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

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Abstract

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

Key words: poly(vinyl chloride), additives, oligomers, mechanical properties, thermal properties

Introduction

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

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

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

Previous studies have shown that polymeric and oligomeric plasticizers tend to resist migration better than low molecular weight ester plasticizers [6, 27-29]. Poly(ε-caprolactone) (PCL)-based plasticizers have been found to exhibit good compatibility with PVC [30, 31], have increased migration resistance (i.e., less leaching) [32-34], and are also biodegradable [35, 36], non-toxic [37], and biocompatible [38]. Recently, a new family of oligomeric additives (see Fig. 1) consisting of a PCL core with ester linkers and alkyl chain caps was shown to be effective at removing surface defects during PVC calendering at concentrations as low as 8 parts per hundred resin (phr, 4.5 wt%) [39]. The previous work investigated the mechanism of surface defect removal, however the performance of the additives as potential plasticizers has not been evaluated.

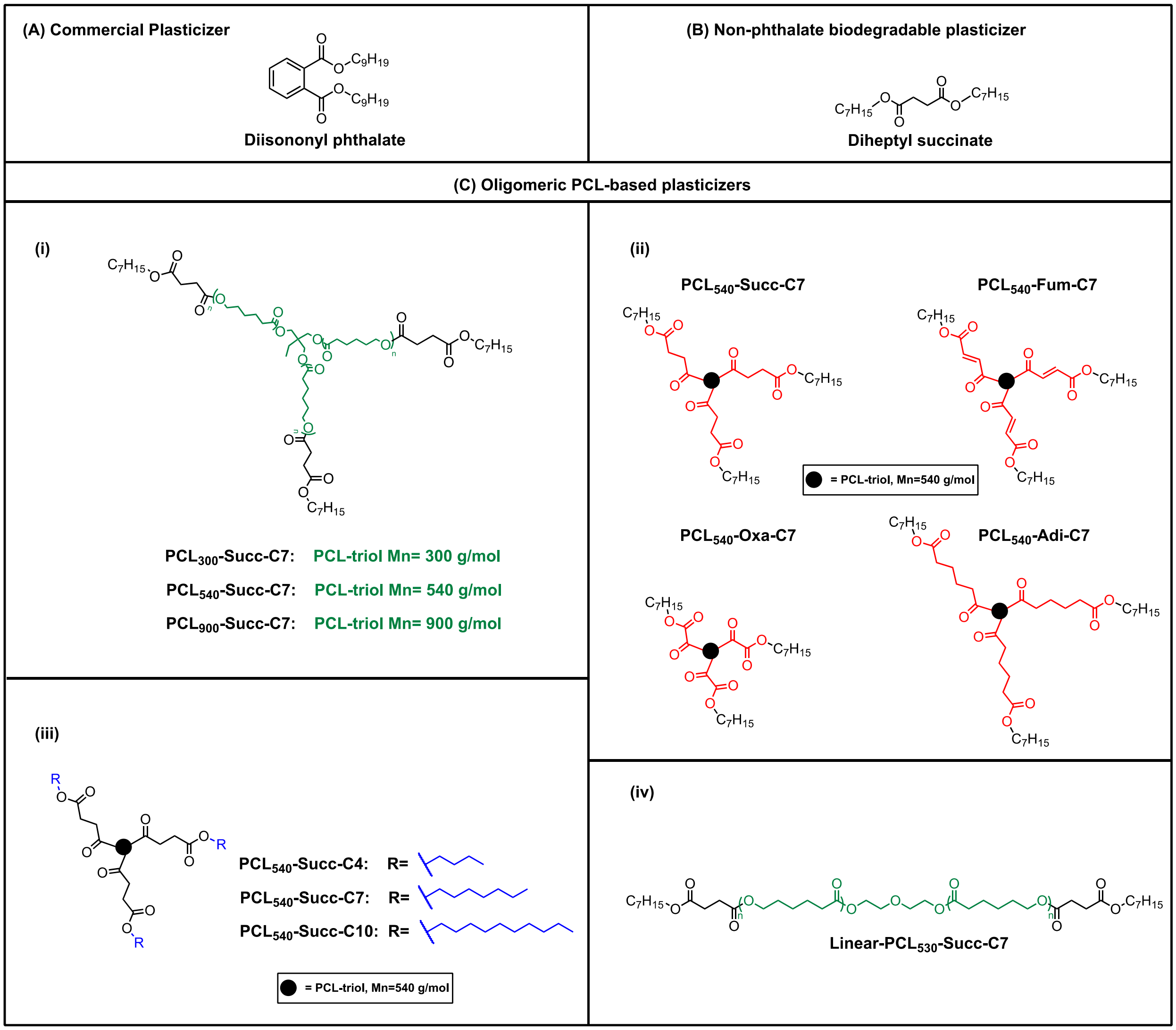

Figure 1. Molecular structures of additives evaluated as plasticizers: (A) di-isononyl phthalate (DINP) (B) diheptyl succinate (DHPS) (C) oligomeric PCL plasticizers with (i) different PCL core sizes, (ii) different ester groups, (iii) different alkyl caps, and (iv) linear structure.

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

Experimental

Materials

Poly(ε-caprolactone) (PCL) triol (M_n = 300, 540) (99%) was purchased from Scientific Polymer Products (NY, USA). PCL triol (M_n = 900) (99%), PCL diol (M_n = 530) (99%), fumaric acid (99%), oxalic acid (98%), adipic acid (99%), 1-butanol (99%), and 1-decanol (98%) were purchased from Sigma Aldrich (Missouri, USA). Renewably sourced succinic acid (99%) was purchased from Roquette (Lestrom, France). Renewably sourced Oleris *n*-heptanol (99%) was purchased from Arkema (Pennsylvania, USA). Sulfuric acid (96%), hexanes (99%), and stearic acid were purchased from Fisher Scientific (Montreal, Canada). Epoxidized soybean oil was purchased from Galata Chemicals (Louisiana, USA). Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), antimony oxide Hi-Tint (99.68%), silica (99%), stearic acid (99%), barium/zinc stabilizer (1.046 specific gravity at 20°C), and acrylic processing aid (99.8%) were supplied by Canadian General-Tower Limited (CGT Ltd., Ontario, Canada). Unplasticized PVC pellets (K58, product code: IH014/G045/AA) were provided by Solvay Benvic (Chevigny-Saint-Sauveur, France). All chemicals and reagents were used as received without further purification.

Plasticizer synthesis

Diheptyl succinate (DHPS) was synthesized in a one-step, solvent-free reaction, as previously reported [40]. Tributylsuccinate-terminated poly(caprolactone) (PCL_{540}-Succ-C4) was synthesized using the same method described previously [39]. The remainder of the star-shaped PCL analogs were synthesized using a two-step reaction method similar to a previously described method [39], but modified to remove any use of the solvent benzene, and subsequent solvent removal steps through rotary evaporation. In a first step, PCL triol (one stoichiometric equivalent) and the diacid reagent (three equiv.) were added to a three-necked round bottom flask fitted with a Dean-Stark trap and a condenser. The mixture was then stirred at room temperature for 5 min. A catalytic amount of sulfuric acid (0.15 equiv.) was added to the reaction mixture and the mixture was heated to 110 °C and stirred continuously. Once at temperature, nitrogen gas was bubbled through the mixture for 90 min to promote the removal of water. The mixture was then cooled to room temperature. The alcohol reagent (three equiv.) was then added directly to the flask and the mixture was re-heated to 110 °C, at which point nitrogen gas was again bubbled through the mixture for 90 min. The mixture was then cooled to room temperature. The resulting viscous oils were not further purified. Table 1 shows the reagents used to synthesize each plasticizer as well as the abbreviated plasticizer names that will be used hereinafter. The linear PCL analog was synthesized using the same procedure as the star-shaped PCLs except for the use of two stoichiometric equivalents of diacid and alcohol reagents, respectively, instead of the three equivalents used for the star-shaped molecules. The resulting linear-PCL_{530}-Succ-C7 was obtained as a viscous oil and was not further purified.

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

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

Blending of Plasticizers with PVC

Roll Milling and calendering

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

The milled film was then fed into a lab-scale calender (d=180 mm, T=160-170°C, P=45 psi hps, 50 rpm) for 1 min, set to achieve a film gauge of 0.4 mm +/- 0.05 mm. All plasticized PVC films were prepared to a final concentration of 55 phr (32.5 wt%) plasticizer. Each blend contained 100 phr PVC 70K suspension resin, 55 phr plasticizer, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid.

Extrusion and compression molding

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

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

Tensile testing

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

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

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

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

Differential scanning calorimetry (DSC)

The glass transition temperature of plasticized PVC blends was measured using a TA Instruments Q2000 differential scanning calorimeter. A previously-established temperature-modulated differential scanning calorimetry (MDSC) protocol was used [41]. Briefly, between 5-10 mg of sample was weighed and loaded into a Tzero Hermetic aluminum pan then into the DSC sample holder. The MDSC protocol comprised two cool-heat cycles. In the first cycle, the sample was cooled to -90°C and held isothermally for 5 min. The cooled sample was then exposed to a linear heating ramp of $2°C \cdot min^{-1}$ with a superimposed modulated heating (amplitude=1.27°C, period=60s) until it reached 100°C and was held isothermally for 5 min. This cycle was repeated a second time. DSC results were analyzed using TA Universal Analysis software (V4.5A). Glass transition temperature was determined from the reversible heat flow curve of the second heating cycle using the T_g tool.

Leaching

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

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

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

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

Statistics

Statistical analyses were performed using GraphPad Prism 8 software. The mechanical and leaching properties of the PCL plasticizers were compared controls (DINP and DHPS) using a one-way analysis of variance (ANOVA) followed by Dunnett's post-test. Differences between the PCL plasticizers were analyzed by one-way ANOVA followed by the Holm-Sidak multiple comparison test. The effect of plasticizer concentration on elongation at break and tensile strength was determined by two-way ANOVA. In all comparisons, $P<0.01$ was considered statistically significant.

Results & Discussion

Synthesis

We aimed to optimize the synthesis of the PCL-based additives by avoiding the use of organic solvent with the goal of developing a set of conditions that reduced reaction waste and were amenable to large-scale production. Fig. 2 shows the successful incorporation of the heptyl-succinate groups onto the PCL core of PCL_{540}-Succ-C7, as observed through ^1H NMR, using our modified one-pot method that was based on the solvent-free method previously described by Elsiwi et al. [40]. Thus, we showed that this was a viable method of synthesizing the plasticizers in this study.

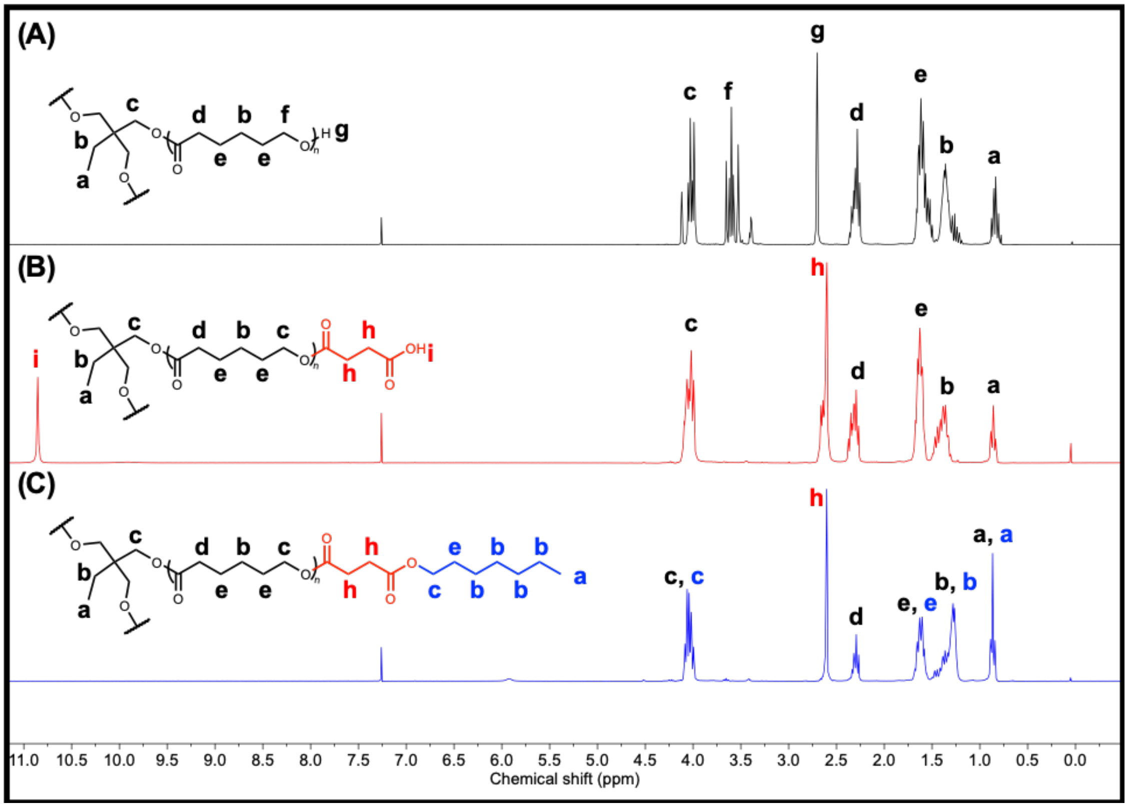

Figure 2. ^{1}H-NMR spectra showing the reaction progress of PCL$_{540}$-Succ-C7: (A) commercially available PCL-triol (M_n of 540 g/mol); (B) reaction intermediate after first step; (C) PCL$_{540}$-Succ-C7.

Mechanical properties

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

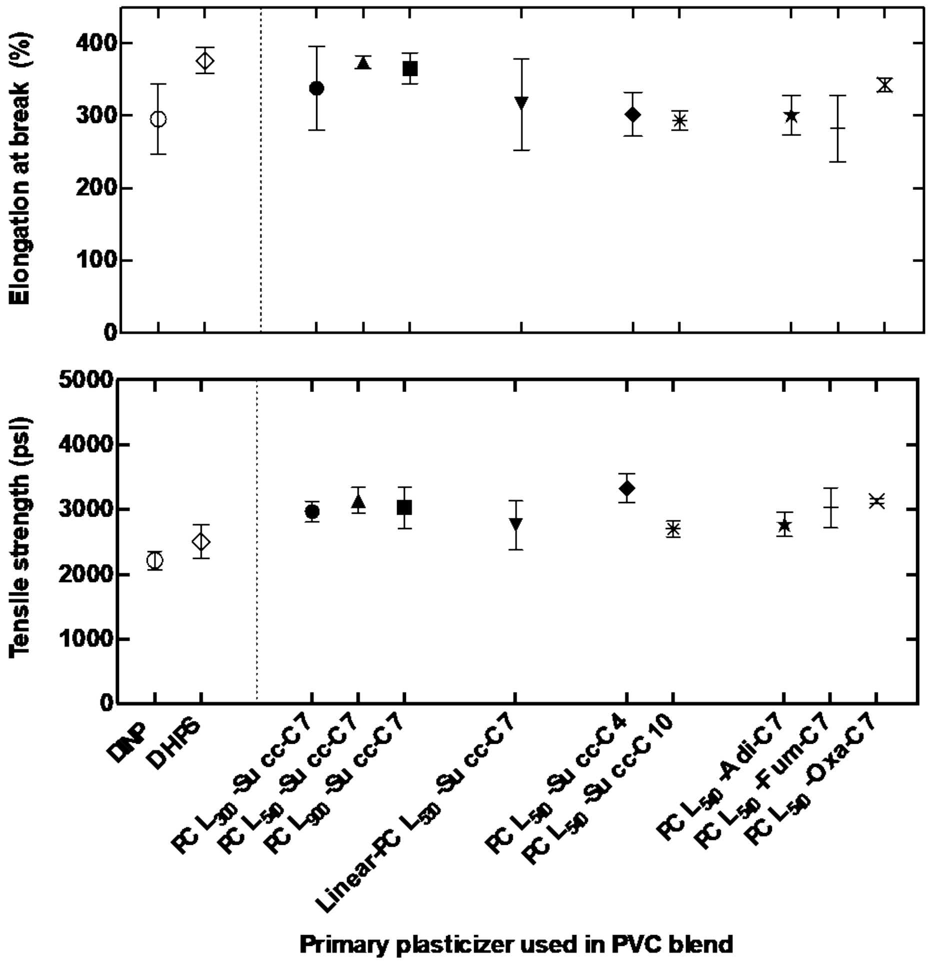

Figure 3. Elongation at break and tensile strength of calendered PVC films prepared with 55 phr of various PCL plasticizers, and compared to DINP and DHPS controls.

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

The effect of concentration of the PCL-based additives on mechanical properties was assessed on extruded PVC blends. A family of three additives (Fig. 1 C) of increasing molecular weight (PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, and PCL_{900}-Succ-C7) were blended with PVC at concentrations of 20, 40 and 60 phr. Fig. 4 shows a trend of increasing elongation at break and decreasing tensile strength with increasing plasticizer concentration for all three compounds. There was no effect of molecular weight over the range studied (P>0.01) however concentration had a significant effect (P<0.0001). These results are consistent with multiple previous reports of increasing elongation and decreasing tensile strength with increasing plasticizer concentration for various polymer-plasticizer systems [45-48]. This finding is important in establishing the feasibility of using these additives commercially given the need to be able to quickly fine-tune material properties by altering plasticizer concentration [49]. The elongation at break of the 40 phr blends (94%-113%) was shown to be comparable with previously published elongations for DEHP (96%)[43] and DHPS (93%)[40] blends of the same formulation with PVC (Fig. 4). Therefore, we have shown that the PCL-based plasticizers exhibit equivalent efficiency in controlling PVC mechanical properties by altering concentration when compared with DEHP and DHPS. We also demonstrated the successful blending of the additives with PVC using a second compounding technique (extrusion) under the same conditions used for phthalate plasticizers, with no observation of phase separation or exudation. Furthermore, we found no significant effect of molecular weight on elongation, with all three plasticizers performing comparably, seen in Fig. 4.

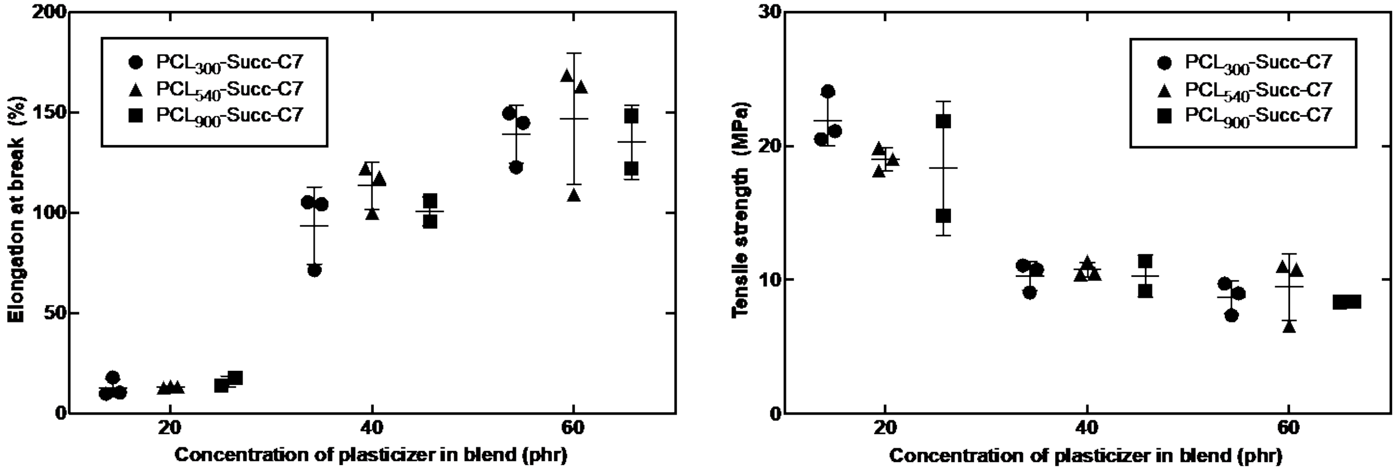

Figure 4. Effect of plasticizer concentration on elongation at break and tensile strength of extruded PVC blends.

Thermal properties

To investigate the effect of additive concentration on the thermal properties of PVC, the T_g of blends prepared with PCL_{300}-Succ-C7, PCL_{540}-Succ-C7, and PCL_{900}-Succ-C7 was evaluated at concentrations of 20, 40, 55 and 60 phr. A decrease in T_g with increasing additive concentration was seen for all the additives, as shown in Fig. 5. This trend holds true even when comparing samples that were prepared by different techniques and with different blend formulations. For example, the T_g of the 55 phr PCL_{540}-Succ-C7 blend prepared by calendering (-13°C) falls between the T_g of 10°C for the 40 phr and the T_g of -16°C for 60 phr blends prepared by extrusion and compression molding. The thermal properties of the plasticized blends agree with the mechanical findings (see Figs. 3 and 4), and support previous work that shows the T_g of plasticized PVC to be correlated with tensile properties such as elongation at break [41]. Similarly to the mechanical properties, the effect of concentration on T_g is significant while the effect of molecular weight, within our studied range, is not.

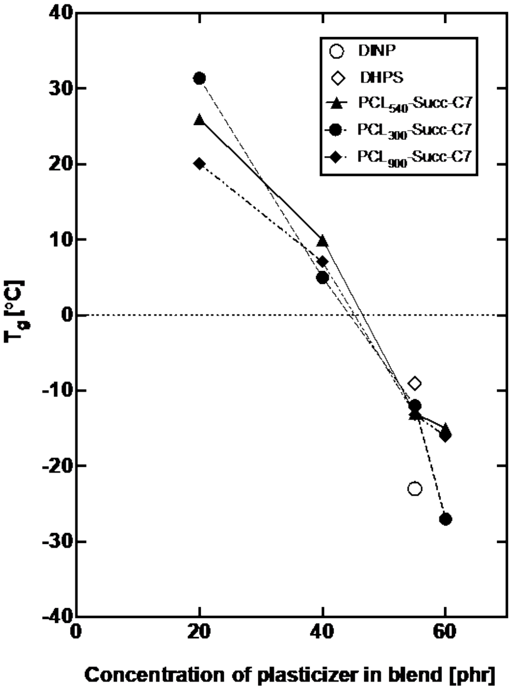

Figure 5. Effect of plasticizer concentration on glass transition temperature (T_g).

The T_g of the blends at 40 phr (5 to 10°C), 55 phr (-9 to -23°C) and 60 phr (-15 to -27°C) were all found to be below room temperature. Since polymer blends are expected to be flexible at temperatures above T_g and rigid below T_g, the T_g results coupled with the elongation results obtained at room temperature suggest that at concentrations between 40 and 60 phr the PCL-based additives are effective plasticizers. Additionally, the T_g of the blends prepared with PCL-based additives were found to be between the T_g for DINP and DHPS. Therefore, the thermal behavior of PVC blends prepared with the PCL-based additives further supports their efficacy as primary plasticizers.

Leaching

Having established the efficiency of the PCL-based additives in altering mechanical and thermal properties of PVC blends, we sought to investigate their resistance to migration. It was found that all the PCL-based plasticizers demonstrated significantly lower leaching into hexanes after 6 h compared with DINP and DHPS controls ($P<0.01$, Fig. 6). While DINP and DHPS blends demonstrated 41% and 28% plasticizer loss, respectively, the leaching of PCL-based plasticizers ranged from 2%-14%.

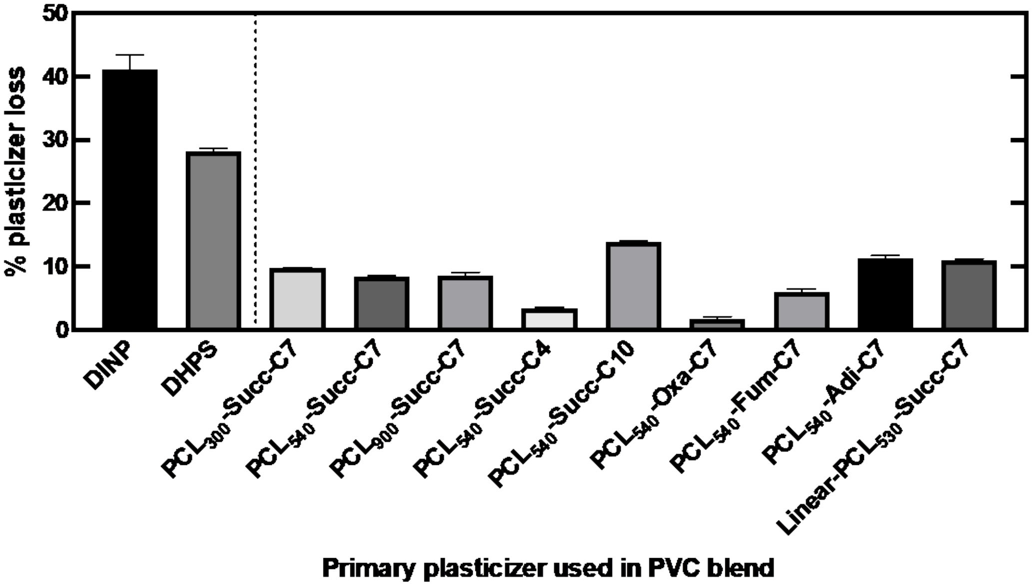

Figure 6. Leaching of plasticizers into hexanes after 6 hrs at 50°C. All blends were prepared with a plasticizer concentration of 55 phr.

Effect of molecular weight

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

Effect of alkyl chain length

A significant effect of alkyl chain length on migration was found when comparing PCL$_{540}$-Succ-C4, PCL$_{540}$-Succ-C7, and PCL$_{540}$-Succ-C10 (molecular structures shown in Fig. 1 C). We observed a trend of increasing leaching (3%, 8%, and 14%) with increasing alkyl chain length from four to ten carbons ($P < 0.01$, see Fig. 6). All three additives contained an identical PCL-triol core, with M_n of 540 g/mol, and a succinic acid linker, however they were synthesized using alcohols of increasing chain lengths (i.e., butanol, heptanol, decanol). The increase in leaching with alkyl chain length is likely the result of a decrease in the relative proportion of polar groups on the plasticizer, which are thought to provide strong points of interaction with the polymer through the formation of solvating dipoles on the PVC chain [2, 50]. Thus, having longer non-polar aliphatic functional groups on the plasticizer means that fewer points of attraction exist between polymer and plasticizer, resulting in increased migration. This agrees with previously reported findings for dibenzoate, succinate, maleate, and monoglyceride plasticizers that report lower migration of plasticizers with shorter alkyl chain groups [51, 52].

Effect of acid type

Similarly, a significant effect of the dicarboxylic acid on migration resistance was observed ($P < 0.01$, see Fig. 6), with increasing leaching with increasing length of aliphatic group within the acid. All four structures, PCL_{540}-Oxa-C7, PCL_{540}-Succ-C7, PCL_{540}-Fum-C7, and PCL_{540}-Adi-C7, are comprised of two ester functional groups, with differing carbon chain lengths between the esters. PCL_{540}-Oxa-C7, which is made from oxalic acid, the smallest dicarboxylic acid, is comprised of two adjoining esters with no aliphatic group between them and exhibited the lowest leaching of the four plasticizers at 2%. Conversely, PCL_{540}-Adi-C7, made from adipic acid, which contains two carboxylate groups separated by four methylene groups, has the longest aliphatic linker of the four plasticizers, and exhibited the highest leaching at 11%. There was no statistical difference in the amount of plasticizer leached between PCL_{540}-Succ-C7 and PCL_{540}-Fum-C7, which demonstrated 6-8% leaching, and both contain two linking carbons. Succinic acid, which contains a C-C single bond is simply the saturated analog of fumaric acid which contains a C=C double bond. While previous studies have reported differences between the performance of some fumarate and succinate plasticizers due to the stiffness imparted by the fumarate double bond [41, 43], this does not appear to play a significant role in their resistance to migration. The use of different acids modifies the ratio of polar to non-polar groups in each plasticizer, with an increase in the ratio of non-polar groups (i.e., longer aliphatic chains) corresponding to higher levels of leaching, which is consistent with the trend observed for the different alkyl capping groups.

Effect of branching

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

Conclusion

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

Acknowledgment

This research was funded using grants from the Natural Sciences and Engineering Research Council of Canada (NSERC; Collaborative Research and Development Grants, CRDPJ 543853-2019 and Discovery Grants Program, RGPIN 05948-2019, RGPIN 06161-2018, 2016-03792) and the James McGill Chair program of McGill University. Student support was provided through McGill Engineering Doctoral Awards (MEDA) of the Faculty of Engineering of McGill University. The authors acknowledge Canadian General-Tower Limited for their donation of materials and use of their laboratory equipment, specifically their lab-scale polymer mill, calender, and tensile tester.

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