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# Soil and Microbial Degradation Study of Poly(ε-caprolactone) – Poly(vinyl butyral) Blends

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**Summary:** Biodegradation of blends of poly(ε-caprolactone) [PCL] with poly(vinyl butyral) [PVB] was studied in the soil and by bacterial strains of *Bacillus subtilis* and *Escherichia Coli* isolated from the soil. Miscibility of the blends was also analyzed using FT-IR and optical microscopy at room temperature. Biodegradation of the blends was followed by weight loss, visual observations and scanning electron microscopy [SEM]. Blends with low polyester concentration, i.e., 30 wt% PCL and less, were clear and transparent and no spherulite formation was observed. Above 30 wt% PCL spherulites appeared, the size of which increased with increasing PCL concentration. Infra-red studies of the blends with less than 30 wt% PCL showed that only the amorphous phase of PCL was present. Above 30 wt% PCL indicated the presence of both crystalline and blended PCL. The second derivative of the carbonyl peak of PCL also supported the presence of two phases in blends with more than 30 wt% PCL and only one peak for blends with 30 wt% or less PCL. Weight loss was observed in all the blends. PCL rich blends showed more degradation, which was faster in the natural environment than in the laboratory. Physical appearance and microscopic examination showed the films deteriorated in soil. Blends in the *Bacillus subtilis* strain showed more degradation as compared to the *E. Coli.* strain.

**Keywords:** amorphous; biodegradation; blends; FT-IR; polyester

## Introduction

In the last couple of decades, the uses of plastic materials have increased enormously and as a result have worsened the problem of waste disposal. Landfills are now being filled rapidly and the incinerating of plastics releases environmentally harmful chemicals. The best solution to the problem is to use biodegradable plastics. Biodegradable plastics are degraded by the enzymatic action of living micro-organisms such as bacteria, yeast, and fungi. A great deal of research is now being directed towards developing plastics which are biodegradable. Understanding the behaviour of the biodegradation of polymeric materials is of fundamental importance in the development of these new materials.

There are several synthetic biodegradable polymers available. Poly(ε-caprolactone) [PCL] is one of the very few synthetic polymers that has been found to be biodegradable.[1-3] It is

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an aliphatic polyester obtained by self-condensation of the cyclic ester ε-caprolactone.[4] PCL has unique properties such as being water-resistant and having excellent biodegradability and biocompatibility. These properties have made it possible for PCL to be used in a variety of biomaterial applications such as medical devices[5] and biodegradable packaging materials.[1] Its biodegradable blend with starch is available commercially.[6] PCL has not attained commercial importance because of its relatively low melting point of about 60 $^0$C, poor mechanical properties and high production cost. It is often blended with other polymers to improve its mechanical properties and biodegradation rate.

The biodegradability of PCL and its blends have been investigated in many environments such as landfill and compost simulations,[7] soil burial,[8] and microorganisms,[9] etc. The biodegradation was found to depend on several parameters, such as molecular weight, crystalline morphology, film thickness and degradation conditions.[10-12] Microbe enzymes present in soil accelerates biodegradation of aliphatic polyesters by surface erosion. When the polymer films undergo hydrolysis through main chain scission, weight loss of the film takes place, which becomes detectable when water-soluble oligomers produced by microbes diffuse into the surrounding soil.[13] While many investigators using various techniques have studied PCL blends, blending PVB with PCL has not been investigated to a significant extent.

This study investigates a) the miscibility of [PCL] and Poly(vinyl butyral) [PVB] using optical microscopy and FTIR, and b) the biodegradation of blend films by the soil burial method and the microbial action of *Bacillus subtilis* and the *Escherichia Coli.* strain. PVB was selected as one of the polymers to be blended with PCL because it is tough, amorphous and has excellent mechanical properties.

## Experimental

**Materials.** PCL and PVB used in this study were purchased from Aldrich Chemicals. The average molecular weights of the polymers and thermal characteristics are given in Table 1. The polymers were used without further purification. Solvents used were distilled twice.

**Preparation of the blend films.** Blends were prepared by initially making 5% wt/vol solutions of the respective polymers in dichloromethane. The solutions were kept overnight to ensure complete dissolution. By mixing subsequent amounts of PVB solution with PCL solution, the blend solution containing different mass ratios of PCL was obtained.

Table 1. Characteristics of the polymers.

| Polymers | Molecular weight | Thermal |
|---|---|---|
| PCL | 42500 [b] 30300[a] (Mw) | $T_m$= 57 $^0$C, $T_g$ = -63 $^0$C |
| PVB | 36000[b] | $T_g$ = 75 $^0$C |

[a] Determined by GPC.
[b] Obtained from Aldrich Chemicals Company.

The resulting blend solutions were then cast onto glass plates. The solvent was allowed to evaporate slowly at room temperature. The films were peeled off by placing the glass plates in water and dried with tissue paper, placed in paper envelopes and dried in an oven at 40 °C for several days to remove residual solvent or water.

For FTIR analysis blend films were prepared as above but 2% wt/vol solutions were used instead of 5%.

**Optical and visual observation.** The thin films were observed visually for clarity and also with an Olympus 52X ZB12 microscope with a digital camera attached. Scanning electron microscopy (SEM) was also used.

**Miscibility tests.** The phase morphology of the polymer blends was investigated using a Philips XL30S FEGC scanning electron microscope at the University of Auckland, New Zealand. The films were fractured using liquid nitrogen and then the sample was mounted onto the sample holder. The sample was coated with Platinum using a Polaron SC7640 sputter coater, 10 to 12 mA.

**FT-IR.** Infrared spectra of the thin films were obtained on a Perkin Elmer 1000 Fourier transform infrared spectrometer. In all cases, 32 scans with a resolution of 2cm$^{-1}$ were signal averaged, corrected for baseline and normalised before storing.

**Biodegradation tests.** Biodegradability of PCL/PVB was evaluated by soil burial and microbial test methods. The degradation was expressed by the % weight loss of the blend films.

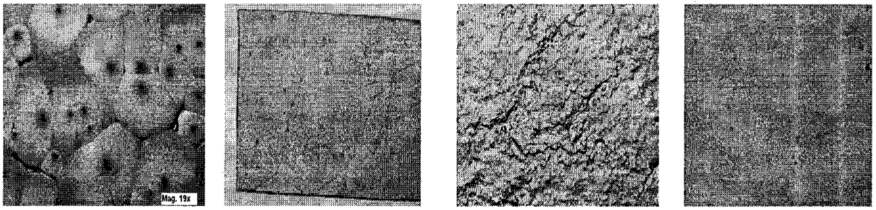
***a) Soil burial method.*** The soil was sieved with a 2-mm mesh size sieve. Maximum water holding capacity of the soil was determined. The experiments in the laboratory were carried out at a water content which was 50% of the maximum water holding capacity. The soil was placed in plastic trays and the blend films were buried in the soil and placed inside the laboratory at ambient temperature. Water was added to the soil daily to maintain the water content. The samples were also buried outside in the open soil to compare the biodegradation rate with that inside the laboratory. The biodegradation was studied by: a) measuring the mass loss of the samples every week, b) visual observation of the films, and c) electron microscopy.

***b) Microbial method.*** PCL/PVB films (4 $cm^2$ x 0.1 mm) were placed in nutrient broth solutions at a pH of 7.0 ± 0.2 containing bacterial strains of *Bacillus subtilis* and *E. Coli.* The films were removed from the broth every 2 days, washed with sterile water, dried, weighed and placed back into freshly prepared broth. One set of films was placed in water only to act as the control. The test was carried out over a period of 15 days.

## Results and Discussion

**Optical and visual microscopy.** Blend films with 30 wt% and less PCL appeared transparent. Opaqueness increased with increasing PCL content. Microscopic study showed that the size of the PCL spherulites was dependent on the PVB concentration. In films with a PCL content of 30 wt% and less, no spherulite formation was observed. For blends with a PCL content of 40 wt% and more, large spherulites were seen. The microphotograph in Figure 1a-d shows that the size of the spherulites is large and distinguished in pure PCL. As the concentration of PVB increases, the spherulite size decreases and disappears at low concentrations of the polyester.

**FT-IR Analysis.** PCL exists in a semi-crystalline state at room temperature and in the amorphous state above its melting point. The spectra of the two phases of PCL are shown in Figure 2. The carbonyl peaks centered around 1725 and 1735 $cm^{-1}$ are attributed



a b c d

Figure 1. Microphotographs of : a) Pure PCL, b) 90% PCL, c) 50% PCL, d) 10% PCL.

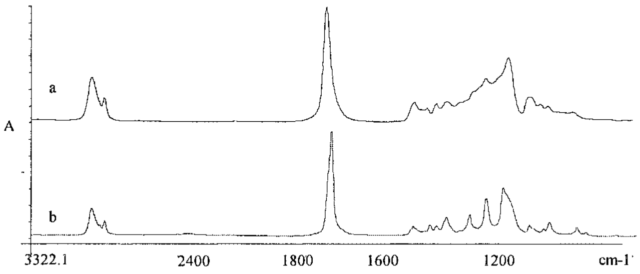


Figure 2. FT-IR spectra of a) PCL above the melting point, b) at room temperature.

to the crystalline and amorphous state of PCL, respectively.[14] Changes were also observed in the C-O-C region.

The second derivatives of the carbonyl band of PCL spectrum at room temperature and above the melting point of PCL are shown in Figure 3. This method[15] is capable of separating overlapping peaks. For the room temperature spectrum, two well resolved inverted peaks were observed, confirming the observation that PCL exists in the semi-crystalline state at room temperature. The second derivative of the carbonyl band of the higher temperature spectrum showed only a single peak at 1735 $cm^{-1}$ indicating that only the amorphous phase was present.

In spectra of the blends containing 30 wt% or less PCL, the carbonyl peak appeared at 1734 $cm^{-1}$ and the second derivative also showed a single peak at this wave number. For blends above 30 wt% PCL, the carbonyl peak appeared at 1725 $cm^{-1}$ and two well resolved peaks appeared in the second derivative. These observations mean that PCL exists in the

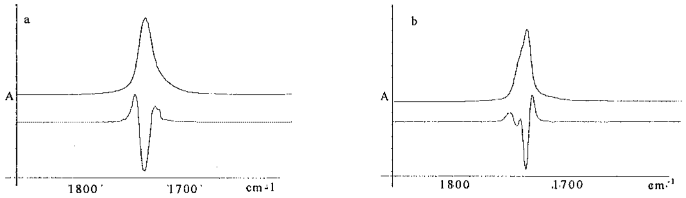


Figure 3. The second derivative of carbonyl peak of a) PCL above the melting point, and b) at room temperature.

amorphous state in blends containing 30 wt% or less PCL for a homogeneous mixture with PVB. However, in blends with more than 30 wt% PCL, the polyester exists in a semi-crystalline state, i.e., crystalline PCL and blended PCL for a heterogeneous mixture.

**Biodegradation.**

***a) Soil burial method.*** Figure 4 shows the comparison in percent weight loss of the blends after being placed in the respective environments. Each set of data is the average of two replicates. These data show that the 50% PCL blend is degraded most, followed by 40% PCL. Pure PVB is not biodegradable, while 10, 20 and 30 wt% PCL blends showed evidence of biodegradation. Weight loss is a clear indication that degradation was taking place.

Biodegradation in the natural environment was faster than biodegradation in the laboratory environment. The biodegradation was faster in the natural environment possibly due to better conditions for the microbes to grow, and some additional factors may have affected the biodegradation rate. PCL rich blends were not tested because the films were not mechanically strong enough to be buried.

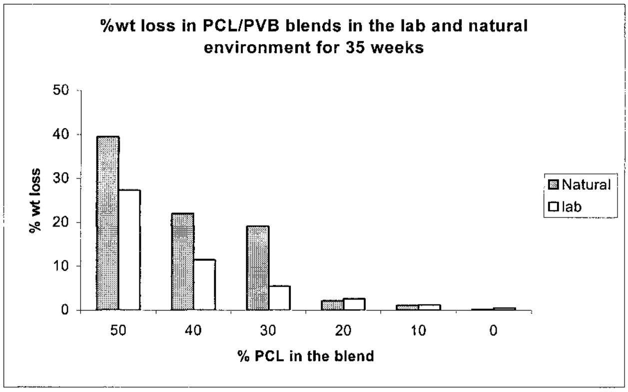
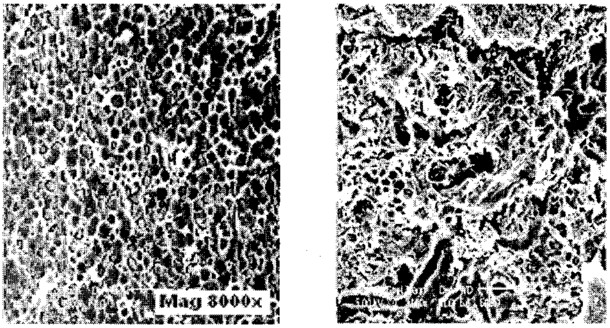


Figure 4. Percentage wt. loss of the blends (a) in the laboratory, (b) in the natural environment.

**Visual observation.** The samples became hard and brittle when removed from the soil. Red spots started appearing on the 50% PCL films, to a greater extent in the outside sample. After two weeks the red spots started appearing in 40% PCL films, and in the third week on 30% PCL films. Other colours such as brown and yellow also appeared, mostly in the outside samples. As time passed these colours spread over the film, and the films in the natural environment were affected the most, as can be seen in the following pictures of the films taken after 12 weeks. The colours may be due to certain microbes growing on the films.

**Scanning Electron Microscopy (SEM).** The surface morphology of the 50 wt% PCL blend film had changed after biodegradation, as is evident from the following figure. A number of holes ~1 μm in diameter were seen on the fractured surface of the blend due to the PCL rich phase being degraded. In addition, the SEM photomicrographs of the surface show evidence of filamentous microorganisms whose hyphae adhered to the polymer surface even after cleaning treatment.



a b

Figure 5. SEM microphotographs of the fractured surface of 50% PCL blend a) before and b) after degradation.

***b) Microbial Degradation.*** The microbial degradation test was carried out with PCL rich films. Figure 6 shows the percentage weight loss after being placed in the bacterial cultures of *Bacillus subtilis* and *Escherichia Coli.* Each set of data is the average of two replicates. These data show that the blends with a higher percentage of PCL degraded most, followed by 90%, 70% and 50 wt% PCL. Degradation was minimal in the beginning. This can be explained in terms of the surface smoothness. During film casting the side that was exposed was rough and the side touching the glass was smooth; therefore, the microbial attack was not the same on both sides of the films. The rough side was degraded more than the smooth surface. The percent weight loss increased as the incubation period increased. Since PVB is tough and gives smooth film upon casting, this may explain why the %wt loss decreases with increasing PVB content in the blend although the percentage of blended PCL increases. Weight loss was seen with all the blends, which is a clear indication that degradation was taking place.

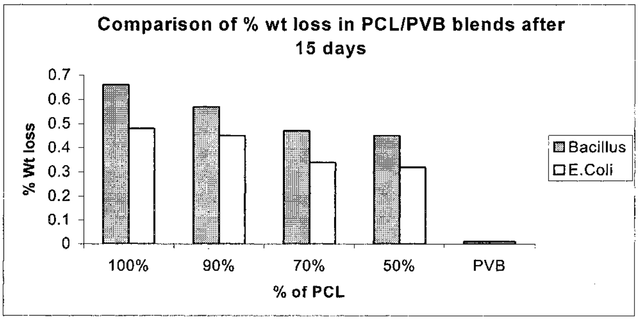


Figure 6. Biodegradation of the blends in the bacterial strains.

## Conclusion

Infrared spectroscopy and optical microscopy showed that blends of PCL/PVB were both in the amorphous phase at concentrations 30wt% and less of PCL at room temperature but in two phases over 40 wt% PCL. This conclusion is based on the fact that the blends were not optically clear and FTIR derivative spectra showed peaks for crystalline and amorphous phases. However, FTIR spectra of the blends with low concentration of the polyester showed a shift in the carbonyl stretching band from 1724 $cm^{-1}$ to 1734 $cm^{-1}$.

The biodegradation of PCL/PVB blends has been investigated by recording the mass and physical appearance of the films left in the soil. The results indicate that the PCL/PVB blends are biodegradable and the rate of biodegradation increases with the percentage of PCL in the blends. Further work is in progress to find out the effect of temperature and moisture content of the soil on the rate of biodegradation of these blends.

## Acknowledgement

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[1] M.F. Koenig, S. J. Huang, *Polymer* **1995**, *36(9)*, 1877.

[2] R. Miettinen, *Poly(ε-caprolactone)*: Manufacture, Properties and Applications. Government Research Announcements and Index. 1990, p. 29.

[3] F. Kazuhiko, "*Biodegradable Polymers and Plastics*", M. Vert, J. Feijen, A. Albertsson, G. Scott, E. Chiellini, Eds., The Royal Society of Chemistry, England 1992. p. 173.

[4] G. Biresaw, C.J. Carriere, *J. Appl. Polym. Sci.* **2002**, *83*, 3145.

[5] M. Yasin, B. Tighe, *J. Biomaterials* **1992**, *13*, 9.

[6] C. Bastioli, A. Cerutti, I. Guanalla, G. Romano, M. Tosin, *J. Environ. Polym. Degrad.* **1995**, *3*, 81.

[7] C. D. Kesel, C. V. Wauven, C. David, *Polym. Degrad. Stab.* **1997**, *55*, 107.

[8] T. Hirotsu, A.A.J. Ketelaars, K. Nakayama, *Polym. Degrad. Stab.* **2000**, *68*, 311.

[9] C. Lefevre, A. Tidjani, C. V. Wauven, C. David, *J. Appl. Polym. Sci.* **2002**, *83*, 1334.

[10] F. Lefebvre, A. Daro, C. David, *J. Macromol. Sci, Pure Appl. Chem.* **1995**, *A32*, 867.

[11] F. Lefebvre, C. David, C. Vander Wauven, *Polym. Degrad. Stab.* **1994**, *45*, 347.

[12] H. Nishida, Y. Tokiwa, *J. Environ. Microbiol.* **1993**, *1*, 227.

[13] H. Tsuji, A. Mizuno, Y. Ikada, *J. Appl. Polym. Sci.* **1998**, *70*, 2259.

[14]. D.F. Varnell, J.P. Runt, M.M. Coleman, *Macromolecules* **1981**, *14*, 1350.

[15]. P. Musto, L. Wu, F.E. Karasz, W.J. MacKnight, *Polymer* **1991**, *32*, 3.