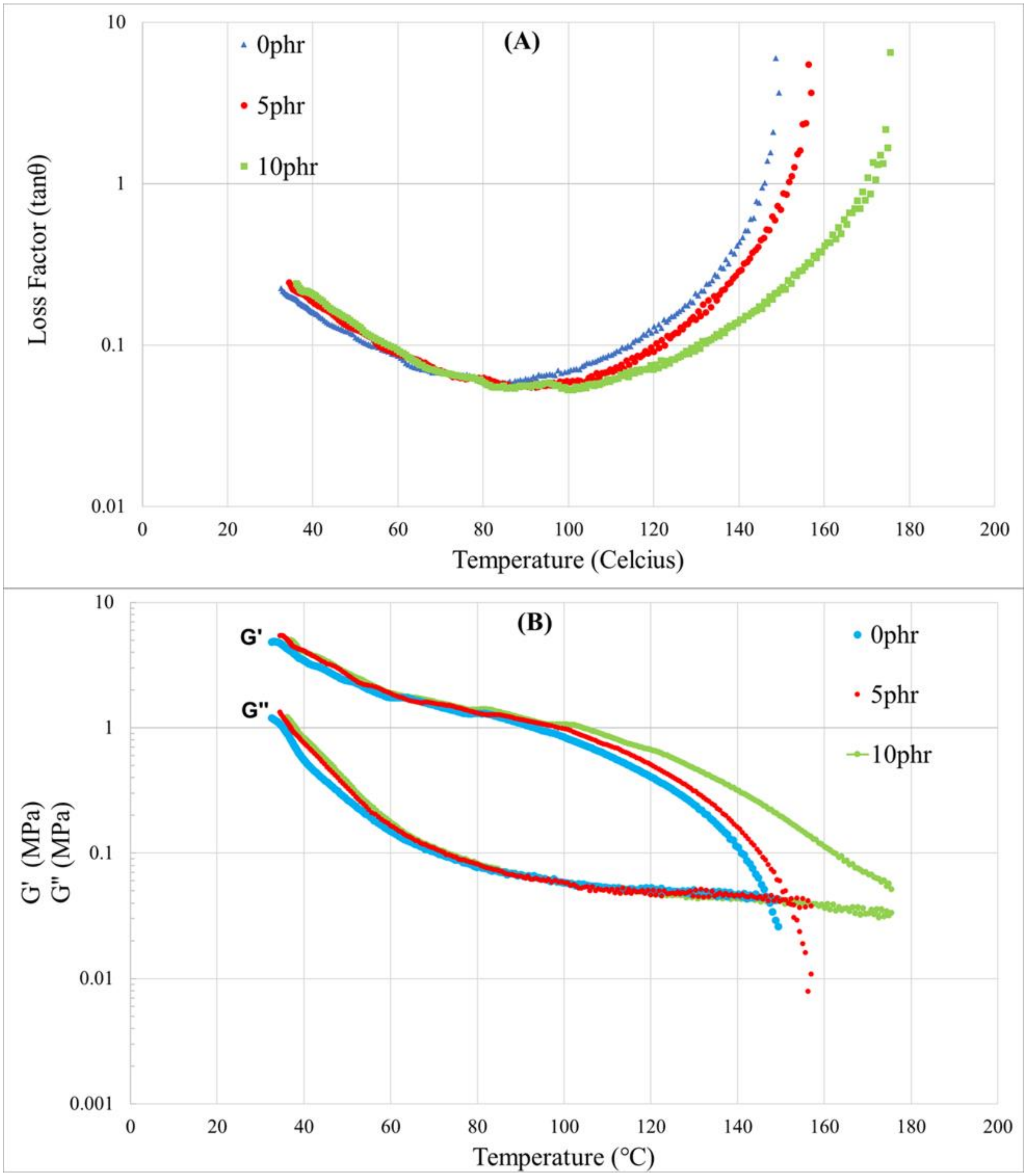

Figure 4.6:Average properties from DMTA for PVC blends with 0, 5, and 10 phr of PCL_{540}-$[(succ)\text{-}C_7]_3$: (A) Loss factor ($n = 3$, $p < 0.01$) and (B) Storage modulus ($n = 3$, $p < 0.01$) and loss modulus ($n = 3$, $p = 0.52$).

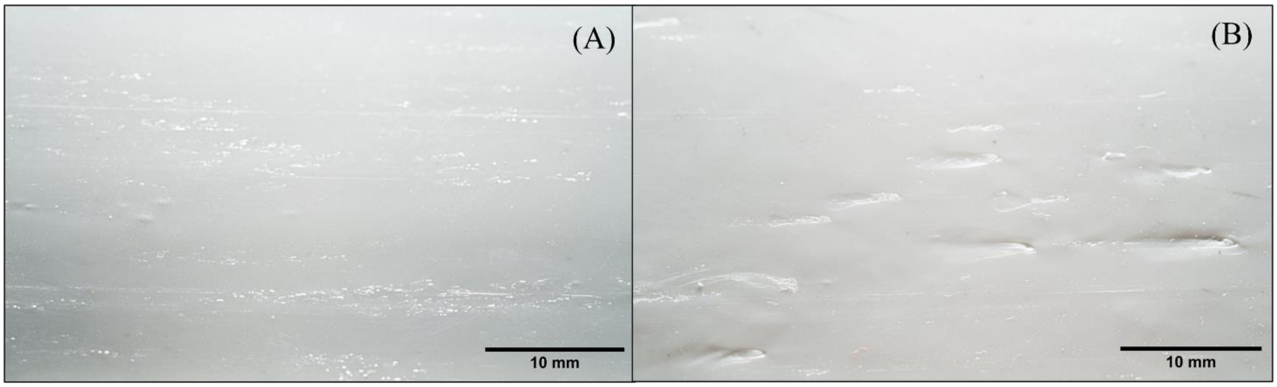

Figure 4.7: Calendered PVC films of 0.8 mm film gauge (A) without PCL$_{540}$-[(succ)-C$_7$]$_3$ and (B) with PCL$_{540}$-[(succ)-C$_7$]$_3$.

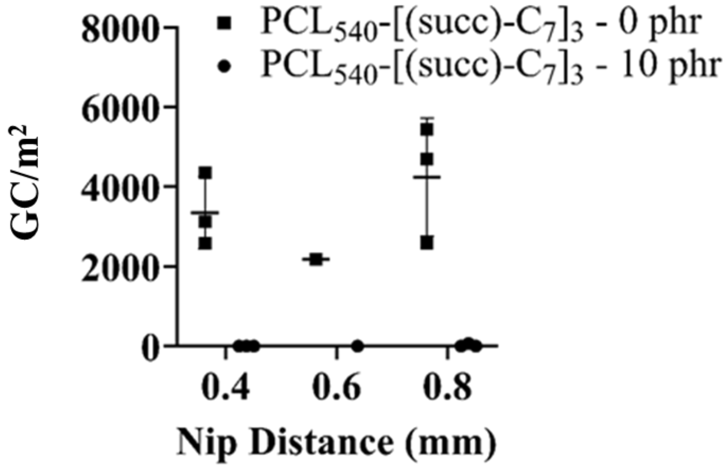

Figure 4.8: Number of gas checks per square meter (Mean ± SEM) for calendered PVC with and without PCL$_{540}$-[(succ)-C$_7$]$_3$ (n = 3 for film gauges 0.4 mm and 0.8 mm, and n = 1 for film gauge 0.6 mm, $p < 0.01$).

4.7 Discussion

Using PCL$_{540}$-[(succ)-C$_7$]$_3$ as a secondary plasticizer and processing aid to remove gas checks could expand the operational conditions of the PVC calendering process [9, 13]. Presently, the standard operating range for the thickness of calendered PVC sheets is between 0.05 and 0.5 mm, as it is difficult to maintain quality and consistency at thicker film gauges [8, 9, 12, 21]. To ensure PCL$_{540}$-[(succ)-C$_7$]$_3$ can be used as a gas check reduction additive in a PVC calendering operation it is important to know how it affects the physical properties of a typical PVC formulation. The effect of using PCL_{540}-[(succ)-C_7]$_3$ as a secondary plasticizer was investigated at concentrations of 0, 5, and 10 phr with the primary plasticizer DINP to achieve a total plasticizer content of 54 phr.

4.7.1 Effect on Mixing Properties

PCL_{540}-[(succ)-C_7]$_3$ loading had no significant effect on any of the measured torque mixing properties ($p > 0.05$, one-way ANOVA). The average time to reach equilibrium from the maximum achieved torque decreased slightly with PCL loading from 320 s at 0 phr PCL_{540}-[(succ)-C_7]$_3$ to 240 s at 10 phr PCL_{540}-[(succ)-C_7]$_3$. The maximum and final average torques increased slightly with PCL_{540}-[(succ)-C_7]$_3$ loading, with maximum and final average torques at 0 phr PCL_{540}-[(succ)-C_7]$_3$ being 13 and 8.0 N·m, respectively, and maximum and final average torques at 10 phr PCL_{540}-[(succ)-C_7]$_3$ being 15 and 8.5 N·m, respectively. These were again however non-significant changes, which indicates that PCL_{540}-[(succ)-C_7]$_3$ could be incorporated into PVC using existing processing operations without additional changes needing to be made to production parameters.

4.7.2 Effect on Thermal Properties

The unchanged degradation onset temperature with PCL_{540}-[(succ)-C_7]$_3$ loading shows that a PVC mixture containing PCL_{540}-[(succ)-C_7]$_3$ as a secondary plasticizer is thermally stable at typical PVC processing temperatures. Calendering typically takes place in a temperature range from 160 to 210°C [7, 8, 22], which is still well below the onset degradation temperature for the PVC mixtures of 265°C.

The increase in T_g with PCL_{540}-[(succ)-C_7]$_3$ loading indicates that this additive is less effective at plasticizing when compared to DINP at the same overall plasticizer loading. This is consistent with previous work which showed T_gs when compared to DINP at equivalent plasticizer concentrations for calendered PVC/PCL_{540}-[(succ)-C_7]$_3$ mixtures [14, 23, 24]. Nonetheless the samples still had

T_gs well below room temperature, thereby showing the mixtures are still plasticized effectively with PCL as a secondary plasticizer.

4.7.3 Effect on Mechanical Properties

The tensile properties of the PVC blends did not change considerably with PCL_{540}-[(succ)-C_7]$_3$ loading, with no statistically significant difference in the maximum strain or elongation at break, and only a small increase in the maximum achieved stress at 10 phr of PCL_{540}-[(succ)-C_7]$_3$. Sample stiffness did increase slightly with PCL_{540}-[(succ)-C_7]$_3$ loading, reflected in the Young's modulus in the initial elastic region increasing with PCL_{540}-[(succ)-C_7]$_3$ content.

Rheological testing revealed a significant change in complex viscosity at a PCL_{540}-[(succ)-C_7]$_3$ concentration of 10 phr, particularly at lower angular frequencies ($w < 1$ rad/s). Overall, the viscosity of the blends generally increased with PCL_{540}-[(succ)-C_7]$_3$ loading, showing that PCL_{540}-[(succ)-C_7]$_3$ is slightly less effective at plasticizing the PVC blend when compared to DINP (Figure 4.5). As w decreases, the G' and G'' for each blend decreases following a power law curve, however at $w < 1$ rad/s, the G' for the blend containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ begins to diverge from the power-law model (Figure 4.5). At low frequencies, the blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ move out of a transitional region and enter a rubbery plateau. The increased complex viscosity of the 10 phr blend at low frequencies could be contributing to the removal of gas checks in calendering processes, as higher viscosity polymers produce fewer air inclusions [9].

As shown in Figure 4.6(B), DMTA showed an increase in the temperature at which G' drops below G'' at a PCL_{540}-[(succ)-C_7]$_3$ content of 10 phr. This point which coincides with the temperature at which the loss factor exceeds unity ($\tan\delta > 1$) is considered here to be the point at which the sample has entered the melt flow region, as seen in Figure 4.6(A) [18-20]. The temperatures at which the loss factors for the different blends exceed one increase with PCL loading; however not all samples with 10 phr of PCL_{540}-[(succ)-C_7]$_3$ entered the melt flow region by the upper temperature of the testing parameters (175°C). The PVC samples with 10 phr of PCL_{540}-[(succ)-C_7]$_3$ did not consistently transition from the rubbery plateau at temperatures below 175°C, meaning PVC blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ undergoing calendering would have increased viscosities at operating temperatures at or below 175°C. This increased viscosity at typical calender operating conditions would help to avoid air inclusions, as it would result in a higher pressure in the calender bank [8, 9, 25]. The PVC samples with 10 phr of PCL_{540}-[(succ)-C_7]$_3$ not entering the melt flow region by 175°C may require calendering to occur at higher temperatures, which would require more energy to heat the polymer melt and may cause thermal degradation of some of the blend components. Interestingly, the opposite effect was noticed during the calendering of the PVC films, as the PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ were able to be processed at temperatures ~10°C lower than those without. As well the fusion times for blends containing PCL_{540}-[(succ)-C_7]$_3$ was ~50% lower than those without. This may because while calendering 10 phr of PCL_{540}-[(succ)-C_7]$_3$ was added in addition to the 54 phr of DINP, while for the mechanical testing 10 phr of DINP was replaced by PCL_{540}-[(succ)-C_7]$_3$, and so the overall melt flow temperature for the blend was lowered.

4.7.4 Effect on Film Properties

The primary focus of the film calendering experiments was to determine whether PCL_{540}-[(succ)-C_7]$_3$ could effectively reduce gas check defects at greater film gauges than previously reported [13]. As mentioned earlier, the broadening of calendering operating conditions could have major benefits in reducing energy consumption in the calendering process given that thicker gauges of films could be produced without multiple calender runs and additional processing steps such as pressing or lamination [8, 11].

The calendered films containing the PCL_{540}-[(succ)-C_7]$_3$ additive had considerably smoother finishes when compared to those without, primarily due to the lack of air inclusions on their surface (see Figure 4.7 and Figure 4.8). There was scratching on the surface of all calendered films, with and without PCL_{540}-[(succ)-C_7]$_3$, which is presumed to be imprints from the calender rolls.

There was no observable trend in the location of gas check defects on the surface of calendered sheets (i.e., at the beginning, middle, or end of the calender run), with gas checks being evenly distributed throughout the sheets not containing PCL_{540}-[(succ)-C_7]$_3$. PVC films containing PCL_{540}-[(succ)-C_7]$_3$ saw a complete reduction in gas checks in nearly all cases, with the number of gas checks per unit area (GC/m^2) being reduced from 3400 GC/m^2 to 0 GC/m^2 at a film gauge of 0.4 mm, and from 4200 GC/m^2 to 23 GC/m^2 at a film gauge of 0.8 mm.

4.8 Conclusion

Overall, the PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ performed comparably to those only containing DINP in both tensile and mixing properties. This shows that PCL_{540}-[(succ)-C_7]$_3$ can be added to existing calender operations without requiring additional substantial changes to the process or significantly altering the PVC product. Rheological testing revealed differences in blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ at higher temperatures and lower angular frequencies when compared to blends with lower PCL_{540}-[(succ)-C_7]$_3$ loading. These differences could conceivably be contributing to the effect of PCL_{540}-[(succ)-C_7]$_3$ on reducing gas checks in PVC calendering, as a higher viscosity at PVC calendering process conditions would lead to higher pressures in the calender bank and thus would result in fewer defects according to the current theories on gas check formation [9, 10]. The mechanism for PCL_{540}-[(succ)-C_7]$_3$ to remove gas checks, however, is still not well understood, and may not be purely resultant of a physical phenomenon but could also be dependent on a chemical interaction between the PCL_{540}-[(succ)-$C_7]_3$ compound and the PVC matrix. This work shows a nearly complete reduction in gas check defects at a film gauge above the typical operating limits of PVC calendering. Were this additive to be utilized in a calendering operation, it could have benefits in process simplification, and waste and energy reduction.

4.9 References

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5 Supplemental Information

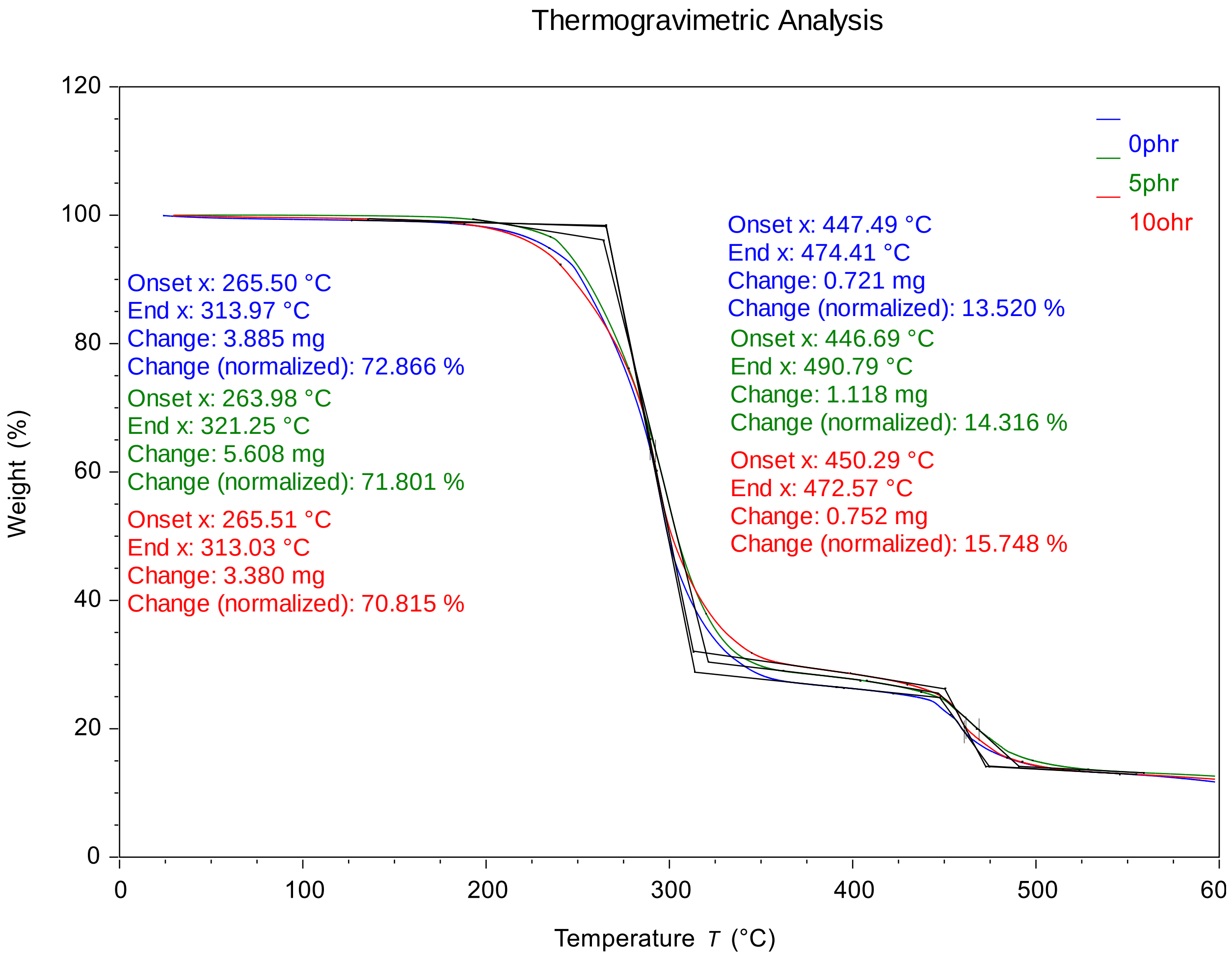

Figure 5.1: Thermogravimetric Analysis for PVC blends with 0, 5, and 10 phr of PCL$_{540}$*-[(succ)-C*$_7$*]*$_3$*.*

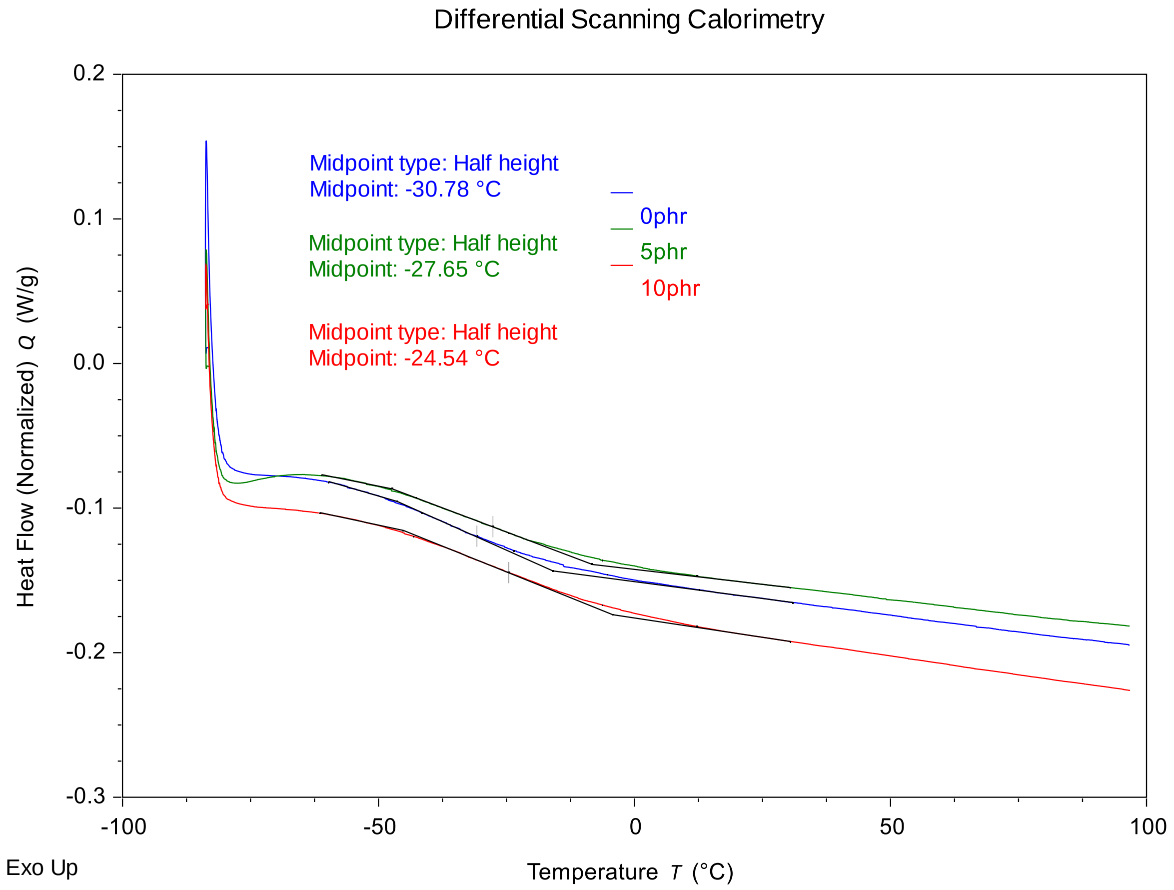

Figure 5.2: Differential scanning calorimetry for PVC blends containing 0, 5, 10 phr PCL$_{540}$*-[(succ)-C*$_7$*]*$_3$*. Analyzed using half-height method and one-way ANOVA (*$n = 3$*,* $p < 0.01$*).*

6 Preliminary LCA Results

The following are preliminary LCA results which were not included in the manuscript. The methods used to complete the preliminary LCA are outlined in section 3.11.

Table 6.1 contains the preliminary LCA data for 1 kg of calendered PVC at varying thicknesses both with and without PCL_{540}-[(succ)-C_7]$_3$. The estimated amount of energy for one calender run of PVC is 6 MJ/kg [87]. Multiple calender runs are required to calender sheets of a thickness greater than 0.5 mm without PCL_{540}-[(succ)-C_7]$_3$ or greater than 0.8 mm with PCL_{540}-[(succ)-C_7]$_3$. This preliminary LCA does not factor in additional energy and labour costs associated with the pressing or lamination stages of processing thick calendered sheets, as industry data for those process steps could not be found. This LCA also does not account for the potential waste reduction from gas check elimination, although an industry partner reported that waste generated from gas checks can range anywhere from 10 to 50% depending on the blend and manufacturing specifications.

Table 6.1 shows the comparative impact to produce 1 kg of calendered PVC with and without PCL_{540}-[(succ)-C_7]$_3$ at varying thicknesses across the CML-IA baseline impact categories. The cells containing an asterix represent a decrease in the observed impact category for calendered PVC containing PCL_{540}-[(succ)-C_7]$_3$. For films with a thickness of 0.4 mm, requiring only one calender run, the blends containing PCL_{540}-[(succ)-C_7]$_3$ had an increase in most impact categories compared to the control, except for abiotic depletion, ozone layer depletion, and terrestrial ecotoxicity. This is due to the amounts of each component in the PVC mix being determined on a per hundred rubber basis, so by adding in 10 phr of PCL_{540}-[(succ)-C_7]$_3$, it decreased the percentage of the total blend which was composed of other components which are especially impactful in those categories. For calendered films of thicknesses greater than 0.8 mm, the benefits of PCL$_{540}$-[(succ)-C$_7$]$_3$ become more apparent with the reduced energy costs from requiring less calender runs. At 0.8 mm, the blends containing PCL$_{540}$-[(succ)-C$_7$]3 have reduced impact scores in the same categories as at 0.4 mm, and also in global warming potential, freshwater aquatic ecotoxicity, photochemical oxidation, and eutrophication. At a film gauge of 1.6 mm, the blends containing PCL$_{540}$-[(succ)-C$_7$]$_3$ have reduced impact scores in all categories except for marine aquatic ecotoxicity. This comes from the synthesis of PCL$_{540}$-[(succ)-C$_7$]$_3$ having a relatively high impact in that category when compared to the other components of the PVC blend, and also electricity generation having a low impact in that category meaning the reduced energy costs do not greatly reduce the impact score of marine aquatic ecotoxicity.

Table 6.1: Preliminary LCA data for 1 kg of calendered PVC both with and without PCL$_{540}$-[(succ)-C$_7$]$_3$.

(*Denotes a relative improvement of calendered PVC sheets containing PCL$_{540}$-[(succ)-C$_7$]$_3$ when compared to those without in their respective impact category)

		Without PCL$_{540}$-[(succ)-C$_7$]$_3$			**With PCL$_{540}$-[(succ)-C$_7$]$_3$**		
Film Thickness	mm	0.4	0.8	1.6	0.4	0.8	1.6
Impact category	**Unit**						
Abiotic depletion	kg Sb eq	9.04E-05	9.42E-05	1.04E-04	8.99E-05*	8.86E-05*	9.36E-05*
Abiotic depletion (fossil fuels)	MJ	6.11E+01	6.49E+01	7.51E+01	6.69E+01	6.56E+01	7.07E+01*
Global warming (GWP100a)	kg CO2 eq	3.88E+00	4.12E+00	4.78E+00	3.95E+00	3.87E+00*	4.20E+00*
Ozone layer depletion (ODP)	kg CFC-11 eq	1.41E-06	1.44E-06	1.52E-06	1.37E-06*	1.36E-06*	1.40E-06*
Human toxicity	kg 1,4-DB eq	1.27E+00	1.34E+00	1.53E+00	1.41E+00	1.39E+00	1.48E+00*
Fresh water aquatic ecotox.	kg 1,4-DB eq	1.59E+00	1.71E+00	2.01E+00	1.63E+00	1.59E+00*	1.75E+00*
Marine aquatic ecotoxicity	kg 1,4-DB eq	4.08E+02	4.74E+02	6.51E+02	6.34E+02	6.12E+02	7.00E+02
Terrestrial ecotoxicity	kg 1,4-DB eq	9.29E-02	9.30E-02	9.33E-02	8.76E-02*	8.76E-02*	8.77E-02*
Photochemical oxidation	kg C2H4 eq	6.77E-04	7.21E-04	8.38E-04	7.20E-04	7.05E-04*	7.64E-04*
Acidification	kg SO2 eq	6.21E-03	6.75E-03	8.19E-03	6.98E-03	6.80E-03	7.52E-03*
Eutrophication	kg PO4--- eq	1.01E-03	1.09E-03	1.31E-03	1.11E-03	1.08E-03*	1.19E-03*

7 Discussion

The development of additives to reduce gas check defects in calendered PVC is expected to have a significant impact on the calendering industry, as it could reduce plastics waste and energy usage, and increase consistency and the operating range for calendering. A better understanding of the mechanism for how these additives function in reducing gas checks would be helpful in developing them further and discovering other compounds with a similar reduction effect. It is also important to know how PCL_{540}-[(succ)-C_7]$_3$ affects the physical properties of commercial PVC blends, and if changes to the blend composition or processing parameters would be required to incorporate PCL_{540}-[(succ)-C_7]$_3$ into a commercial calendering operation.

This work explored the effect of PCL_{540}-[(succ)-C_7]$_3$ on standard PVC mixes to assess its viability as a processing aid for PVC calendering. Calendered PVC films containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ had a nearly complete elimination of gas check defects, with the average gas checks per square meter in 0.4 mm films being reduced from 3400 to 0 GC/m^2, and the average gas checks per square meter in 0.8 mm films being reduced from 4200 to 23 GC/m^2. This came without any effect on any of the measured torque mixing properties, and only small increases in the stress at break (increase of 4 MPa) and the glass transition temperature (increase of 6.2°C). There was a significant increase in complex viscosity, particularly at angular frequencies below 1.58 rad/s, which was largely driven by an increased storage modulus. Dynamic mechanical thermal analysis revealed that PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ had no significant difference in loss modulus from control blends, however at temperatures above 100°C the storage modulus of blends containing PCL_{540}-[(succ)-C_7]$_3$ were higher on average than control blends, resulting in a delayed entry into the melt flow region.

7.1 Possible Mechanisms for Additive Gas Check Reduction Effect

Gas check reduction arising from the use of PCL_{540}-[(succ)-C_7]$_3$ could be due to a variety of factors. The first hypothesis for why PCL_{540}-[(succ)-C_7]$_3$ is effective at reducing gas checks relates to rheological differences of PCL_{540}-[(succ)-C_7]$_3$ compared to other plasticizers. Polymer blends with a higher apparent viscosity produce fewer gas check defects when calendered, due to a high pressures being required to prevent air inclusions in the sheet [21, 48]. PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ are more viscous than those containing DINP, and the differences become more pronounced near processing temperatures (i.e., 165-175°C) and at low angular frequencies ($\omega < 1.58$ rad/s). PVC blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ entered the melt flow region at +175°C, compared to 145°C in control blends. At an angular frequency of 0.1 rad/s, PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ had a 180% higher complex viscosity than control blends. The higher viscosity of PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ could be a major factor in preventing the formation of gas bubbles.

In Mitsoulis's work [57] reporting on the modelling of calendering of viscoplastic fluids, they note that models of the calendering process produce regions of yielded/unyielded viscoplastic material, with increasing unyielded regions based on the Bingham number of the material. Unyielded regions of polymer may prevent air from entering, thereby inhibiting the formation of gas checks. Lower Bingham numbers also correlate with a higher vortex intensity, which may provide the conditions that allow for air to become entrained in the polymer melt, as described in Ancker's work [48]. Mitsoulis [57] also found that materials with a low power-law index produced less vorticity in the calender bank and higher maximum pressures. This suggests that materials with elevated yield stresses and shear-thinning effects would produce fewer gas checks, as they would have higher maximum pressures and decreased vorticity before the calender bank. PCL_{540}-[(succ)-

$C_7]_3$ may be increasing the yield stress or the shear-thinning behaviour of the PVC blends, thereby decreasing the prevalence of gas checks.

There may also be a chemical basis for the gas check reduction effect of PCL_{540}-[(succ)-$C_7]_3$, where the additive may be interacting with the air or PVC mix in some way to dispel the air bubbles from the PVC matrix. PCL_{540}-[(succ)-$C_7]_3$ produced according to our original methods [20], used stoichiometric amounts of the diacid reagent (succinic acid) and alcohol reagent (n-heptanol), however it was observed that when an industry partner changed the formulation to include an excess of n-heptanol in an attempt to drive the reaction further and completely cap the succinic end groups, the effect of gas check reduction effect was lessened significantly. PCL_{540}-[(succ)-$C_7]_3$ synthesized this way had lower acid values than PCL_{540}-[(succ)-$C_7]_3$ produced stoichiometrically, which may have played a role in why it was not as effective at reducing gas checks. PCL_{540}-[(succ)-$C_7]_3$ may also be acting as a lubricant in the PVC matrix, reducing the friction between PVC chains and allowing the air to escape instead of becoming entrained. In summary, at present it remains unclear whether the observed reduction effect is purely rheological, or if there is another reason why PCL_{540}-[(succ)-$C_7]_3$ is so effective.

7.2 Benefits/Applications of Gas Check Reduction Additives

The anticipated benefits arising from the use of PCL_{540}-[(succ)-$C_7]_3$ in a PVC calendering operation would be to reduce operational complexity, increase consistency in product, and decrease energy requirements and machine work. Presently, in order to calender sheets of a thickness greater than 0.5 mm while maintaining product consistency, manufacturers are required to calender several thinner sheets and press or laminate them together. This requires additional calender runs to create sheets thicker than 0.5mm which requires energy, operators, and machine hours. By expanding the operating range for PVC calendering, some of these additional runs could be avoided, reducing the required energy to produce these thicker sheets.

The preliminary results shown in Table 6.1 show promise for PCL_{540}-[(succ)-C_7]$_3$ being beneficial as a processing aid for calendering processes requiring multiple calender runs, however a more detailed and comprehensive LCA is required. The preliminary LCA was performed using stoichiometric estimates for the inventory analysis. While stoichiometric estimates are the most used substitute for plant data, it may be the case that these results underestimate the real impact of using PCL_{540}-[(succ)-C_7]$_3$ as a gas check reduction additive. Obtaining primary data from a manufacturer of poly(caprolactone) would allow for more accurate process calculations for the synthesis of PCL_{540}-[(succ)-C_7]$_3$. Better estimates for the waste generated due to excessive gas check defects in a calendering operation would also provide a better picture of the benefits of PCL_{540}-[(succ)-C_7]$_3$. While a complete LCA was out of the scope of this work, the skills and expertise obtained in formulating these preliminary findings will help to lay the groundwork for a full LCA to be completed in the future.

This preliminary LCA along with the results from mechanical, thermal, and calendering experiments lend support to the contention that PCL_{540}-[(succ)-C_7]$_3$ is a viable product for use as a gas check reduction additive in PVC calendering. It can effectively eliminate gas checks at mid to high film gauges, without considerably affecting the manufacturing process or end product specifications. It may be beneficial to explore alternate synthesis pathways for PCL_{540}-[(succ)-C_7]$_3$ to avoid the more impactful precursor chemicals, which could further increase the environmental benefits of PCL_{540}-[(succ)-C_7]$_3$.

7.3 Future Work

It is recommended that future work include quantifying the environmental impact of using PCL_{540}-$[(succ)\text{-}C_7]_3$ by performing a more in-depth life cycle assessment of the calendering process with and without the use of PCL_{540}-$[(succ)\text{-}C_7]_3$ as a gas check reduction additive. This would involve evaluating the environmental impact of the production of PCL_{540}-$[(succ)\text{-}C_7]_3$ using LCA software and discovering whether this cost would be offset by the reduced energy usage and waste from the utilization of the additive. An in-depth LCA would include an uncertainty analysis to ensure consistency, sensitivity, and completeness of the results. This could also include the evaluation of alternate synthesis pathways for PCL_{540}-$[(succ)\text{-}C_7]_3$ to determine the most environmentally conscious production method while balancing it with the associated economic costs.

The other avenue to consider for future work involves developing a better understanding of the additive gas check reduction mechanism. This may help with the development of other chemicals with a similar effect on reducing gas checks, or with improving the effect observed already with PCL_{540}-$[(succ)\text{-}C_7]_3$. As the calendering process is not completely understood and most research currently is based on empirical evidence and computer simulations, it is difficult to prove the gas check formation mechanism purely theoretically. However further testing would provide more clues on how PCL_{540}-$[(succ)\text{-}C_7]_3$ functions and why it is so effective at reducing gas check defects. Experiments which could be performed to further investigate the mechanism behind the gas check reduction effect include:

1. Rheological testing to find the yield stress, power law index, and consistency index for PVC blends containing PCL_{540}-$[(succ)\text{-}C_7]_3$ and other potential gas check reduction additives. This could be used to calculate the Bingham number for a PVC blend at specific

calender settings. If blends with higher yield stresses and lower power law indexes produce fewer gas checks then it would help to identify new compounds with similar effects.

2. Further increasing the nip distance or reducing the calender roll speed to find the limit for PCL_{540}-[(succ)-C_7]$_3$ to be effective at reducing gas check defects.
3. Synthesizing PCL_{540}-[(succ)-C_7]$_3$ with varying amounts of uncapped succinate end groups to measure the effect of acid value on reducing gas checks. PCL_{540}-[(succ)-C_7]$_3$ could be synthesized with a limiting amount and an excess of n-heptanol, to compare its effectiveness against PCL_{540}-[(succ)-C_7]$_3$ produced with n-heptanol in stoichiometric amounts. There may be an optimal ratio of capped to uncapped end succinate end groups.

8 Conclusion

The objectives of this work were to: (1) show the effect of PCL_{540}-[(succ)-C_7]$_3$ on the processing, mechanical, and thermal properties of PVC blends; (2) evaluate PCL_{540}-[(succ)-C_7]$_3$ effectiveness at reducing gas checks in calendered PVC sheets at thicker film gauges; and (3) perform a preliminary life cycle assessment to determine the comparative environmental impact of producing 1 kg of calendered PVC at varying thicknesses with and without PCL_{540}-[(succ)-C_7]$_3$.

The first objective was met through the batch mixing, mechanical, and thermal testing outlined in the manuscript section of this thesis. Batch mixing experiments were performed to identify if the addition of PCL_{540}-[(succ)-C_7]$_3$ to standard PVC blends would require any additional changes to the manufacturing process. The physical properties of PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ was examined, with testing performed pertaining to their mechanical and thermal properties. The batch mixing experiments showed that PCL_{540}-[(succ)-C_7]$_3$ had no significant effect on the maximum torque achieved, final average torque, or time to achieve complete mixing. This implies that PCL_{540}-[(succ)-C_7]$_3$ could be added without a significant change being made to pre-processing. Analysis of the thermal properties of PVC blends containing PCL_{540}-[(succ)-C_7]$_3$ showed a slight increase in glass transition temperature with PCL_{540}-[(succ)-C_7]$_3$ loading, indicating a sightly higher stiffness for the blends containing PCL_{540}-[(succ)-C_7]$_3$. This was reflected in the tensile testing done, as the maximum stress increased with PCL loading as well. The rheological experiments highlighted the largest differences with PCL_{540}-[(succ)-C_7]3 loading, with blends containing 10 phr of PCL_{540}-[(succ)-C_7]$_3$ having significantly higher complex viscosities than the control blends at low angular frequencies ($\omega < 1.58$rad/s) and elevated temperatures (+100°C)

The second objective of this work was met with the calendering experiments outlined in the manuscript of this thesis. PVC films containing PCL_{540}-[(succ)-C_7]$_3$ up to 0.8 mm were calendered to determine whether PCL_{540}-[(succ)-C_7]$_3$ was effective at reducing gas checks at thicker gauges. These experiments showed a complete elimination of gas checks in nearly all cases, at film gauges thicker than the currently accepted upper limit of 0.5 mm.

The third objective of this work was met and the preliminary LCA findings indicate that at thicker film gauges adding PCL_{540}-[(succ)-C_7]$_3$ to reduce the required number of calender runs could decrease the overall environmental impact over most of the calculated impact categories. A more comprehensive LCA study would need to be conducted to see if the negative impact of PCL_{540}-[(succ)-C_7]$_3$ and human toxicity and marine aquatic toxicity outweigh the benefits in other categories, and to validate whether this preliminary LCA accurately estimated the impact of PCL_{540}-[(succ)-C_7]$_3$ production.

Future work remains to be done to understand the mechanism by which PCL_{540}-[(succ)-C_7]$_3$ reduces gas checks in PVC calendered film. The theories outlined in this work attempt to describe the phenomena through either a rheological difference between the mixes containing PCL_{540}-[(succ)-C_7]$_3$ to the ones that do not, or to a chemical reaction between PCL_{540}-[(succ)-C_7]$_3$ and either the PVC matrix or the air bubbles themselves. It also may very well be a combination of these two effects working together, or other factors not considered here.

Overall, this work outlines the potential benefits of using PCL_{540}-[(succ)-C_7]$_3$ as a gas check reduction additive. It has been shown that this additive can be added to a standard PVC blend without greatly affecting the properties of the finished product or requiring additional preprocessing. The use of PCL_{540}-[(succ)-C_7]$_3$ in PVC calendering could expand the operational range for calendering operations, thereby decreasing operational complexity and energy costs.

PCL_{540}-[(succ)-C_7]$_3$ could also be added to existing processes to increase consistency and decrease waste from inferior product.

The plastic industry is a major contributor to climate change, and any incremental benefits in reducing waste, carbon emissions, and energy usage in a major plastics industry can have a huge overall benefit in reducing our environmental impact. Future research in the calendering process to better understand where modifications and improvements can be made is a step in the right direction to reducing the environmental impact for the PVC industry.

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