Poly(ε-caprolactone)-based ‘Green’ Plasticizers for Poly(vinylchoride)

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Abstract

A series of proposed plasticizers for poly(vinyl chloride) (PVC), based on poly(ε-caprolactone) (PCL) with octanoate and benzoate-terminal groups, were synthesized with various microstructures and molecular weights (MW) and tested for biodegradability as well as for mechanical performance, and leaching resistance in blends with PVC. The plasticization efficiency of each was characterized by measuring the glass transition temperature (T_g) and tensile properties of PCL/PVC blends. The PCL-octanoate plasticizers demonstrated plasticization efficiency similar to di(ethylhexyl) phthalate (DEHP) with the same plasticizer loading. PCL-benzoate/PVC blends had much higher T_gs (~ 20 °C higher) compared to PCL-octanoate/PVC and DEHP/PVC blends. Yield stresses were about two times higher for PCL-benzoate/PVC blends compared to PCL-octanoate/PVC and DEHP/PVC blends, reflecting the stiffer nature of such blends. Biodegradation was rapid for all PCL-octanoates, with the exception of linear PCL-octanoates with arm molecular weights > 10^3 g·mol^{-1}. Biodegradation rates of PCLs by *Rhodococcus rhodocrous* were not affected by microstructure for the range of PCL topologies studied (linear versus three or four arms) but were slower for PCLs made from commercial PCL-diols that had a central ether linkage due to the initiator used to make these compounds. Leaching resistance was higher as PCL molecular weight increased and, for pairs of comparable sized species, significantly less PCL-benzoate leached out compared to the PCL-octanoate. For the range of PCL topologies studied, the number of arms did not significantly affect leaching resistance. In summary, both the end group and the molecular weight influenced the leaching resistance of the PCL. PCL-octanoates were comparable plasticizers to DEHP in terms of the mechanical properties examined, and were rapidly degraded by a common soil microorganism.

1. Introduction

Poly(vinyl chloride) (PVC), when blended with plasticizers, is one of the most versatile thermoplastics, being widely applied in construction, toys, medical devices and food packaging materials [1,2]. The most commonly used plasticizers in PVC formulations have been the phthalates, at production rates of about 5 million tonnes per year, which account for more than 75% of the current global plasticizer production [2,3]. The low molecular weight phthalates are not chemically bound to the PVC matrix and can migrate into the surrounding environment, particularly after disposal, resulting in environmental accumulation [4,5]. Recent studies have shown that phthalate plasticizers, such as di(ethylhexyl) phthalate (DEHP), are suspected of being endocrine disruptors and carcinogenic agents [5,6]. Phthalate plasticizers are incompletely degraded when exposed to microorganisms, leaving stable metabolites that are often more toxic than their parent compounds [7,8]. Phthalates and their metabolites have been found in soils, rivers, air, aquatic ecosystems and even in the human body [4,5]. The accumulation of phthalates and their metabolites has raised serious concerns. As a result, many countries have introduced strict regulations or bans regarding the use of phthalates in many specific applications such as children's toys [9].

The widespread use of DEHP-plasticized PVC has made it difficult to find an alternative plasticizer capable of substituting for DEHP universally. Researchers have been modifying PVC or developing alternative 'green' plasticizers, with varying degrees of success. For example, surface modification of PVC by grafting [10] or cross-linking [11] has been used to restrict the migration of plasticizers, but these modifications negate the improvement in flexibility of the PVC due to the plasticizer [11]. Several alternative, low molecular weight plasticizers, including citrates (such as Citroflex® B-6 (Morflex Inc.) and benzoates (such as Benzoflex® 2888, by Velsicol Chemical Corporation) have been developed, but the possible toxicity, especially the long-term effect on organisms, is still largely unknown [12,13].

The ideal 'green' plasticizer for PVC should display the following properties: (1) facile biodegradation; (2) non-toxicity of both the plasticizer and the possible metabolites; (3) miscibility with PVC; (4) plasticization efficiency comparable to DEHP; (5) good processability and high performance in PVC products; (6) high resistance to leaching from PVC and (7) relatively low cost.

Biodegradable poly(lactones), such as US Food and Drug Administration (FDA)-approved poly(glycolide) (PGA), poly(lactide) (PLA), and poly(ε-caprolactone) (PCL), have been widely studied in biomedical applications such as absorbable sutures, artificial organs, controlled drug delivery and tissue regeneration and they have been shown to be biocompatible and easily biodegraded [14-16]. PCL is deemed attractive as a 'green' plasticizer for PVC due to the following: (*1*) the well-known biodegradation behaviour and non-toxicity of PCL; (*2*) its low glass transition temperature (T_g) (around –60 °C) that provides low-temperature flexibility, which is enhanced by using oligo(caprolactones) [14-16]; (*3*) the miscibility of PCL with PVC, which facilitates processing and mechanical performance [17,18]; (*4*) the relatively simple synthesis and low cost of PCL make it possible for large-scale production. PCL is often used to lower the cost and improve the performance of other polymers by copolymerization [15] or by blending [19]. Furthermore, the use of PCL plasticizers, since they are longer chain molecules, is expected to reduce greatly the plasticizer migration from PVC and enhance the fatigue resistance of PVC articles [20,21].

The aim of this study is to develop a simple PCL-based 'green' plasticizer for PVC and evaluate the biodegradation, leaching and blend mechanical properties as a function of PCL microstructure and molecular weight.

2. Materials and methods

Chemicals and reagents

Three poly(caprolactone) triols (PCL-$(OH)_3$), number average molecular weight M_n = 300, 540 and 900 g mol^{-1}) were purchased from Scientific Polymer Products Inc. (Sp^2, Ontario, NY, USA). Poly(caprolactone diol) (PCL-(OH_2), M_n = 3000 g mol^{-1}) was also obtained from the same source. Octanoyl chloride (99%), benzoyl chloride (99%), pentaerythritol (98%) and activated carbon powder (Darco G-60, -100 mesh) were obtained from Sigma-Aldrich. ε-caprolactone monomer (99%) was acquired from Acros. Toluene (99.9%), pyridine (99%), n-hexane (99.9%), tetrahydrofuran (THF, 99.9%) and anhydrous magnesium sulfate (97%) were obtained from Fisher Scientific. Deuterated chloroform ($CDCl_3$, >99%, Cambridge Isotopes Laboratory) was used as a solvent for proton nuclear magnetic resonance (^1H NMR). A commercial poly(vinyl chloride) (PVC) without any plasticizer was obtained from Solvay Benvic France. The PVC (Catalogue # 1H014GH045AA) contained a calcium-zinc heat stabilizer, typically a complex mixture of calcium and zinc salts of fatty acids, but which was not specified. The resin also contained an unspecified coloring agent. Epoxidized soybean oil (ESO) was also used as a secondary additive and heat stabilizer (Drapex 6.8, Chemtura Corp.) while stearic acid was added as a lubricant (Fisher Scientific). Bacto Brain/Heart infusion and yeast extract were obtained from Difco Microbiology (Montreal, QC, Canada) and Fisher Scientific, respectively.

2.1. Synthesis of PCL plasticizers

Various plasticizers were made using commercially available PCL diols or triols or PCLs made from suitable bi-, tri- and tetra-functional alcohols, which were then reacted with acid chlorides (benzoyl chloride or octanoyl chloride) to add the end groups.

As an example, synthesis of the three-armed PCL with octanoate end groups ($(OPCL)_3$) is described here. Commercial PCL triol (PCL-OH$)_3$ and octanoyl chloride in pyridine and toluene were reacted at room temperature under nitrogen atmosphere. The molar ratio of PCL triol to octanoyl chloride was 1:3.6 (20% molar excess of hydroxyl to acid chloride). 20 g PCL triol (M_n = 540 g mol^{-1}, 37 mmol) and 22.8 mL octanoyl chloride (133 mmol) were dissolved in 200 mL toluene and 16.1 mL pyridine (160 mmol) in a 500-mL reactor. After 24 hours, activated carbon was added to the reaction mixture and stirred for 1 hour followed by the addition of magnesium sulfate. The mixture was filtered, the filtrate was collected and the solvent was removed by rotary evaporation. The final product was dried under vacuum at 60 ºC until constant weight and stored in a desiccator. The final yield was 28.3 g (83%).

The octanoate and benzoate-terminated PCL structures were characterized by ^1H NMR with a Varian Oxford-400 MHz spectrometer using $CDCl_3$ as a solvent. In each case, the samples were shimmed and scanned 16 times.

2.2. Biodegradation of $(OPCL)_3$

2.2.2. Culture of bacterium

Rhodococcus rhodochrous, American Type Culture Collection (ATCC) 13808, was used to study the biodegradation of plasticizers. The bacterium was cultured in a 500 mL Erlenmeyer flask with a foam cap containing 100 mL of sterilized BHI broth (Bacto Brain/Heart infusion medium, 37 g/L in distilled water) and incubated in a rotary shaker (Series 25, New Brunswick Scientific, Edison, NJ, USA) at 200 rpm and 30 ºC. Every 7 days, 1.0 mL of cell broth was transferred into a fresh flask.

2.2.2. Biodegradation test

For the biodegradation medium, each Erlenmeyer flask contained 100 mL of minimum mineral salt medium (MMSM, as shown in Table 2), 0.5 g/L of yeast extract and 2.0 g/L plasticizer. The plasticizer was the only carbon source. After sterilization in an autoclave (at 17 psig and 120 ºC for 30 min), 5 mL of cell broth (7-day culture) were added to each flask, which were then incubated in a rotary shaker at 200 rpm and 30 ºC.

Measurements were performed every few hours at the beginning and every few days thereafter.

Each measurement was done with the extract of the entire contents of one flask with chloroform. Prior to extraction, the biodegradation medium in the flask was acidified to a pH 2-3 with sulfuric acid. The organic fraction was recovered using a separatory funnel, passed through a 0.22 µm PTFE filter and stored in a glass vial at -15 °C. Uninoculated flasks containing plasticizer were used as controls. The composition of the minimum mineral salt medium in distilled water was: 4.0 $g \cdot L^{-1}$ NH_4NO_3, 4.0 $g \cdot L^{-1}$ KH_2PO_4, 6.0 $g \cdot L^{-1}$ $NaHPO_4$, 0.2 $g \cdot L^{-1}$ $MgSO_4 \cdot 7H_2O$, 0.01 $g \cdot L^{-1}$ $CaCl_2 \cdot 2H_2O$, 0.01 $g \cdot L^{-1}$ $FeSO_4 \cdot 7H_2O$ and 0.014 $g \cdot L^{-1}$ disodium ethylenediamine tetraacetic acid (EDTA).

2.3.3. Characterization by gel permeation chromatography

The biodegradation samples were analyzed with the aid of gel permeation chromatography (GPC, Waters Breeze HPLC). Tetrahydrofuran (THF) was used as the mobile phase with a flow rate of 0.3 $mL.min^{-1}$. The GPC was equipped with a guard column followed by three Waters Styragel® HR columns in series heated to 40 °C (HR1 with molecular weight measurement range of 10^2-5×10^3 $g.mol^{-1}$, HR2 with molecular weight measurement range of 5×10^2-2×10^4 $g.mol^{-1}$ and HR4 with molecular weight measurement range 5×10^3-6×10^5 $g.mol^{-1}$). The molecular weights were calculated after calibration with standards having a narrow molecular weight distribution of linear poly(styrene) (PS). The detector used was a differential refractive index (RI 2410) detector.

The procedure to use GPC was based on measuring the area of the degraded plasticizer, after its extraction from the biodegradation broth with chloroform, relative to a known amount of PS reference. Prior to GPC analysis, the sample solution, in chloroform, was transferred into a glass vial. The solvent was evaporated until constant weight. THF was added to this with the PS reference (obtained from SP^2, $M_n = 10^5$ $g\ mol^{-1}$, 2.0 g L^{-1}) as an internal standard. The ratio of the peak area of the degraded sample to the area of the PS reference peak provided the weight loss of the degraded sample. This ratio of the degraded sample was then calibrated relative to the peak ratio of a known amount of PS reference relative to a known amount of virgin plasticizer. Alternatively, gravimetric estimates were by using the relative weight (R_W, %), which was defined as the weight ratio of the biodegraded samples (W_1) to the virgin plasticizer sample (W_0). The procedure was identical to that shown above for the samples analyzed by GPC. After extraction with chloroform, the samples were dried until constant weight and then compared to that of a virgin plasticizer sample.

2.3. Plasticizer Mechanical Testing

2.3.1. Extrusion of plasticizer in PVC

A conical intermeshing twin-screw extruder (Thermo Electron Corporation, Haake Minilab) was used to produce the plasticized PVC blends [22]. The concentration of PVC additives, $C_{Additive}$, was characterized in parts per hundred parts resin (PHR). $C_{Additive}$ is the ratio of its weight, $W_{Additive}$, to that of the PVC resin, W_{PVC}. All of the PVC blend formulations consisted of 100 PHR PVC, 4 PHR epoxidized soybean oil (ESO, used as secondary plasticizer) and 0.8 PHR stearic acid (used as processing lubricant). A step-wise approach was used to prepare the plasticized PVC blends with steps of 20 PHR of plasticizer. For example, to make a 60 PHR plasticized PVC blend, the first step created 20 PHR plasticizer/PVC. This blend was then mixed with more plasticizer to prepare a PVC blend with 40 PHR of plasticizer with the PVC, which was further increased to 60 PHR by adding more plasticizer in the final step. To do the extrusion, the size of each sub-batch was 3 g and each batch consisted of 10 sub-batches. The threads from each sub-batch were chopped, mixed and re-passed through the extruder in 3 g portions. The extrusion temperature was 140 °C for 20 PHR, 120 °C for 40 PHR and 110 °C for 60 PHR PVC, respectively.

2.3.2. Glass transition temperature (T_g)

A differential scanning calorimeter (DSC, TA instruments, Q2000) was used to measure the glass transition temperature T_g of the plasticized PVC blends. A heat-cool-heat cycle method was applied where the second heating cycle was used for the T_g measurement. The heating/cooling rate used was 15 °C min^{-1} and the temperature range was from –90 to 100 °C.

2.3.3. Tensile testing

A hot press (Carver, 25 ton capacity) was used to prepare the tensile bars according to ASTM standard method D638. The extruded PVC blends were pre-heated and pressed for 20 min at 10 tons of pressure and 160 °C. A Shimadzu EZtest tester equipped with a 500 N load cell was used to evaluate the tensile properties of the plasticized PVC bars. The pressed bars were conditioned for a minimum of 48 h in a desiccant chamber at room temperature prior to testing. The tensile test bars were then loaded into the tensile tester and subjected to a strain rate of 5 mm min^{-1} until the specimen fractured. The force imposed on the specimen and the corresponding strain were recorded with a computer. The strain, ε, was reported in units of percent elongation (%*El*) which was calculated with Equation 1, where L_o is the initial grip separation and L is the grip separation at any time. The tensile stress, σ, imposed on the sample was calculated by Equation 2, where F is the tensile force and T_o and W_o are the initial thickness and width of the center region of the tensile bar. This procedure was based on the ASTM D638 [Standard test method for tensile properties of plastics].

Equation 1:

$$\varepsilon(\%El) = \frac{L - L_0}{L_0} \times 100$$

Equation 2:

$$\sigma(MPa) = \frac{F(N)}{T_0(mm) \times W_0(mm)}$$

2.4. Leaching tests

The hot press was used to prepare plasticizer/PVC disks for leaching tests. Each disk was 2.5 cm in diameter and 1.2 mm thick. The leaching experiments were performed based on the ASTM Designation D1239-98 guidelines (Standard Test Method for Resistance of Plastic Films to Extraction by Chemicals). The plasticized PVC disks were dried under vacuum until constant weight prior to the experiment. The leaching test was done in a 500-mL flask filled with 200 mL of n-hexane and shaken at 125 rpm at room temperature. After 1 week, the disks were washed with n-hexane three times and then dried under vacuum until constant weight. For each plasticizer, the leaching test was repeated at least 3 times. DEHP and PVC experiments were also done for comparison. The relative weight loss of additives was reported as a measure of leaching and defined as the weight ratio of the leached additives to the amount added.

3. Results

3.1. Poly(caprolactone) Plasticizer Synthesis

The characteristics of the various PCLs are summarized in Table 1. Figure 1 shows a typical ^{1}H NMR spectrum of one of the PCLs synthesized. NMR analysis detected no hydroxyl groups in the octanoate plasticizers, showing that the hydroxyl-terminated PCL was fully converted to the ester. Figure 2 compares the ^{1}H NMR spectra of linear PCL-$(OH)_2$ derived from commercial sources and one that was synthesized. Figure 3 shows the ^{1}H spectra of two benzoate terminated PCLs, one of which is a linear PCL-dibenzoate made from a commercial PCL-$(OH)_2$ and the second is a three armed PCL-tribenzoate made from commercial PCL-triol.

3.2. Mechanical Properties of Poly(caprolactone) (PCL)/Poly(vinylchloride) (PVC) Blends

The plasticizing performance of a plasticizer was evaluated by measuring the glass transition temperature (T_g) and the stress-strain behavior of the plasticized PVC blends. The T_g results of all of the PCL/PVC blends and the DEHP/PVC blends are shown in Figure 4. At 20 PHR, all the flexible PVC blends had similar T_gs, all about 20 ºC. With the increase of plasticizer loading to 40 PHR and 60 PHR, the octanoate plasticizers such as $(OPCL)_2$ and $(OPCL)_3$ resulted in blends with PVC with similar T_gs to the average of the DEHP/PVC blends at the same concentration. As expected, the T_g of the PCL-octanoate/PVC blends increased with increasing total molecular weight of the PCL. Although the effect of the number of arms was not significant, the influence of the end-group was important. When the PCL chains were terminated with benzoate groups instead of octanoate groups, the T_g values were increased.

The strain at break and stress at break results from tensile tests of plasticizer/PVC blends are shown in Figures 5 and 6, respectively, for a plasticizer loading of 60 PHR. There was no significant difference between the octanoate and benzoate terminated PCLs for the strain at break (Figure 5). There was also no significant effect of molecular weight or of number of PCL arms on the strain at break.

The yield stress of the various PVC/plasticizer blends versus molecular weight of plasticizer, for plasticizer loadings of 60 PHR, is shown in Figure 6. The PCL-based plasticizer blends generally have similar yield stresses compared to the PVC/DEHP blend. In this case, for the octanoate-terminated PCLs blended with PVC, the number of arms seems to affect the yield stress, with an increasing number of arms leading to higher yield stresses.

3.3. Biodegradation

Since the PCL was polymeric, changes in molecular weight and molecular weight distribution were followed with GPC. The sample contained a known concentration of reference polymer so the relative amount of plasticizer remaining was determined by comparison of peak areas of plasticizer to reference polymer. Figure 7 shows typical GPC chromatograms where Figure 7a) shows the peak corresponding to the DEHP plasticizer from samples taken at various times while Figure 7b) shows similar data for a linear benzoate-terminated PCL. It is clear that the PCL peak area is decreasing with time and its molecular weight distribution is changing. In contrast, DEHP plasticizer samples taken at various times indicated little change in peak area or molecular weight distribution (Figure 7a). Figure 8 compares the fraction of degraded PCL determined by the GPC method (Figure 8a) and by the gravimetric method (Figure 8b) for linear octanoate terminated PCLs of various molecular weights. The methods gave results that are in very good agreement. This was generally true as can be seen in Table 2, which contains data for all of the compounds tested for biodegradation. Similar results were found for benzoate terminated PCLs although the degradation was slightly slower compared to the octanoate terminated PCLs of comparable molecular weight. Figure 9 compares the fraction of degraded PCL determined by the GPC method (Figure 9a) and by the gravimetric method (Figure 9b) for benzoate terminated PCLs.

3.4. Leaching

Figure 10 shows the fraction of the original blend that is lost by leaching as a function of plasticizer molecular weight in formulations with 60 PHR plasticizer. The control samples of PVC without plasticizer but containing all of the other additives exhibited a negligible relative additive loss of 0.7% in hexane. Thus, the weight loss data in Figure 10 is almost exclusively due to the loss of PCL. The weight loss from the samples into hexane decreased as the molecular weight of the plasticizer increased. There is also a subtler trend due to the end groups attached to the PCL plasticizer. Plasticizers having octanoate end groups were lost more easily compared to plasticizers with benzoate end groups.

4. Discussion

Our goal was to develop a ‘green’ plasticizer with high plasticizing efficiency for PVC blends and resistance to leaching from these blends. Our criteria for a ‘green’ plasticizer required that it, or its possible metabolites, should be environmentally friendly, biodegradable, and non-toxic. This paper considered the use of poly(ε-caprolactone) (PCL)-based plasticizers because they have been approved by the FDA for use in materials that would be in contact with humans.

The chain length of the PCL arms was expected to be an important parameter, influencing both the mechanical properties (*eg*. the T_g of the blend) and the tendency to leach from the blend. The linear PCLs that were purchased had been derived from commercially available PCL-diols and the ^{1}H NMR showed that the initiator used to make these compounds must have been diethylene glycol. This is important as previous biodegradation work involving dibenzoate plasticizers (eg. diethylene glycol dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB)) with ether linkages showed that such a functionality made the plasticizer much more resistant to biodegradation [23, 24].

In this previous work, replacing the ether linkage by using aliphatic diols such as hexanediol or pentanediol as the central unit allowed β-oxidation pathways to be operative and these resulted in rapid biodegradation without the accumulation of toxic metabolites. This prompted us to use pentanediol as the initiator for producing a different series of linear PCL-diols.

All of the PCL plasticizers tested were compared to the properties of DEHP/PVC blends. Comparing results for T_g and the tensile properties demonstrated that overall, our PCLs were as good as DEHP in performance as plasticizers for PVC at similar plasticizer loadings. There are, however, trends in the data showing the effect of structure on the properties.

The measurements of T_g were lower for the various octanoate-terminated PCL/PVC blends using PCL molecular weights up to 10^3 g·mol^{-1} than those for the DEHP/PVC blends. It was expected that the number of arms on the PCL would be a significant parameter because an increase in the number of chain ends would result in more free volume and the T_g would decrease. However, the number of branches/end groups did not have a significant influence on the blend T_g. The PCLs with aliphatic octanoate end groups when blended into PVC resulted in materials with lower T_gs compared to PVC blended with PCLs having benzoate end groups. At plasticizer loadings of 40 and 60 PHR with similar plasticizer chain lengths, T_gs were nearly 20 °C lower for PCL plasticizers with octanoate end groups compared to benzoate end groups. This difference can be attributed to the fact that the aliphatic octanoate end group would be expected to have greater flexibility compared to the stiffer aromatic benzoate end group. Overall, based on T_g measurements, PCL-octanoates with M_n up to 10^3 g·mol^{-1}, whether linear, three or four-armed, have comparable plasticizing properties to those of DEHP in PVC blends.

The strain at break data shown in Figure 5 indicates that all of the PCL/PVC blends were comparable to DEHP/PVC blends. Neither the number of arms nor the molecular weight has a significant effect on the strain at break. It is conceivable that the nature of the PCL end group (benzoate versus octanoate) may have a slight effect on the strain at break, with the PCL-benzoates having slightly higher strain at break.

In Figure 6, the PCL-benzoate/PVC blends had slightly higher yield stresses compared to the DEHP/PVC and PCL-octanoate/PVC blends. This suggests that the aromatic end groups contributed to making the PCL-benzoate/PVC blends slightly stiffer, which is in agreement with the obvious trends in the blend T_g data. Figure 6 also suggests that increasing the number of PCL arms from a linear chain to three or four armed PCLs, resulted in an increase in the yield stress for the series of PCL-octanoate/PVC blends.

The biodegradation studies were done with the various octanoate PCLs and with three different benzoate PCLs. There was good agreement between the two methods of monitoring the rate of disappearance of the plasticizers. Most of our new plasticizers degraded very quickly and over 70% had disappeared within a few days, which is an important property for a 'green' plasticizer. The one exception was O_2-1069, which barely degraded. This compound was not the largest but it was the longest with only two arms. Possibly this structure was significantly less soluble in water than the other compounds.

Within the two series of compounds there were trends in biodegradability. This was particularly noticeable for the two arm linear compounds for which the smallest compound disappeared the fastest. This same trend was less obvious for the three arm compounds but the two smaller members degraded faster than the longest in the series. The introduction of the ether bond resulted in a compound that could be biodegraded but it disappeared more slowly than most of the other compounds. This is consistent with earlier reports that the ether bond could make similar compounds in a series more difficult to biodegrade. [23, 24]

The linear benzoate PCLs degraded more slowly compared to the linear octanoate PCL of comparable molecular weight. As noted previously, the use of diethylene glycol as the initiator for the commercial PCL-diols could be a problem for biodegradation as the central ether linkage from the diethylene glycol blocked β-oxidation pathways, as has been shown for diethyleneglycol dibenzoate and dipropyleneglycol dibenzoate. [23,24] If the initiator instead was an aliphatic diol, like pentanediol, biodegradation is much faster. This effect of structure was noticeable in our biodegradation studies of the linear benzoate plasticizers as the PCL-benzoate made with pentanediol initiator resulted in faster biodegradation compared to the PCL-dibenzoate made with diethylene glycol initiator (Figure 9). The degradation of the three-armed PCL-tribenzoate was the slowest among the benzoates studied. This could be due to the structure of the PCL where the three bulky aromatic end groups may make it more difficult for the enzymes to get access to the ester groups to degrade them.

Most of the compounds degraded much faster than DEHP. All of the smallest compounds, that did not contain an ether bond, had completely disappeared within a week. Furthermore, no stable metabolites were observed during the biodegradation of any of these PCLs. The importance of relative size is quite noticeable in the estimated times of complete biodegradation. At least trace amounts of the largest compounds were still present even after a week.

Many reports have focused on using PCLs as plasticizers for PVC in order to impart better resistance towards leaching. Different strategies have been employed to do this, such as using hyper-branched PCLs or multi-block PCL copolymers. [25, 26] These authors stressed that such compounds were effective plasticizers for PVC and also were highly resistant to leaching. Instead of using such PCLs, we focused on using linear, three or four-armed PCLs that were terminated with groups such as the aliphatic octanoates or aromatic benzoates. The degree of leaching of all of these compounds was no worse than the leaching of DEHP (Figure 10). The effect of molecular weight was also clear. Increasing molecular weight of the PCL resulted in lower weight loss of PCL from the blend. There did not seem to be a significant effect on weight loss due to the number of branches. The key observation from Figure 10 is the effect of the end group on the weight loss. The PCL-benzoates were much more resistant towards leaching into hexane than were PCL-octanoates. Diffusion of the PCL-benzoates from the polymer matrix may be slower due to the bulkier aromatic groups at the chain ends. The octanoates may also be more soluble in the hexane than are the more polar aromatic groups of the PCL-benzoates.

Conclusions

Most of the PCLs tested were readily biodegraded and none of them resulted in the accumulation of metabolites. In general, these properties were much better than those of the control plasticizer DEHP.

The benzoate compounds were the more resistant to leaching and the larger compounds showed the least leaching. However, all of them were at least as stable in the formulations as DEHP.

Plasticizing properties of PCL/PVC blends were comparable to DEHP/PVC blends. However, blends with PCLs terminated by benzoate groups tended to be stiffer (higher blend T_gs and higher yield strengths) compared to blends with PCLs terminated with octanoate groups. The effect of PCL microstructure (linear versus three-arm or four-arm chains) was not significant in the range of molecular weights studied.

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Figure Captions

Figure 1: ^{1}H NMR spectra of a) the commercial poly(caprolactone) triol (PCL-$(OH)_3$, M_n = 540 g mol^{-1}) and b) the three-armed PCL with octanoate end groups $(OPCL)_3$ derived by esterification of PCL-$(OH)_3$ with octanoyl chloride.

Figure 2: Comparison of ^{1}H NMR spectra of linear poly(caprolactone) diols obtained from a) commercial sources and b) synthesized by initiating caprolactone ring-opening polymerization with 1,5 pentane diol and tin octanoate catalyst.

Figure 3: ^{1}H NMR spectra of poly(caprolactone) (PCL) terminated with benzoate groups: a) linear benzoate terminated PCL synthesized from a commercial PCL-diol and b) three-armed PCL-tribenzoate synthesized from a commercially available PCL-triol.

Figure 4: Glass transition temperature (T_g) of poly(vinylchloride) (PVC)/plasticizer blends versus molecular weight of plasticizer for a) 40 parts per hundred (PHR) plasticizer in PVC and b) 60 PHR plasticizer in PVC. The symbols are defined in Table 1 for the various plasticizers. Note that "O" refers to octanoate terminated poly(caprolactone) plasticizers while "B" refers to benzoate terminated poly(caprolactone) plasticizers.

Figure 5: Strain at break versus molecular weight of plasticizer (M_n) in poly(vinylchoride) (PVC)/plasticizer blends at 60 parts per hundred (PHR) plasticizer. Note that "O" refers to the series of octanoate terminated poly(caprolactone) while "B" refers to the series of benzoate terminated poly(caprolactone).

Figure 6: Yield stress of various poly(vinylchoride) (PVC)/plasticizer blends versus molecular weight of plasticizer (M_n) with a plasticizer loading of 60 parts per hundred (PHR) plasticizer. Note that "O" refers to the series of octanoate terminated poly(caprolactone) while "B" refers to the series of benzoate terminated poly(caprolactone).

Figure 7: Typical gel permeation chromatograms (GPC) of a) DEHP and b) a typical poly(caprolactone) (PCL) plasticizer in samples taken after various times of biodegradation. The PCL shown is a linear benzoate terminated poly(caprolactone) (plasticizer ID B_2-769) compared to the poly(styrene) reference. Note the change in molecular weight distribution and peak area of B_2-769 as it is being degraded.

Figure 8: Relative weight of various octanoate-terminated linear poly(caprolactone)s derived from gel permeation chromatography (GPC) (a) and from gravimetry (b) after biodegradation by *R. rhodocrous* for 2 weeks.

Figure 9: Relative weights of various benzoate-terminated poly(caprolactone)s derived from gel permeation chromatography (GPC) (a) and from gravimetry (b) after biodegradation by *R. rhodocrous* for 2 weeks.

Figure 10: Leaching of the plasticizer according to ASTM test procedure D1239-98 in terms of % weight loss versus molecular weight (M_n) of the plasticizer in the PVC blend at a loading of 60 PHR plasticizer. The leaching experiments were all done at ambient conditions for 1 week using n-hexane.