

Performance of cellulose acetate propionate in polycaprolactone and starch composites: biodegradation and water resistance properties

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ABSTRACT

Introducing starch into some polymers such as polycaprolactone (PCL) has been used to produce biodegradable plastics. The existence of a derivative of cellulose such as cellulose acetate propionate (CAP) with starch and PCL combinations might affect the degradation rate of starch when only mixed with PCL. To check whether this was the case, different investigations such as enzymatic degradation, composting trial and water resistance performance over a wide range of different compositions of such composites were studied. It is deducible that the use of cellulose acetate propionate can improve the performance of such composites without a big significantly changing their whole biodegradability. It was found that the presence of cellulose acetate propionate improved the water resistance properties which enable such composites to be used in the packaging industry.

Keywords: Starch; polycaprolactone; biodegradable polymers; cellulose acetate propionate; enzymatic degradation, water resistance and composting trial.

1. INTRODUCTION

Starch is a low-cost biopolymer obtained from renewable resources and can produce a variety of products with good properties when processed with different kinds of polymers to enhance its biodegradable features [1-6]. Lot of products of food and non-food articles can be made from starch-based polymers using the present manufacturing techniques [7, 8]. It has been proved that the mixing of starch with PCL can improve film formation and promotes its biodegradation [9]. Polycaprolactone has been used with starches from many sources such as corn,

wheat and sago. The composites have been made using granular, non-granular or thermoplastic forms of starches [10-14]. Esters of cellulose are products derived from natural polymers and are useful in different applications [15].

The present paper illustrates different investigations of the biodegradation behavior and water resistance performance of polycaprolactone, starch and cellulose acetate propionate composites.

2. MATERIALS AND METHODS

2.1. Materials.

Poly-ε-caprolactone, PCL, (Mw=80.000), (Aldrich), Hylon - a starch with high amylose - (National Starch), cellulose acetate propionate, CAP, (Acros Organics), the enzymes amylase (from *Aspergillus*) and lipase (from *Mucorjavanicus*) (both from Fluka Biochemika), were all used as supplied.

2.2. Preparation of the PCL/CAP/starch composites.

During this work, different experiments were done at a different temperature range from 80 °C to 150 °C, different rotor speed range from 30 rpm to 50 rpm and different hydraulic pressure range in the compression moulder from 5 MPa to 20 MPa. Previous work on composites has typically worked with similar temperature and pressure ranges [16-20]. The best conditions to give good homogeneous mixtures and good moulded sheets were at 130 °C, 50 rpm and 10 MP. Components proportions were mixed together in the dry solid states. Composites were prepared in a Brabender mixer model PL 2200 with 50 rpm and 15 minutes of 130 °C. At 10 MPa hydraulic pressure for 10 minutes at 130 °C each composite was moulded as 10 cm x 10 cm x 1 mm sheets. For simplicity, the way the weight percentage of each component is reported here is x% A - y% B -

z% C where A, B and C are the components and x, y and z are corresponding to the weight % in each composition as shown in table 1. In each case, PCL added with starch and then the starch was progressively replaced with CAP until starch and CAP had equal shares. Since the aim of this work was to research high-starch composites, compositions in which CAP had a higher content than starch were not investigated.

2.3. Measurements.

2.3.1. Enzymatic degradation (hydrolysis).

The specimens tested were 0.5 mm thick and prepared by compression moulding using a hydraulic press. The sheets were cut into squares (20 mm) and dried in an oven with vacuum at 40 °C to constant weight. Each sample was placed in a bottle containing 5 ml of phosphate buffer solution (pH = 7.2) with 5 ml of enzyme (amylase or lipase) and sealed. The bottles were incubated at 37 °C for 96 hrs. After incubation samples were removed, washed with fresh water and dried to constant weight. The degree of degradation was estimated from the percentage weight loss in the test specimen with time.

2.3.2. Composting trial.

The specimens tested were 1 mm thick and prepared by compression moulding using a hydraulic press as described above. The sheets were cut into squares (40 mm × 40mm) and dried in an oven with vacuum at 40 °C to constant weight. The specimens, having the same initial shape (i.e. the same surface to exposure to the biodegradation treatment), were buried inside the containing mature compost made from autoclaved municipal solid waste using a seed mixture of compost made from green waste (garden waste). The compost was held in a 240 litre laboratory composter (picture 1) at room temperature with a minimum air flow rate. The degree of maturity of the compost meant that the temperature was never significantly above room temperature (25 ± 2) °C. Samples were removed, washed and dried to constant weight. The degree of degradation was referred to as the weight loss percentage.

Table 1. Composites compositions.

Code	composition (%) by weight		
	PCL	Starch	CAP
C-1	20	80	0
C-2	20	70	10
C-3	20	60	20
C-4	20	50	30
C-5	20	40	40
C-6	20	0	80
C-7	40	60	0
C-8	40	50	10
C-9	40	40	20
C-10	40	30	30
C-11	40	0	60
C-12	60	40	0
C-13	60	30	10
C-14	60	20	20
C-15	60	0	40
C-16	80	20	0
C-17	80	10	10
C-18	80	0	20

2.3.3. Water Resistance.

The samples were dried in an oven with vacuum at 40°C until a constant weight then immersed in water at room

temperature, removed at specific intervals, gently blotted using tissue paper to dry any water on the surface, and then weight was recorded.

This process was repeated at several time intervals up to 60 days (initially every 2 days and then every 5 days). In order to ensure no leaching had occurred, different compositions were dried on completion of the test and compared after weighting against the original sample weight. The water resistance percentage of samples was determined by using the equation below [21].

$$\% \text{ water uptake} = (W_w - W_i) / W_i \times 100\%$$

Where W_i is the initial weight of the sample and W_w is the weight of the wet sample at different times.



Picture 1. Bin used for composting trial, with air supply system.

3. RESULTS

3.1. Enzymatic degradation.

The weight loss for uncompatibilized and compatibilized composites with amylase and lipase enzymes after 96 hours is shown in Table 2.

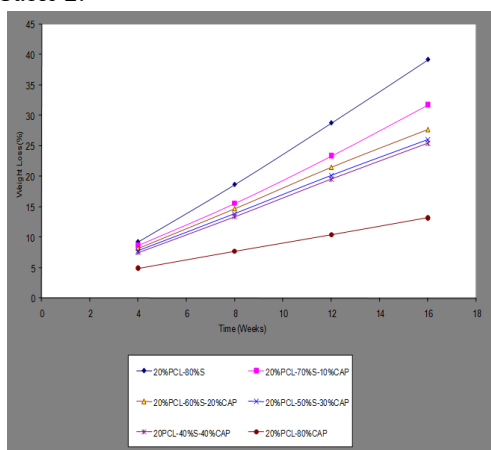


Figure 1. Composting trial of 20% PCL composites.

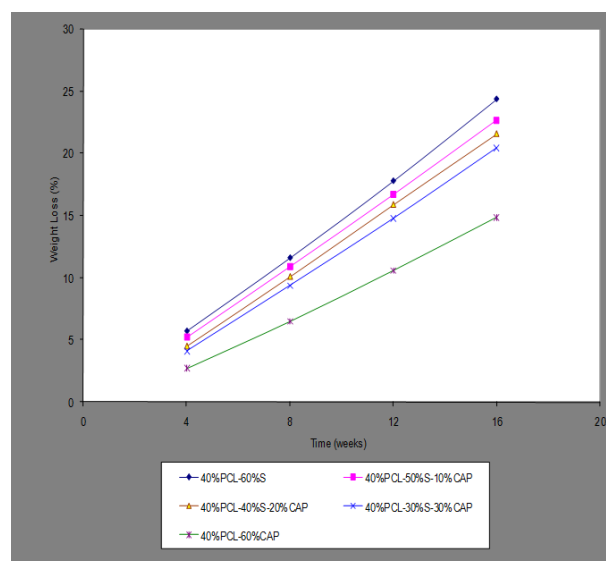


Figure 2. Composting trial of 40% PCL composites.

It can be seen that in the case of amylase enzyme, the weight loss decreased with the reduction of starch content from 80% to 60%, 40%, and 20% in the composites. Amylase is a fungal, exo-splitting enzyme that attacks 1, 4- and 1, 6- glucoside linkages in starch. The branching points, however, are hydrolyzed at a slow speed. The enzyme's action releases glucose which causes the complete conversion of polysaccharides into glucose. The weight loss increases with the increase of starch content, this is because the enzyme selectivity hydrolyzes starch so, enzyme activity increases with the increase in starch content [22].

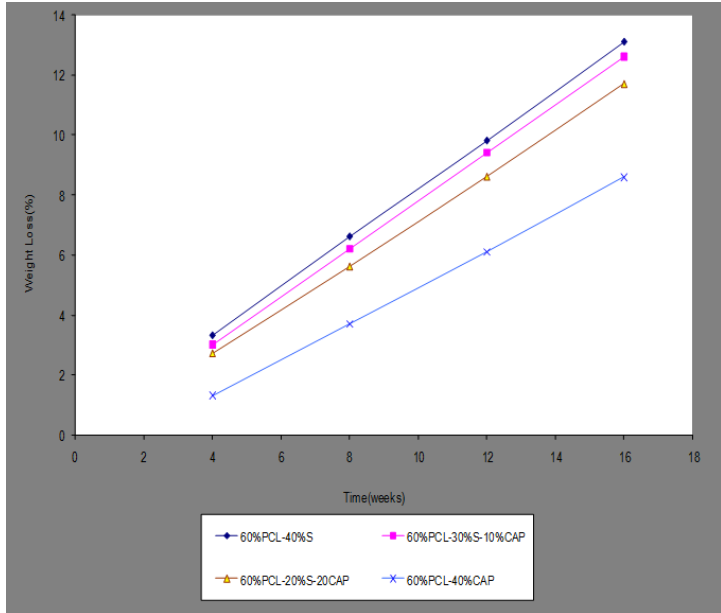


Figure 3. Composting trial of 60% PCL composites.

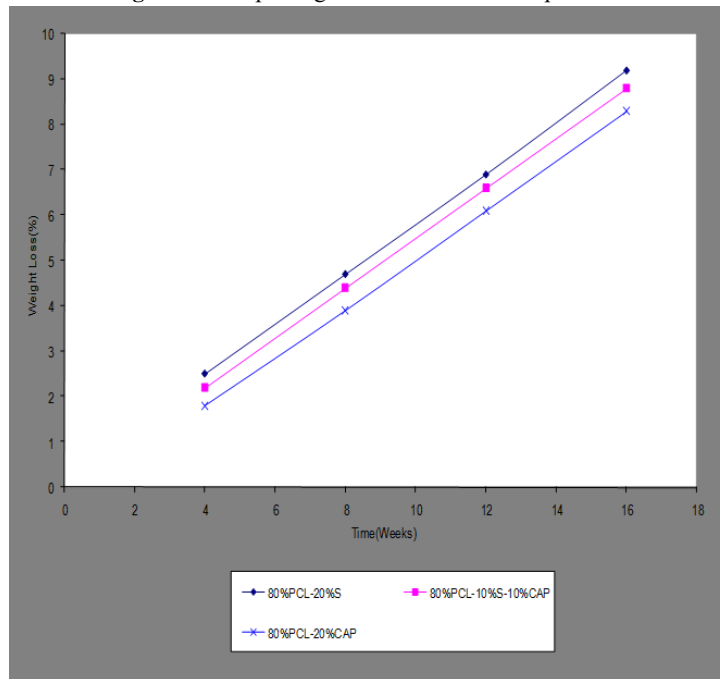


Figure 4. Composting trial of 80% PCL composites.

Also, it was found that composites containing different amounts of CAP undergo considerable weight loss indicating that the presence of CAP enhances the biodegradability of such composites.

This can be because of CAP improves the adhesion between polycaprolactone and starch and increases the compatibility among the components of each composition and affects biodegradable properties. Lipases enzymes can degrade

polycaprolactone in a very short time via degrading the ester bonds of macromolecular chains in a random way. The mechanism for the hydrolysis of the ester bonds is suggested to form an acyl-enzyme intermediate and then hydrolyzed to give fatty acid and enzyme regeneration [23]. In the case of lipase enzyme, it was found that the weight loss increased when the content of PCL increased from 20% to 40%, 60% and 80%, this may due to the enzyme activity which increases with the increasing of ester content, and may be for this reason the weight loss of the composites containing CAP in case of lipase enzyme is higher than in case of amylase enzyme.

3.2. Composting.

The temperature in the bin was kept at the room temperature to avoid the effect of higher temperatures on the polymer composites. Samples were introduced to the compost test and the weight loss % was evaluated at different intervals during the process of biodegradation. Figures 1 to 4 show the weight loss data for the different polymer composites.

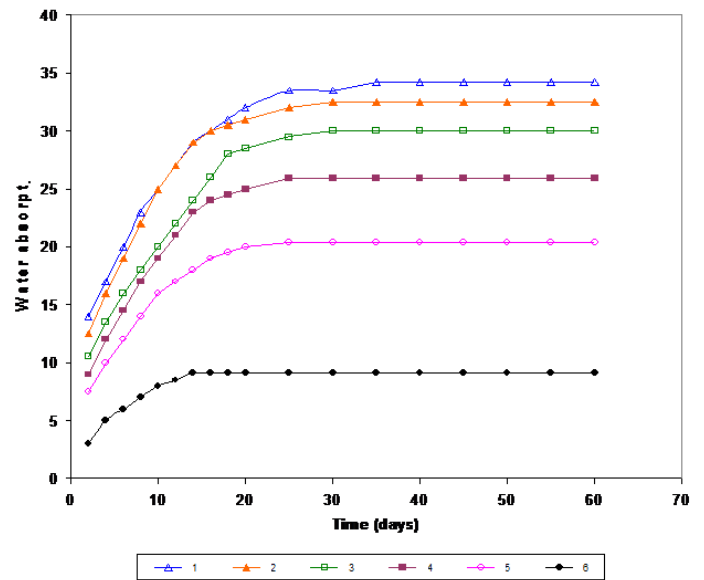


Figure 5. Water absorption behaviour of: C-1 C-2 C-3 C-4 C-5 C-6

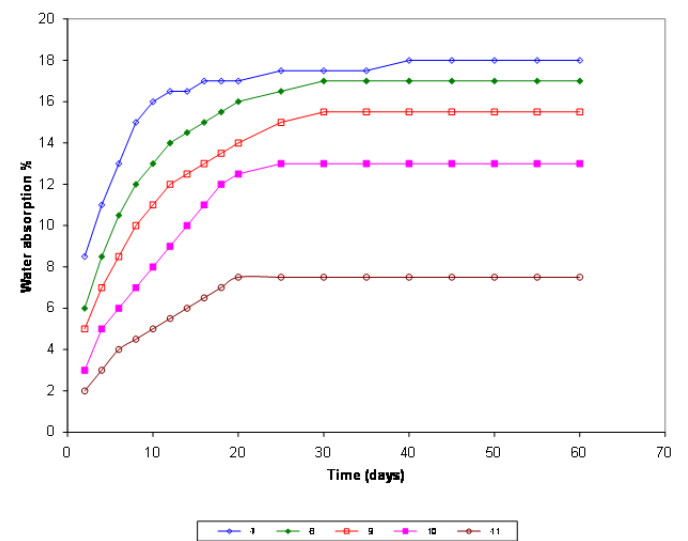


Figure 6. Water absorption behaviour of: C-7 C-8 C-9 C-10 C-11

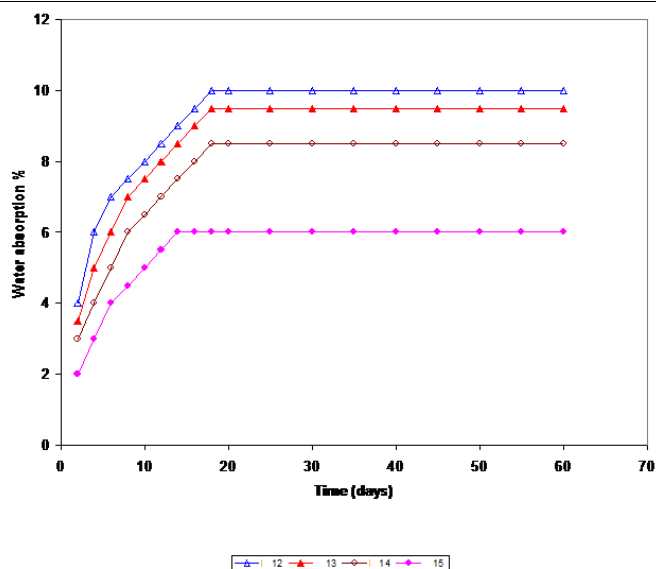


Figure 7. Water absorption behaviour of:
C-12 C-13
C-14 C-15

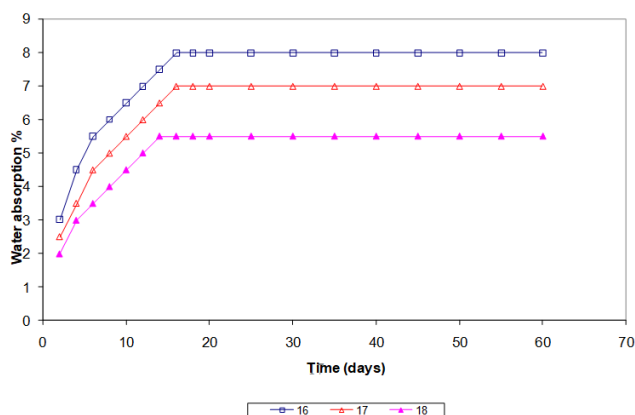


Figure 8. Water absorption behaviour of:
C-16 C-17
C-18

The weight loss % decrease from 39.2 for 20% PCL-80%starch to 24.4 for 40% PCL-60%starch, 13.1 for 60% PCL-40%starch and 9.2 for 80% PCL-20%starch which means that the degradation decreases with the decreasing of starch content; this is because the microorganism’s activity in the compost increases with the increasing of starch content which used as microorganism’s food. The compost test performed on PCL/starch compatibilized composites indicated that the presence of cellulose acetate propionate enhance the biodegradability of the composites where the weight loss % decrease from 39.2 for 20% PCL-80%starch to 31.8 for 20% PCL-70%starch-10CAP, from 24.4 for 40% PCL-60% starch to 22.7 for 40% PCL-50% starch-10% CAP, from 13.1 for 60% PCL-40% starch to 12.6 for 60% PCL-30% starch-10% CAP and from 9.2 for 80% PCL-20% starch to 8.8 for

80% PCL-10% starch-10% CAP. This may be due to CAP acts as a compatibilizer which generates an interaction between the components of such composites and enhances their biodegradability.

Table 2. Weight losses (%) with amylase and lipase enzymes after 96 hours.

Composite	Weight Loss %-Amylase	Weight Loss %-Lipase
C-1	30.1	21.6
C-2	29.9	21.8
C-3	29.4	21.8
C-4	23.8	21.9
C-5	23.4	21.9
C-6	8.8	21.2
C-7	24.6	23.8
C-8	24.5	23.8
C-9	22.7	23.7
C-10	22.1	23.8
C-11	8.5	23.4
C-12	19.5	26.5
C-13	19.4	26.6
C-14	15.1	26.7
C-15	6.9	26.2
C-16	14.2	27.8
C-17	10.8	27.6
C-18	6.4	27.3

3.3. Water Resistance.

The characteristics of water absorption of different composites are shown in figures (5-8). It has been found that the equilibrium water absorption for composites depended on the content of starch. The equilibrium water absorption decreased from 34.2 for 20% PCL-80% starch to 18.0 for 40% PCL- 60% starch, 9.9 for 60% PCL- 40% starch and 8.0 for 80% PCL-20% starch. The equilibrium water absorption decreased with the decrease in starch content because of the hydrophilic nature of starch. Water absorption tendency is one of the major drawbacks in the use of starch in polymer composites and any limitation to water absorption is highly appreciated. The hydroxyl groups in starch suggest forming hydrogen bonds with water and thus composites containing high starch content absorbed more water. The moisture resistance of starch was improved by mixing with hydrophobic biodegradable polymers such as polycaprolactone (water absorption % = 5.5±0.5 after 14 days) [14] so, the composites which have high PCL content have significantly better water resistance because of its hydrophobic nature. The composites which included cellulose acetate propionate absorbed less water than those of PCL/starch composites because CAP acts as a compatible partner between the components of such composites and decreases the overall equilibrium water absorption of PCL/CAP/starch composites.

4. CONCLUSIONS

We expect these composites materials, that is, biodegradable plastics, to be useful as one method of solid waste-management although cellulose acetate propionate enhances the biodegradability of these composites. It can be seen the use of cellulose acetate propionate (CAP) in composites of PCL/starch can improve the performances without a big significantly changing their whole biodegradability. Also, it was found that the

presence of cellulose acetate propionate (CAP) reduced the amount of water absorbed and improved the water resistance properties of these composites. These environmentally compatible materials are characterized by less cost than the neat PCL and display good requires of disposable plastic.

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