Mechanical Testing and Biodegradation of an Alternative Dibenzoate Plasticizer

by

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ABSTRACT

Plasticizers are ubiquitous environmental contaminants. Biodegradation of some of these chemicals, such as di(2-ethylhexyl) phthalate (DEHP or DOP), has been shown to lead to the accumulation of toxic metabolic breakdown products. As a result there is a desire to produce new, fully biodegradable, “green” plasticizers. With this goal in mind, a series of tests were developed to be used to measure the plasticizing efficiency of potential green plasticizers. The base resin selected for the study was poly(vinyl chloride (PVC). Plasticizers were mixed with the polymer using a small-scale, twin-screw extruder. The glass transition temperature (T_g) of the plasticized polymer was measured by temperature-modulated differential scanning calorimetry (TMDSC). Tensile tests were carried out on injection-molded samples of the material from which the tensile strength and the strain at break of the material were measured. The $T_{g,}$, the tensile strength and the strain at break were measured for PVC plasticized with the commercial plasticizers DEHP, diethylene glycol dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB) at plasticizer concentrations of 20, 40, 60 and 80 parts per 100 parts resin (PHR).

1,5 pentanediol dibenzoate (PDDB) was synthesized and evaluated as a plasticizer by comparing results for this compound with those for the commercial plasticizers using the developed tests. The depression in Tg and tensile properties were comparable at a fixed composition for blends with PDDB relative to blends with DEHP, DEGDB, and DPGDB. PDDB was subjected to biodegradation unsing co-metabolism by the common soil bacterium *Rhodococcus rhodocrous* (ATCC 13808). After 16 days of growth, nearly all the PDDB was degraded and only small amounts of transient, unidentified, metabolites were observed in the growth medium during the experiment.

1 INTRODUCTION

Plasticizers are additives used to impart desirable properties in polymeric materials. They facilitate processing and improve the performance of plastics. Measurable properties of a polymer such melt viscosity, second order (or glass) transition temperature (T_g) and mechanical properties such as tensile strength typically decrease with increasing plasticizer concentration. [1]

In 2004 the global production of plasticizers was 6 billion tonnes, worth approximately CAD $11billion [2]. Of the plasticizers produced worldwide in the early part of this decade, 92% were esters of phthalic acid [3]. The most commonly plasticized polymer is poly(vinyl chloride) or PVC due to the high quantities of plasticizer needed to make the PVC workable for many applications. Formulations with PVC account for roughly 80% of all plasticizers consumed [3]. Other commonly plasticized polymers are poly(vinyl acetate) or PVA, nylon, acrylics and polyamides. These mixtures are used in a wide range of products such as insulation for electrical wire, children's toys, plastic food wrap and medical items. [3]

Plasticizers are not typically chemically bonded to the polymer matrix and, as a result, they can be released from the material while being used or after disposal.[1] This has raised considerable concern in recent years as studies have suggested that common plasticizers may not be entirely benign and completely biodegradable, as originally thought. [3, 4]

As a result, there is now an interest in producing biodegradable and non-toxic plasticizers capable of achieving performance similar to traditional plasticizers. There are now a few plasticizers commercially available, such as some citrate and dibenzoate plasticizers, that are reputed to have these properties. Some intended applications of these include children's toys, medical devices and food packaging. [3]

As mentioned above, PVC is the most commonly plasticized polymer. It is therefore often used as a system in which to evaluate the performance of plasticizers. The mechanical properties of PVC containing various plasticizers in PVC were measured in the 1960's by producers of these chemicals and were compiled by Matthews in his PVC handbook 1994 [4]. The elongation at break, ultimate tensile strength (also known as tensile strength at break), modulus at 100% elongation and British standard softness are shown with varying concentrations of plasticizers such as phthalates, sebacates, adipates and others. The glass transition temperatures for PVC with varying concentrations of DEHP were published in the journal *American Laboratory* in 1988 [5] and were reprinted in Rodriguez's *Principles of Polymer Systems* 5th edition. [6]

The tensile strength of a polymer is generally expected to decrease with increasing plasticizer concentration while the strain at break increases with increasing plasticizer content. Few studies provide curves of these parameters at plasticizer concentrations over 100 parts by weight per 100 parts resin (PHR), as the applications of such materials are limited. Curves of these properties for PVC plasticized with additions of DEHP from zero to nearly 100 wt% are provided in Sears' authoritative text, *The Technology of Plasticizers.* [1] It is shown that while the tensile strength continues to decrease over the entire range of concentrations, the strain at break actually goes through a maximum, in this case at around 150 PHR DEHP. The strain at break decreases at higher concentrations until it ultimately reaches zero, at which point the polymer is essentially in solution in the plasticizer and there is no tensile strength at all.

Tensile testing of PVC with traditional plasticizers, such as DEHP, has been undertaken in recent studies to compare their behavior with that of novel plasticizers. Studies examining the behavior of poly(butylene adipate) [7] and thermoplastic polyurethane [8] as internal plasticizers in PVC used DEHP and DIDP as a bench mark for performance. Another group studied the mechanical behavior of various plasticizers for the purpose of PVC ion-selective membranes [9, 10]. Mechanical tests were performed on membranes plasticized with sebacates, adipates and azelates. These were compared to three citrate plasticizers (see next section).

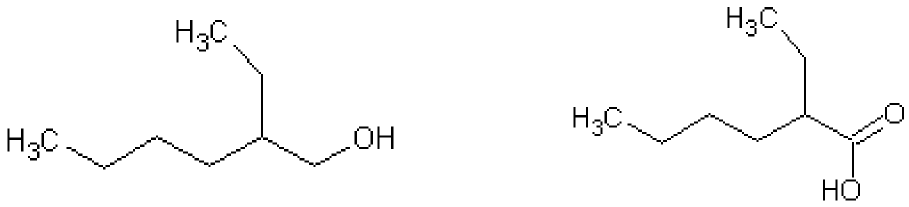
As mentioned above, because plasticizers are not bound to the polymer matrix into which they were added, these additives can be released over time from the material, and into the surroundings. Major sources of these chemicals include plastic manufacturing plants and landfills. Other common sources are consumer goods such as construction materials [11]. Plasticizers and their metabolites have been found in environmental samples of soil [12-15] and surface water [16-19] and their presence is considered ubiquitous in the environment [20].

Plasticizers have also been found in the tissue of mammals [20-22]. They have been shown to have bio-concentrated and bio-accumulated in some aquatic species of fish and amphibians, where they were found to be carcinogenic and to interfere with reproduction [20].

Phthalates in particular have been scrutinized because of their suspected endocrine-disruption activity in laboratory rats [23]. Further, in 1980 the International Agency for Research on Cancer classified DEHP as "a possible carcinogenic to humans". [3] One study found phthalate esters in the serum of young Puerto Rican girls with premature breast development and suggested that these compounds may have esterogenic activity. [21]

Humans may be exposed to elevated levels of plasticizers by ingesting food which had been wrapped in plasticized food film [24] and also during blood transfusions [25]. Plasticizers have been found to leach from plastic bags used for storing blood and also from medical tubing [3].

Biodegradation of DEHP, DEHA and other common plasticizers has been studied under co-metabolism by a variety of microorganisms (bacteria, yeast and fungi). [26-28] In these studies the plasticizers were found to degrade leaving behind metabolic products (metabolites) which were more toxic than the parent compound and accumulated in the growth medium. For instance 2-ethylhexanoic and 2-ethylhexanol (see Figure 1-1), which were found to accumulate during the biodegradation of DEHP and DEHA, exhibited acute toxicity by a number of assays [29]. These chemicals have been found to be present in samples of surface waters, river sediment, freshly fallen snow and tap water [29] and, in a more recent study, in all streams, including effluent, of the physiochemical wastewater treatment plant of Montréal, Canada [30]. These results make a very convincing connection between plasticizer degradation in the laboratory with pure cultures and the fate of these plasticizers in the environment.



A **B**

Figure 1-1-Chemical structure of 2-ethylhexanol (**A**) and 2-ethylhexanoic acid (**B**), metabolites from the biodegradation of DEHP and DEHA.

Because of potential toxicity problems recent plasticizer development has focused on creating biodegradable, non-toxic products. The Velsicol Chemical Corporation offers a series of dibenzoate plasticizers as non-toxic alternatives to traditional plasticizers. Benzoflex® 2888 for instance, was developed in response to the problem posed by using toxic, leachable plasticizers in children's toys. It is a blend of diethylene, triethylene and dipropylene glycol dibenzoates (Figure 1-2). Phthalate esters were once used in flexible children's toys, however the health risk associated with these compounds and the ban on the use of many phthalate plasticizers in such products in the European Union [7] caused toy manufacturers to find alternatives. Benzoflex® 2888 has been found to be a good alternative due to its low toxicity, good material performance and rapid biodegradation. [3] The physical properties of PVC with a some popular benzoate plasticizer blends were compared to those of PVC containing DPGDB as well as butyl benzyl phthalate (BBP) in an article by Arendt. [31]

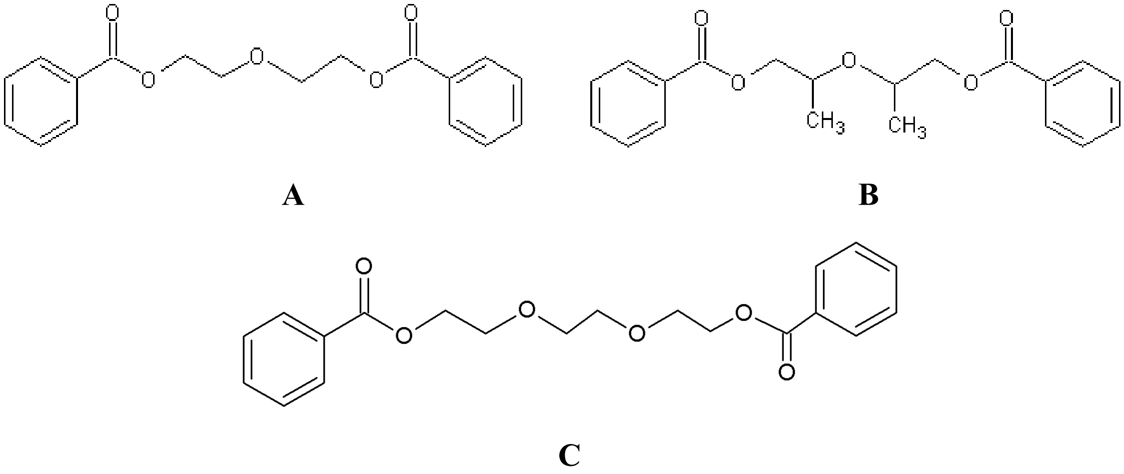


Figure 1-2-Structures of diethylene glycol dibenzoate (DEGDB) (**A**), dipropylene glycol dibenzoate (DPGDB) (**B**), and triethylene glycol dibenzoate (**C**).

A recent study [28] has shown that the biodegradation of DEGDB and DPGDB can be incomplete leading to accumulation of toxic metabolic products. This means these compounds are likely to have the same incomplete breakdown issue associated with DEHP and DEHA. For both of the above dibenzoates, the metabolite in question was the monobenzoate version of the parent compound. The biodegradation pathway suggested by the authors in presented in Figure 1-3.

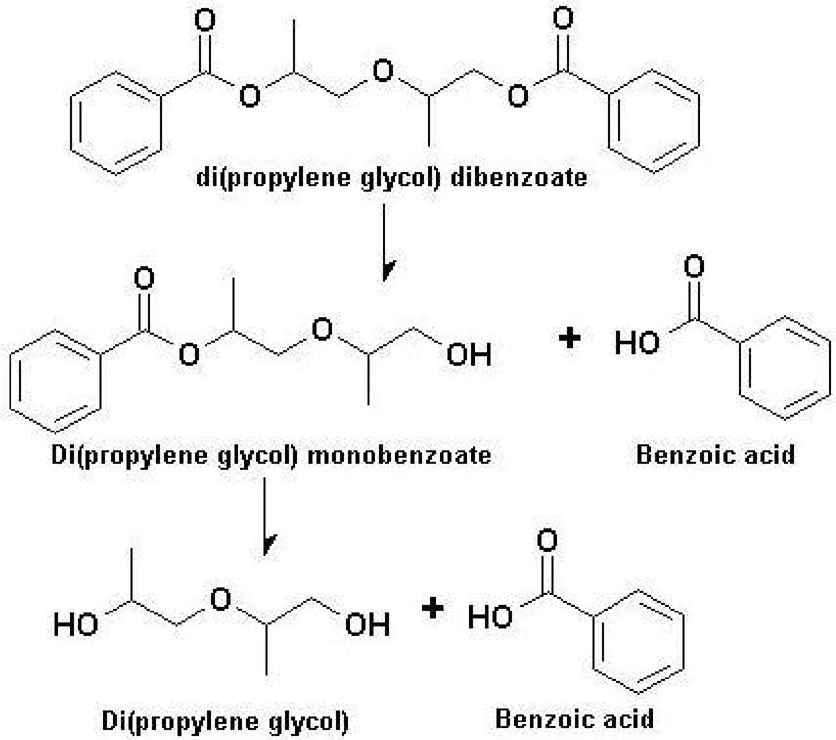


Figure 1-3-Pathway proposed for the partial biodegradation of DPGDB. [28]

A broad range of pentanediol-based diesters, including 1,5 pentanediol dibenzoate (PDDB), were patented in the 1950's as plasticizers for vinyl polymers [32]. This compound is identical to DEGDB (Figure 1-2 **A**) except for the elimination of an ether bond (Figure 1-4). This implies that this compound is also likely to be more easily biodegraded than DEGDB because these bonds are typically difficult for microorganisms to degrade [33]. At the moment there is one diester of pentanediol offered industrially: 2,2,4-trimethyl-1,3-pentanediol dibenzoate. It is offered by the Velsicol Chemical Corporation as a specialty plasticizer for silk screen ink applications. Material properties of PVC plasticized with this chemical to various concentrations are reported and compared to properties of PVC plasticized with di-isodecyl phthalate in a report. [34]

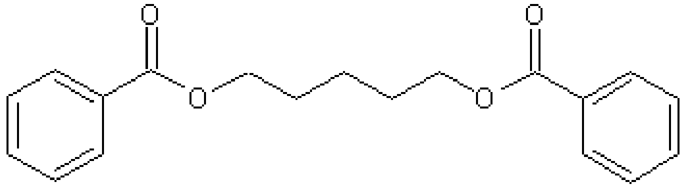


Figure 1-4-Chemical structure of PDDB.

2 MATERIALS AND METHODS

2.1 Synthesis of 1,5 Pentanediol Dibenzoate

The synthesis of the potential ‘green’ plasticizer, 1,5 pentanediol dibenzoate (PDDB), was performed by esterification via the acid chloride route. The chemicals listed in Table 2-1 were placed in a 2 L round bottom glass reactor fitted with a reflux condenser. The mixture was stirred and heated at reflux for 6 hours under the flow of nitrogen (Megs, Montreal, QC).

Table 2-1-Starting materials used in the synthesis of 1,5 pentanediol dibenzoate as well as the amounts used, purities and suppliers.

Material	Amount	Purity	Supplier
Benzoyl Chloride	113g	99%	Sigma-Alrich, Oakville, ON
1,5 Pentanediol	33g	96%	Sigma-Alrich, Oakville, ON
Acetone	500 mL	>99%	Fisher Scientific, Montreal, QC

The reaction mixture was allowed to cool and was then diluted with chloroform (ACS certified, Fisher Scientific, Montreal, QC), to which a saturated solution of sodium bicarbonate (Fisher Scientific, Montreal, QC) was added. This was left stirring for 2 hours. The organic fraction was separated using a separatory funnel, and washed with water purified previously by reverse osmosis (RO). The organic fraction was washed a second time with saturated sodium bicarbonate solution, separated, and washed with RO water. Finally, the solvent was removed using a rotary evaporator (Buchi, Rotovapor R200) and the oily product was collected. The structure of the product was confirmed via NMR (McGill University Chemistry Department service), and the presence of impurities was found to be negligible.

2.2 Biodegradation Study

2.2.1 Microorganism, Growth and Sample Preparation

The microorganism used to study the biodegradation of PDDB was *Rhodococcous rhodochrous*, American Type Culture Collection (ATCC) 13808. All cell culturing was performed in 500 mL Erlenmeyer flasks fitted with foam caps (Fisher Scientific, Montreal, QC). The flasks contained 100 mL of MSM medium (composition shown in Table 2-2), 0.1 g/L yeast extract (YE) (Difco brand, Fisher Scientific, Montreal, QC), 2 g/L n-hexadecane (99%, Sigma-Aldrich, Oakville, ON) and 2 g/L PDDB (synthesis outlined in Section 0). The flasks were sterilized in an autoclave (AMSCO, Model 3021-S) at 17 psig and 121 °C for 30 min and then inoculated with 1 mL of cell broth from a previous culture in a laminar fume hood (Baker Company, Model VBM600) using sterile techniques. The flasks were then kept in a rotary incubator shaker (New Brunswick Scientific, Model G-25) at 200 RPM and 30 °C.

Table 2-2-Minimum Salt Medium (MSM) salt concentrations in RO water.

Chemical	Concentration (g/L)	Supplier
Ammonium Nitrate, NH_4NO_3	4.0	Fisher Scientific, Montreal, QC
Potassium Phosphate, KH_4PO_4	4.0	Fisher Scientific, Montreal, QC
Sodium Phosphate dibasic, Na_2HPO_4	6.0	Fisher Scientific, Montreal, QC
Magnesium Sulphate Heptahydrate, $MgSO_4$•$7H_2O$	0.2	A&C American Chemicals, Montreal, QC
Calcium Chloride Dihydrate, $CaCl_2$•$2H_2O$	0.01	Fisher Scientific, Montreal, QC
Iron Sulfate Heptahydrate, FeSO4•7H2O	0.01	Fisher Scientific, Montreal, QC
Disodium Edetate, Na_2EDTA	0.01	Fisher Scientific, Montreal, QC

Several flasks were inoculated at the same time from a cell culture of *R. rhodochrous* acclimatized to the substrates being studied. The degradation of the hexadecane and PDDB was followed over time by extracting the entire contents of one flask every 3 or 4 days. In addition two abiotic control flasks were prepared, the first was extracted immediately, the other was exposed to the same conditions as the biotic flasks and then was extracted at the end of the experiment.

Prior to extraction the cell broth in a flask was acidified to a pH between 2 and 3 using hydrochloric acid (Fisher Scientific, Montreal QC) and was then mixed with 20 mL of chloroform (ACS certified, Fisher Scientific, Montreal QC) containing 1 g/L n-pentandecane (99%, Acros Organics brand, Fisher Scientific, Montreal, QC) as the internal standard for gas chromatography (GC). The mixture was shaken for 30 seconds and the chloroform fraction was separated using a 250 mL seperatory funnel. The chloroform fraction was stored in a glass vial with aluminum foil under the cap, at a temperature of -15 °C until it was analyzed. Prior to analysis by GC, a small volume of the sample was diluted by a ratio of 1:20 in chloroform containing 1g/L n-pentadecane.

2.2.2 Gas Chromatography

The samples were injected into the GC (Varian, model CP 3800), using a 10 µL syringe (Hamilton brand, fisher scientific, Montreal QC). The column used was a Restek RTX®-5 (30m, 0.32 mm internal diameter, 0.25 µm film) and the detector was of the flame ionization variety (FID).

The concentrations of the analytes were related to the ratio of the area under their respective peaks on the GC chromatogram, to that of the internal standard. Calibration curves relating area ratio to concentration were generated for both PDDB and hexadecane.

2.3 Polymer Processing and Testing

2.3.1 Materials

A commercial sample of poly(vinyl chloride) (PVC) that did not contain any plasticizer was obtained from Solvay Benvic France. This was used as the base polymer in this study. Various properties of this resin are listed in Table 2-3. The exact concentrations of calcium-zinc heat stabilizer, typically a complex mixture of calcium and zinc salts of fatty acids [35], and of the colouring agent were not specified.

Table 2-3-Properties of PVC compound.

Property	Value[a]
Supplier	Solvay Benvic France
Catalogue number	IH014GH045AA
Stabilizer	Calcium-zinc
Colour	Grey
Density at 20°C	1.4 kg/dm^3
Yield stress at 23°C	41 MPa
Elongation at break at 23°C	120%
Recommended extrusion temperature	160-180°C

a-all properties taken from supplier data sheet

One of either three different commercially used plasticizers or the compound synthesized for this study, alone with a heat stabilizer and a processing lubricant were incorporated into the PVC resin by way of extrusion (section 2.3.2). Table 2-4 includes a list of these additives along with their respective functions, purities and suppliers.

Table 2-4-Plasticizers and other additives, functions, purities and suppliers.

Additive	Function	Purity	Supplier
Di(2-ethylhexyl) phthalate (DEHP)	Plasticizer	99%	Sigma-Aldrich, Oakville, ON
Di(propylene glycol) dibenzoate (D(PG)DB)	Plasticizer	96%	Sigma-Aldrich, Oakville, ON
Di(ethylene glycol) dibenzoate (D(EG)DB)	Plasticizer	98%	Sigma-Aldrich, Oakville, ON
Epoxidized soybean oil (ESO) (Trade name: Drapex 6.8)	Heat stabilizer/ plasticizer	-	Chemtura Corporation, Middlebury, CT, USA
Stearic Acid (SA)	Heat stabilizer	-	Fisher Scientific, Montreal, QC

2.3.2 Unit of Concentration for Polymeric Additives

The concentrations of all polymeric additives in this study were expressed in parts per hundred parts resin (PHR), that is the ratios of their weights, $W_{Additive}$, to that of the resin, W_{PVC_Resin} (see Equation 1). The weight of the resin included the polymer itself, the Ca/Zn heat stabilizer and the colouring additives included in the resin by the manufacturer.

Equation 1:

$$\frac{W_{Additive}}{W_{PVC\_Resin}} \times 100 = C(PHR)$$

2.3.3 Extrusion

A conical intermeshing twin-screw extruder (Thermo Electron Corporation, Haake Minilab) was used to create the plasticized blends of PVC. These devices have been shown be capable providing mixing comparable to other larger extruders and mixers [36]. The product was a continuous cylindrical piece of polymer, henceforth referred to as a ‘thread’.

The plasticizer concentrations used, as well as the concentrations of other additives in this study are listed in Table 2-5. A stepwise approach was used to incrementally increase the plasticizer concentration in the PVC by 20 PHR per step to each desired level of plasticization. For example, to make an 80 PHR-plasticizer PVC blend, 20 PHR-plasticizer PVC was first made. This material was then mixed with more plasticizer to increase the concentration to 40 PHR. The concentration of this material was then further increased to 60 PHR and finally to 80 PHR. This approach was necessary as it was impossible to absorb large concentrations of plasticizer in one pass through the extruder (see section 3.2.1).

Table 2-5-Concentrations with respect to PVC resin of various additives.

Additive	**Concentration (PHR)**
Plasticizer	20,40,60 and 80
ESO	4
SA	0.5

There were 2 controlled parameters for the extruder: the rotation rate of the screws and temperature of the walls. The former was 30 min^{-1} for all experiments; the latter was set according to the target plasticizer concentration. The extrusion temperatures used are listed in Table 2-6.

Table 2-6-Extrusion temperature used for various target plasticizer concentrations.

Target Plasticizer Concentration (PHR)	Extrusion Temperature (°C)
20	140-160
40	140
60	110-120
80	90-110

The individual components were weighed in an aluminum dish (Fisher Scientific, Montreal, QC) using a balance (Denver Instruments, Apx-203) and then fed together into the extruder in sub-batch sizes of 3 g. The weights of each individual component for a sub-batch of a given level of plasticization are listed in Table 2-7. The resulting thread was pelletized and recycled through the extruder. A batch consisted of 10 sub-batches. The threads from each batch were collected and pelletized. The pellets were then mixed together and passed once more through the extruder in 3 g portions. The same aluminum dish was used to collect and mix the pelletized material during the entire batch This procedure was used for each 20 PHR increase in plasticizer concentration. The number of extruder passes increased by 3 for each step of the increasing plasticizer concentration as shown in Table 2-8. All residual material was removed from the extruder when going from one plasticizer concentration to another. For each plasticizer and each level of plasticization 2 batches of material were made. A small portion of this material was set aside for analysis by differential scanning calorimetry (section 2.3.6) while the rest was molded into tensile test bars (section 2.3.4).

Table 2-7-Weights of various components used per 3g extrusion sub-batch.

20 PHR Plasticizer PVC			
PVC Compound (g)	**Plasticizer (g)**	**ESO (g)**	**SA (g)**
2.41	0.48	0.096	0.014
40 PHR Plasticizer PVC			
20 PHR Plasticizer PVC (g)	**Plasticizer (g)**		
2.58	0.42		
60 PHR Plasticizer PVC			
40 PHR Plasticizer PVC (g)	**Plasticizer (g)**		
2.64	0.36		
80 PHR Plasticizer PVC			
60 PHR Plasticizer PVC (g)	**Plasticizer (g)**		
2.67	0.33		

Table 2-8-Number of extruder passes for each plasticizer concentration

Plasticizer Concentration (PHR)	20	40	60	80
Extruder Passes	3	6	9	12

2.3.4 Injection Molding

The plasticized PVC was molded into tensile test bars using an injection molder (A&B Machinery, AB400 Workstation). The temperature of the barrel was set depending on the plasticizer concentration of the material being molded; these temperatures are listed in Table 2-9. A compressed air line at 100 psig powered the hydraulic injection piston, the injection time was 30 seconds.

Table 2-9-Injection molder barrel temperatures used for each plasticizer concentration.

Plasticizer Concentration (PHR)	20	40	60	80
Barrel Temperature (°C)	193-204	182	175	162

The barrel was initially filled with pelletized extrudate and the piston was forced into the barrel without the mold in place, thereby keeping the valve of the nozzle closed. This had the effect of compressing the material in the barrel and removing void spaces. After this start-up procedure the next injection was done with the mold in place and the first bar was molded. The dimensions of the molded bars are shown in Figure 2-1. The barrel was filled to the top with material after every injection until it was completely used. Injections continued until an incomplete bar was molded, indicating that no material remained. The heater was then disengaged, the device was disassembled and any residual material was removed while the apparatus was still warm. The only material remaining in the device after being cleaned was in the nozzle and for this reason, the first bar of a new batch was always discarded. It was then assumed that the nozzle was cleared of any residual material and that subsequently molded bars were uncontaminated.

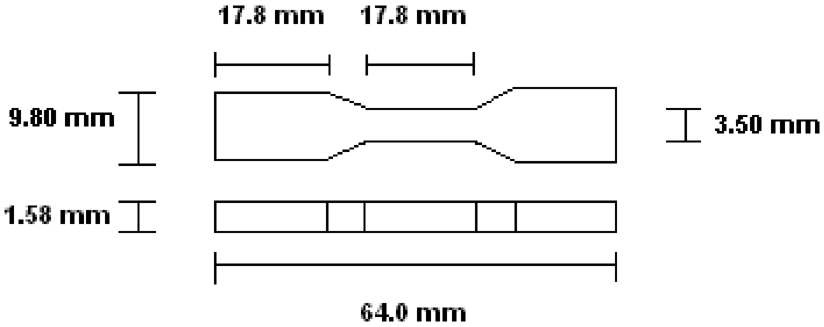


Figure 2-1-Dimensions of the tensile test bars. Top and side views shown.

2.3.5 Tensile Testing

Tensile testing of the plasticized PVC bars was done using a Shimadzu EZtest tester equipped with a 500 N load cell. The molded bars were allowed to rest for a minimum of 7 days after molding before being tested. The specimens were conditioned for a minimum of 48h in a desiccant chamber (Drierite brand, Fisher Scientific, Montreal, QC) at a temperature between 21-25.5°C.

The tensile test bars were loaded into the tensile tester in such a way that the grips were clamped onto the wider end sections of the test bar (see Figure 2-1). The tests were performed at temperatures between 21-25.5 °C. The initial separation of the grips, as well as the initial width and thickness of the thin center part of the bar were measured using a digital caliper (PPRI Aerospace) and recorded. The bars were subjected to a strain rate of 5 mm/min until the specimen fractured. The force imposed on the specimen and the corresponding strain were recorded with a computer over the course of the experiments.

The strain, ε, was reported in units of percent elongation (%El) which was calculated with Equation 2, 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 3, where F is the tensile force and T_o and W_o are the initial thickness and width, respectively, of the center region of the tensile bar.

Equation 2:

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

Equation 3:

$$\sigma(MPa) = \frac{F(N)}{T_o(mm) \times W_o(mm)}$$

The parameters of interest generated from the tensile tests were the tensile strength, σ_U, which was the stress at break, and the strain at break, ε_U. For a given plasticizer, at each concentration, the average value of a minimum of 4 samples was reported along with a 95% confidence interval. This procedure was adapted from the ASTM standard form tensile testing [37].

2.3.6 Differential Scanning Calorimetry

A temperature modulated differential scanning calorimeter (TMDSC) (TA instruments, Q100), was used to measure the glass transition temperature (T_g) of the plasticized blends of PVC. The extruded thread of material to be tested was sliced into very thin discs, 4 or 5 (10-20 mg) of which were placed flat on the bottom of a standard DSC pan (TA instruments, model # 070221). The samples were only manipulated with tweezers to minimize the chances of contamination. The weight of material was recorded (Sartorius CP225D) and a lid was crimped on. The pans containing the samples were loaded into the instrument's auto-sampler for testing. The calibrating material was simply an empty pan and lid assembly.

TMDSC involves superimposing a sinusoidal modulation on the constant heating rate typically applied in conventional DSC. The heat flow necessary to achieve the imposed heating rate and modulation thereof is recorded. As a result of the modulation the reversing and non-reversing heat flows may be separated [38].

The heating rate used was 2 °C/min, the amplitude of modulation was 1.272 °C and the period was 60 sec. The temperature range scanned depended on the level of plasticization, these ranges can be seen in Table 2-10. The samples were quenched to the minimum temperature of the scan range, held at this temperature for 5 minutes, heated to the maximum temperature at the specified heating rate and then held at this temperature for 5 min. This thermal cycle was then repeated. The first cycle was done to erase the sample's previous thermal history and the second was used for the T_g measurement.

Table 2-10-TMDSC temperature range used for each plasticizer concentration.

Plasticizer concentration (PHR)	0	20	40	60	80
Temperature Range (°C)	-10 - 125	-40 - 90	-90 - 45	-90 - 45	-90 - 45

Using the TA instruments software package (TA Universal Analysis) the reversing heat flow measured by TMDSC was plotted versus temperature. Tangents to the three linear regions of the curve were drawn, the intersection points of which were identified as extrapolated onset temperature, T_{eig}, and extrapolated end temperature, T_{efg}. The midpoint between T_{eig} and T_{efg}, labeled T_{mg}, was taken as the T_g of the material in this study. This method was adapted from the ASTM standard for transition temperatures using DSC [39].

3 RESULTS

3.1 Biodegradation of 1,5 Pentanediol Dibenzoate

The results of the co-metabolism of PDDB and hexadecane by *R. rhodochrous* (ATCC 13808) are shown in Figure 3-1. By day 6 a large amount of the hexadecane had been degraded. By day 9 nearly all of the hexadecane had degraded but significant amounts of the PDDB remained. Further degradation of the PDDB was noticed in the flask extracted on day 12 and by day 16 nearly all of it had been degraded.

Over the course of the biodegradation, two new peaks appeared in the chromatograms. These were presumed to be metabolites extracted from the growth medium. Metabolite 1 appeared only in the chromatogram for the flask extracted on day 3. This peak appeared just over a minute after the hexadecane peak and the area ratio was very small relative to those of the substrates. Metabolite 2 was observed in the chromatograms for the flasks extracted on days 6, 12 and 16. This peak appeared between the peaks for hexadecane and the internal standard. The area ratio was again very low relative to those of the substrates and was roughly the same in all 3 flasks, although a decreasing trend was observed.

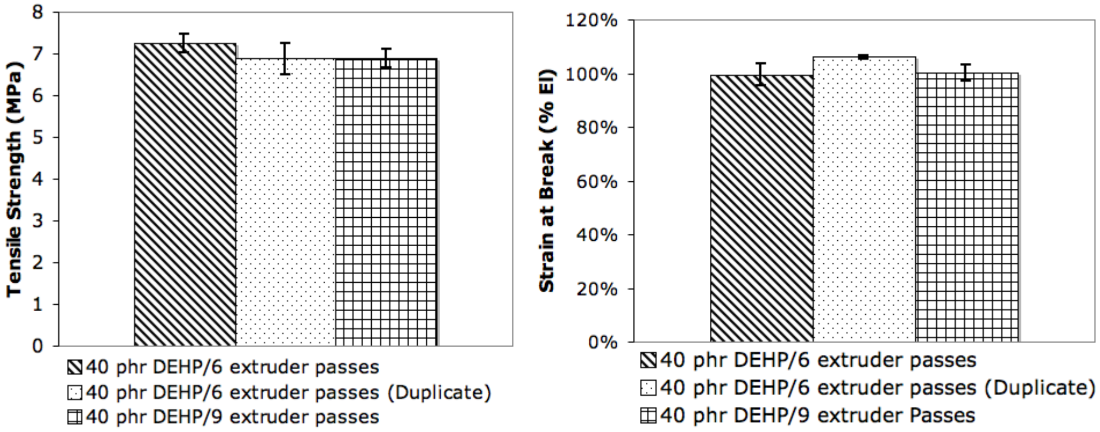
Figure 3-1-Concentrations of PDDB (◆) and hexadecane (✧) and area ratios of metabolites 1(△) and 2(○) during the growth of *Rhodococcous rhodochrous* (ATCC 13808). At each time the data were generated by the complete extraction of the total contents of one shake flask.

3.2 Tensile Testing

3.2.1 Validation of Blending Method

This study required a method of incorporating large amounts of liquid plasticizer into the PVC matrix using a small-scale twin-screw extruder. It quickly became apparent that it would not be possible to simply feed the solid polymer resin and liquid plasticizer together in the desired proportions into the extruder because some of the plasticizer did not mix uniformly with the PVC and accumulated in the extruder as subsequent batches were fed through. This is a problem commonly ecountered in polymer compounding described as phase inversion, where the less viscous phase will coat and lubricate the other phase, inhibiting its heating and mixing. Eventually the desired matrix phase's viscocity will be sufficiently reduced and will invert to become the continuous phase. [40]

It was found that an amount of plasticizer corresponding to 20 PHR could safely be fed into the extruder along with the PVC resin without any visible accumulation. A staged approach was used in which the concentration of plasticizer was increased by 20 PHR per cycle to concentrations of 80 PHR. The validity of this approach was tested with the tensile tests of 3 different batches of PVC containing 40 PHR DEHP (Figure 3-2). The first 2 are duplicate batches of material, which had been passed through the extruder the normal 6 times. The tensile strength of the material was close to 7 MPa for both batches and the mean values obtained are statistically equal at a level of confidence of 95% ($p=0.05$). The strain at break was close to 100% for both batches, although the mean values are not statistically equal ($p=0.05$), this would appear to be due to the abnormally low error on the mean value of the second batch. Regardless, the results are close enough to conclude that this method of blending the polymer and plasticizer is sufficiently repeatable.



A **B**

Figure 3-2-Effect of the number of extruder passes on the tensile strength (**A**) and strain at break (**B**) of PVC containing 40 PHR of DEHP. The striped bars and dotted bars represent duplicate data for material having experienced 6 extruder passes and the checkered bars represent 9 extruder passes. Error bars represent 95% confidence intervals.

The third batch of PVC containing 40 PHR DEHP (Figure 3-2) was subjected to 3 extra passes through the extruder, for a total of 9 passes. This is equivalent to the number of passes that are performed when making 60 PHR PVC. This was done as a control experiment to verify that the extra processing was not affecting the material's properties. The tensile strength and strain at break of this batch are statistically equal to the first 6-pass-batch and to the tensile strength of the second 6-pass-batch (p=0.05). The elongation at break of the second 6-pass-batch was very close to that of the 9-pass-batch, although not statistically equal (p=0.05). This demonstrates that the extra processing does not significantly affect the tensile properties of the material. Any difference observed in these properties between PVC containing different amounts of plasticizer can be attributed solely to the plasticizer concentration.

3.2.2 Mechanical Properties

The tensile strength at break and strain at break obtained from the tensile tests performed on PVC plasticized to 20, 40, 60 and 80 PHR with DEHP, DEGDB, DPGDB or PDDB are shown in Figure 3-3 and Figure 3-4 respectively. In general, as the concentration of plasticizer was increased the tensile strength of the material decreased. The tensile strengths of the various plasticizer-PVC blends at a given plasticizer concentration were quite similar relative to the differences observed at different plasticizer concentrations. The change for each subsequent 20 PHR increase of plasticizer was observed to decrease. For example the decrease in tensile strength from 20 PHR to 40 PHR was greater than 10 MPa, while it was no more than 5 MPa when the concentration was increased from 40 PHR to 60 PHR.

The trend for the strain at break was not continuous over the range of concentrations tested. It increased at low plasticizer levels, reached a plateau at intermediate levels and then decreased as the levels were further increased (Figure 3-5). At 20 PHR the strain at break of the PDDB and DEHP blends were statistically equal (p=0.05) and were around 85 %El while those of the DEGDB and DPGDB blends, also statistically equal at the aforementioned confidence level, are close to 100 %El. The strain at break of the DEGDB and DPGDB blends are again statistically equal (p=0.05) at 40 PHR; the mean values were close to 150 %El and 130 %El respectively. For the same concentration, the mean strain at break of the specimens plasticized with PDDB was about 110 %El and was near 100 %El for those with DEHP. At a concentration of 60

PHR the strain at break of the PDDB blend was higher than it was at 40 PHR and was statistically equal (p=0.05) to those of the other two dibenzoates. The strain at break values did not change significantly (p=0.05) between 40 and 60 PHR concentrations for the 3 other plasticizers, although the means all decreased. The strain at break of the DEGDB blend was significantly higher (p=0.05) than that of the DPGDB blend at 60 PHR. The strain at break for the 3 dibenzoate plasticizers were very similar at 80 PHR, around 110 %El, while that of the DEHP blend of the same concentration was considerably lower at 80 %El.

Figure 3-3-Tensile Strength (MPa) at break for PVC plasticized with DEHP (◆), DEGDB (◇), DPGDB(△) and PDDB (○) at concentrations of 20, 40 60 and 80 PHR. Error bars represent 95% confidence intervals.

Figure 3-4-Strain (%El) at break for PVC plasticized with DEHP (◆), DEGDB (✧), DPGDB(△) and PDDB (○) at concentrations of 20, 40 60 and 80 PHR. Error bars represent 95% confidence intervals.

3.3 Glass Transition Temperature Measurements

The glass transition temperatures of the plasticized PVC blends, as a function of plasticizer concentration, are shown in Figure 3-5. The overall trend was that the Tg decreased with increasing plasticizer content. A Tg measurement was performed on unplasticized PVC. This material contained the same amount of heat stabilizer and lubricant as all the other blends, these were mixed with the resin using the extruder. The Tg measured for this material was 67 °C.

Figure 3-5-Glass Transition Temperature (Tg) for unplasticized PVC (0 PHR) and PVC plasticized with DEHP (◆), DEGDB (✧), DPGDB(△) and PDDB (○) at concentrations of 20, 40 60 and 80 PHR. All material contained 4 PHR ESO and 0.5 PHR SA. Error bars represent 95% confidence intervals.

For all four plasticizers, the Tg of the 20 PHR PVC were the same, about 25 °C. At 40 PHR the Tg values diverged, with the DEHP blend having the lowest Tg at -18 °C and the mean Tg measured of the DEGDB and DPGDB blends were -3 and 3 °C respectively and were significantly different. The Tg of the PDDB blend was nearly the same as that of the DEGDB and was not significantly different than that of the DPGDB. At 60 and 80 PHR the Tg of the DEHP blends continued to be quite a bit lower than the others, -33 °C and -42 °C respectively. The glass transition temperatures of the PDDB and DEGDB blends were nearly identical at these concentrations as well, with Tg values of around -18 °C and -27 °C. The glass transition temperatures recorded for the D(PG)DB blends were higher than those of the other dibenzoates: -11 °C at 60 PHR and -17 °C at 80 PHR.

4 DISCUSSION

4.1 Biodegradation of PDDB

The biodegradation of PDDB by *R. rhodochrous* was nearly complete after 16 days and took place without the accumulation of metabolic products (see Figure 3-1). Two metabolites were observed during the fermentation and they appeared at very low levels relative to the substrates. Metabolite 1 was only observed before there was any perceptible degradation of PDDB. It is, therefore, unlikely that this metabolite is a product of the biodegradation of PDDB. Metabolite 2 appeared after substantial degradation of PDDB had been observed. This metabolite is therefore more likely to be associated with the break down of PDDB. This metabolite was only seen at very low levels.

These results are very promising because under similar conditions the biodegradation of both DEGDB and DPGDB was shown to lead to the accumulation of toxic metabolites. In both cases the metabolite was identified as the monobenzoate version of the corresponding plasticizer [28].

There is only one structural difference between PDDB and DEGDB. The ether bond in the DEGDB is replaced by CH_2 in PDDB. The ether bond was likely the reason for the incomplete breakdown of DEGDB in the previous studies. This particular chemical bond is notoriously resistant to biodegradation [33]. By replacing it with a carbon atom, the monoester produced after the first hydrolysis step should become susceptible to beta-oxidation, and is therefore easier to biodegrade. This suggests that PDDB would be a better plasticizer choice than DPGDB or DEGDB because once released into the environment it would be easier to biodegrade completely without leaving a residue of toxic intermediates.

4.2 Development of Plasticizing Tests

In order to evaluate the plasticizing properties of a potential green plasticizer, it was necessary to develop a method of blending plasticizer into polymer resin. A series of test procedures were also needed to characterize these materials. Blends of resin containing plasticizers used industrially were created and subjected to the developed test procedures. This was necessary to be able to compare the plasticizing properties of a new plasticizer to those of commonly used plasticizers because the measurements are highly dependant on the resin used and the conditions under which the tests were carried out.

The trends of the material properties were not always predictable. It was found that sometimes these trends were less or more pronounced than would have been expected from the literature. This can be attributed mainly to the nature of the type of PVC that was available for these tests.

The values of tensile strength at break for PVC containing the three commercial plasticizers all exhibited expected trends (Figure 3-3). As the concentration of any of these was increased in the formulations, the tensile strength decreased and most of this decrease occurred with the first two additions. This was expected from earlier work [1, 4] but the total reduction was lower than reported in these studies as can be seen in Figure 4-1. Some discrepancies were expected because the polymer resin used in this study was an unplasticized PVC resin which was a commercial sample, designed make rigid PVC products.

Figure 4-1- Tensile strength of plasticized PVC at various plasticizer concentrations measured in the present study (○) compared to values reported in the literature; (□) adapted from Sears [1] and (△) adapted from Mathews [4].

The trends in the strain at break (Figure 3-4) were more surprising. For all of the commercial plasticizers, there was a small but perceptible maximum in the strain at break as the concentration of each of these was increased. This is surprising when compared to the general increasing trends seen in the data from Mathews and the even more dramatic increase seen in the data from Sears (Fig. 4-2).

Figure 4-2-Strain at break of plasticized PVC at various plasticizer concentrations measured in the present study (○) (O PHR point from resin data sheet) compared to values reported in the literature; (□) adapted from Sears [1] and (△) adapted from Mathews [4].

The trends observed for T_g's of the plasticized blends (Figure 3-5) were all of decreasing T_g with increasing plasticizer concentration. This was expected based on what is seen in the literature. This is demonstrated in Figure 4-3 in which the T_g's measured for PVC containing DEHP are compared to the corresponding data published by Brennan [5]. The curves are simply shifted by approximately the difference in T_g's of the base resins, the decreases in T_g with increasing plasticizer concentration in both sets of data agree quite well with each other.

Figure 4-3-Tg's of plasticized PVC at various plasticizer concentrations measured in the present study (○) compared to values reported in the literature; (□) adapted from Brennan et al. [5].

As mentioned previously, the PVC resin used in this study was obtained as a commercial sample, designed to make rigid PVC products. The manufacturer did not specify the average molecular weight of the resin in the product specifications. The literature suggests however, that PVC to be used in a flexible, plasticized product would typically have a higher viscosity (and hence higher molecular weight) than if the product was to be an unplasticized, rigid one [4]. It is assumed that this is the case for the resin used in this study. The low yield strength of the resin used (see Table 2-3), which is 41MPa, gives weight to this argument as that of typical rigid PVC ranges from 55-69 MPa [38]. The T_g measured in the present study for unplasticized resin was 67 °C (Figure 4-3), which further supports this claim, as that of typical PVC is 87 °C [38]. Both of the parameters can be indicative of molecular weight when comparing values for the same type of polymer.

As was mentioned in the introduction the strain at break of plasticized PVC is known to reach a maximum with increasing plasticizer concentration since "at higher concentrations there are relatively few macromolecules and these tend to flow apart under tensile stress" [1]. It is likely that polymers having a lower molecular weight, and therefore shorter polymer chains could suffer from this effect at lower plasticizer concentrations, as there are fewer entanglements. This may explain the relatively flat response of the strain at break encountered in this study (Figure 4-2). It is expected that if the plasticizer concentration were to have been increased higher than 80 PHR, both the tensile strength and strain at break would have continued to decrease and eventually have reached zero, likely at a lower concentration than in the case presented by Sears [1].

Generally, the 2 commercial dibenzoate plasticizers, DEGDB and DPGDB affected the tensile properties of the PVC in similar ways. The tensile strength at 20 and 40 PHR-plasticizer were nearly always higher than they were for the DEHP blends (see Figure 3-3). At 60 and 80 PHR plasticizer the tensile strengths of all the blends became nearly identical.

Although the strain at break data did not follow the typical trend over the range of concentrations tested, important information can be extracted nonetheless. At all plasticizer concentrations tested, the PVC specimens plasticized with DEGDB and DPGDB had higher strain at break than those plasticized with DEHP (see Figure 3-4). This result is particularly interesting at 60 and 80 PHR because, as mentioned above, the tensile strength of the materials were virtually the same at these concentrations. At almost all plasticizer concentrations the tensile strength and strain at break of the materials plasticized with DEGDB and DPGDB were very similar. When they were not equal, the DEGDB specimens tended to have higher strain at break and lower tensile strength at break. Furthermore, the T_g's measured (Figure 3-5) for the DEGDB specimens were lower than those for the DPGDB specimens at all concentrations except for at 20 PHR. This suggests that DEGDB is slightly more efficient as a plasticizer than DPGDB, although this is difficult to confirm from literature data as DEGDB is typically only ever offered commercially as part of a mixture of several plasticizers [41]. This result suggests that the additional methyl groups in the DPGDB (Figure 1-2) cause it to be less effective than DEGDB at lowering the T_g of PVC. These methyl groups hinder the rotation of the plasticizer molecules and therefore cause the T_g of the material plasticized with DPGDB to be higher than the material plasticized with DEGDB. This may also explain the differences observed in the tensile properties between the two materials mentioned above.

The tensile properties of samples plasticized with PDDB were, for the most part, quite similar to the other dibenzoate plasticizers tested in this study (Figure 3-3, Figure 3-4). This is not surprising as their chemical structures are very similar. The most pronounced differences observed between the PDDB specimens and the specimens with one of the other two dibenzoates were at concentrations of 20 and 40 PHR where the strain at break of these specimens was somewhat lower. In fact, the plateau in strain at break observed in the cases of the three other plasticizers between 40 and 60 PHR was not encountered. Instead, the strain at break of the PDDB specimens increased over this interval. The T_g's of the PVC specimens plasticized with PDDB and DEGDB were virtually identical (see Figure 3-5). This implies that the ether linkage replacing the carbon atom in the 3rd position of the 1,5 pentanediol (Figure 1-2) does not have a significant effect on the compound's ability to lower the T_g of the PVC. As mentioned above a wide range of diesters of pentanediol, including PDDB, were patented in the 1950's as plasticizers for vinyl-type polymers [32]. It was therefore anticipated that PDDB would be a good plasticizer for PVC. The findings here confirm this.

5 CONCLUSION

A reliable method was developed for incorporating plasticizers into the matrix of PVC resin using a small-scale twin-screw extruder. Formulations of PVC were made with the commercial plasticizers di(2-ethylhexyl) phthalate (DEHP), diethylene glycol dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB) at plasticizer concentrations varying from 20-80 parts per hundred were made.

Tensile tests were carried out on injection-molded samples of these materials from which the tensile strength and the strain at break of the material were measured. The glass transition temperature (T_g) of these materials was also measured. Generally, the tensile strength and T_g of the PVC decreased with increasing plasticizer concentration while the strain at break increased at low concentrations, then reached a plateau and finally decreased at high concentrations.

1,5 pentanediol dibenzoate (PDDB) was synthesized and compared as a plasticizer to the currently used compounds using the developed tests. The T_g of PVC plasticized with PDDB was found to be virtually identical to that of DEGDB plasticized resin at all concentrations. The tensile strength of the PVC with PDDB was very similar to that of the other two dibenzoates and DEHP, especially at higher concentrations, while the strain at break of this material was between that of the two commercial dibenzoates and DEHP at low concentrations and virtually the same as the commercial dibenzoates at higher concentrations. Overall, PDDB performed very similarly to the other plasticizers, especially the dibenzoates.

PDDB was biodegraded under co-metabolism by the common soil bacterium *Rhodococcus rhodocrous* (ATCC 13808). After 16 days of growth, nearly all the PDDB was degraded and only small amounts of unidentified transient metabolites were observed in the growth medium. This is important because the accumulation of toxic metabolites was observed during the biodegradation of DEHP, DEGDB and DPGDB in previous studies.

The results obtained in the present study suggest that PDDB is a good candidate "green" plasticizer as it can be biodegraded without the accumulation of metabolites and it performs similarly to the commercial plasticizers tested based on T_g and tensile test measurements. Furthermore, techniques have now been established in our laboratory to blend and evaluate new green plasticizers.

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