

Biodegradation Study of poly (ϵ -caprolactone)/poly(vinyl butyral) Blends

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ABSTRACT

Blends of poly (ϵ -caprolactone) (PCL) with poly(vinyl butyral) (PVB) were studied for biodegradation in soil and the results of the investigation are reported. Films of PCL/PVB blends of different compositions were buried in soil in the laboratory and in the outside environment. The films were examined for any changes in the physical appearance and mass loss every week. Electron microscope of some of the films was recorded to see changes on the surface of the films.

1 INTRODUCTION

Due to the increasing environmental concerns about plastic waste pollution, biodegradable polymers are now attracting much attention from researchers and industries. In the recent past many researchers have reported that biodegradable polymers can be degraded effectively into non-toxic water soluble oligomers and carbon dioxide by the action of different microorganisms in the environment through several metabolic pathways (Amin *et al.*, 2002). Besides solving the environmental waste-problem, biodegradable polymers have also found application in other spheres of life, which range from medical to industrial applications (Chandra and Rustagi, 1998; Goodwin *et al.* 1998 and Calandrelli *et al* 2000).

Biodegradable polymers are of two origins: native and synthetic. Native biopolymers include proteins, polysaccharides, nucleic acid and lipids. Synthetic biodegradable polymers have resulted from extensive research and development, for example polymers containing hydrolysable backbone polyesters. Aliphatic polyesters have been recognized as one of the most environmental friendly biodegradable polymers. Microorganisms are also used to produce biodegradable polymers and often biodegradable additives are used to promote environmental degradation, for example starch in polyethylene (Amass *et al.* 1998).

PCL is one of the very few synthetic polymers which has been found to be biodegradable (Koenig and Huang, 1995; Miettinen, 1990 and Kazuhiko, 1992). It is linear polyester with a low melting point of 60°C and has poor mechanical properties. It is often blended with other polymers to improve its mechanical properties. A large number of polymers have been blended with PCL and properties of the resulting blends have been studied using various experimental techniques (Varnell and Coleman, 1981; Clark *et.al.* 1991; Varnell *et al.* 1981). The blends of PCL with starch, poly(hydroxy styrene) PHS, poly(hydroxy butyrate) PHB and poly(hydroxy butyrate-co-valerate) PHB-HV studied for biodegradation demonstrated the blends to be biodegradable and exhibit improved thermal properties

(Takagi *et al.* 1994). While many investigators using various techniques have studied PCL blends, blending PVB and PVF with PCL has not been investigated to a significant extent.

Microbe enzymes present in soil accelerate biodegradation of aliphatic polyesters by surface erosion. When the blend films undergo hydrolysis through main chain scission, weight loss of the film will take place, which becomes detectable when water-soluble oligomers produced by microbes diffuse into the surrounding soil (Tsuiji *et al.* 1998).

This paper investigates the biodegradation study of blends of poly (ϵ -caprolactone) with poly(vinyl butyral) in soil inside the laboratory (controlled conditions) and outside environment (natural condition).

2 MATERIALS AND METHODS

The polymers were purchased from Aldrich Chemicals and used without further purification.

2.1 Preparation of the Films

Solution cast films of PCL and PVB were prepared by initially making 5% solutions of the respective polymers in dichloromethane. The solutions were kept overnight to ensure complete dissolution. 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 the oven at 50°C for several days to remove residual solvent or water.

2.2 Preparation of soil

Soil was dug from open space near the School of Pure and Applied Sciences (SPAS) car park. The soil was sieved in a sieve with 2-mm mesh size. Maximum water holding capacity of the soil was calculated as follows:

$$\text{Maximum water holding capacity} = W_a/W_b \times 100$$

where W_a is the maximum water the dry soil can hold and W_b is weight of dry soil after drying in oven. The

experiments in the laboratory were carried out at a water content which was 50% of the maximum water holding capacity.

2.3 Degradation Test

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 everyday to maintain the water content. The samples were also buried outside in the open space near the SPAS car park to compare the biodegradation rate with that inside the lab. The biodegradation was studied by:

- Measuring the mass of the samples every week
- Visual observation of the films

2.4 Scanning electron microscopy.

The phase morphology of the polymer blends was investigated using Philips XL30S FEGC scanning electron microscope at 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.

3 RESULTS

3.1 Mass loss.

The following figures (Figure 1a and 1b) show percent weight loss after being placed in the respective environments. Each 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% PCL blends showed evidence of biodegradation. Weight loss is a clear indication that degradation was taking place.

From the figures it can also be concluded that biodegradation in the natural environment was faster than biodegradation inside the laboratory. The average weight loss in the blend with 50% PCL in the laboratory was 27% while the weight loss in the same period in the natural environment was 38%. The biodegradation was faster in natural environment possibly due to better conditions for the microbes to grow, and some additional factors may have affected the biodegradation rate.

3.2 Visual observation

The samples were harder when they were removed from the soil. After one week 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

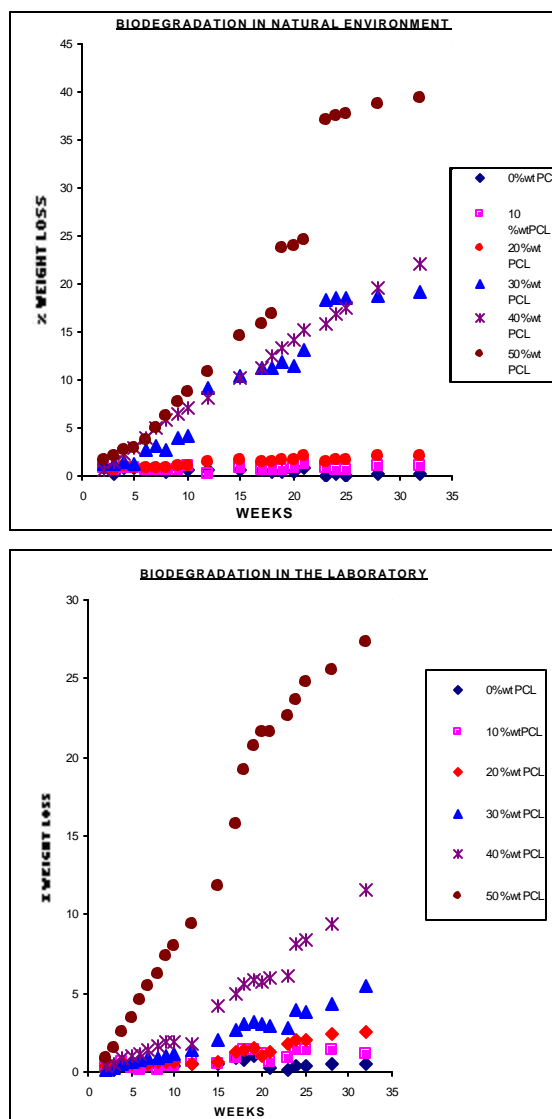


Figure 1 Biodegradation of the blends a) in the laboratory b) in the natural environment.

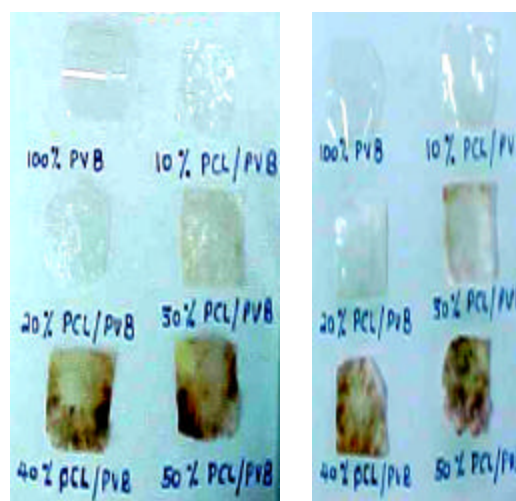


Figure 2 Photographs of the films after 12 weeks. a) in the lab b) in the natural environment.

most as can be seen in the pictures of the films taken after 12 weeks (Fig. 2).

This supports the results obtained from the determination of the weight loss. On the 0, 10 and 20 % PCL films no such colours were observed, but they had hardened. 30 – 50% PCL films also crinkled. The colours may be due to certain microbes growing on the films, or due to production of biodegradation product.

3.3 Scanning Electron Microscopy

The following figure shows the SEM of pure PVB film before and after degradation. It is obvious that there are no change in the morphology of the film.

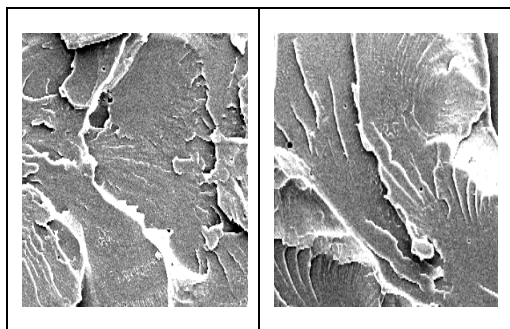


Figure 3 SEM of PVB at 2000x magnification a) before and b) after biodegradation

However, the surface morphology of the 50% PCL blend film has changed after biodegradation as is evident from the following Figure. A number of holes $\sim 1\mu\text{m}$ in diameter were seen on the fractured surface of the blend due to the PCL rich phase being degraded. Moreover, the SEM micrographs of the surface show evidence of filamentous microorganisms whose hyphae adhered to the polymer surface even after cleaning treatment.

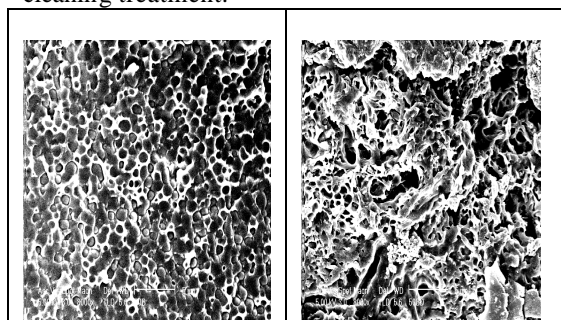


Figure 4 SEM photographs (8000x) of fractured surface of 50% PCL blend before and after degradation.

4 CONCLUSION

The biodegradation of PCL/PVB blends have 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 rate of biodegradation increases with the percentage of PCL in the blends. Further work is in progress to find out effect of

temperature and moisture content of the soil on the rate of biodegradation of these blends.

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