

Mechanical and thermal properties of promising polymer composites for food packaging applications

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Abstract. Blending starches with biodegradable polycaprolactone (PCL) was used as a route to make processable thermoplastics. When developing biodegradable polymer composites it is important to use high concentrations of starch for legislative and cost reasons. The addition of starch has a significant effect on all physical properties including toughness, elongation at break and the rheological behaviour of the melt. To enhance the physical properties, we used cellulose acetate propionate (CAP) as a cellulose derivative with high amylase starch and PCL blends. It is suggested that the PCL/starch/CAP blends are partially miscible. It was found that the yield tensile strengths of most PCL/Starch/CAP blends were higher than that of pure PCL itself. There was a big difference between glass transition temperature values of PCL/Starch/CAP blends and the pure PCL glass transition temperature which indicates that no phase separation occurs. Addition of CAP to starch and PCL blends improved the mechanical and thermal properties even at high content of starch.

1. Introduction

Polycaprolactones (PCLs) are a particularly promising class of biodegradable polymers for blending with starches as they are readily available on an industrial scale. PCL is a biodegradable polymer with very high flexibility, and films of polycaprolactone have been reported to have an elongation and tensile strength at break more than 1000% and 32 MPa [1]. These values are very high compared with the elongation and tensile strength at break of a non biodegradable polymer such as low density polyethylene which has values in the range 500-725% and 9.7-17.2 MPa respectively [2]. PCL has melting point (~ 60 Celsius) which makes some processing routes difficult e.g. film production and the range of applications of PCL-based polymers and blends made using PCL is limited because of their low softening temperature [3]. Reducing the amount of expensive PCL employed through mixing with starch reduces its cost. Cellulose esters are thermoplastic materials used in films, moulded products, and fibres. In general cellulose esters are used in applications need good properties at temperatures above 60°C e.g. modulus and tensile strength [4]. To achieve good properties (modulus and tensile strength) in the temperature range 60 -120°C requires the components of a blend to have appropriately high softening and melt temperatures.

This paper reports the results of the mechanical and thermal properties of a range of different compositions of polycaprolactone, starch and cellulose acetate propionate.



2. Experimental& characterization

2.1. Materials&preparation

Polycaprolactone (Mwt=80,000), (Aldrich), Hylon VII - a high amylose starch (National Starch) and cellulose acetate propionate (Acros Organics), were all used as supplied. PCL, CAP and starch were first mixed in the dry solid states in known proportions and the blends were prepared using Brabender mixer model PL2200 at 50 rpm for 15 minutes at 130 °C. Each component was compression moulded into 10cm x 10cm x 1mm sheets at a hydraulic pressure of 10 MPa for 10 minutes at 130 °C. All blend compositions were produced on a weight basis of the components. The different blends and their content of PCL, starch and CAP are shown as a percentage by dry weight in Table 1.

The percentage of PCL was 20, 40, 60 and 80% and the starch%being progressively replaced against CAP% until both have equal proportions. As the aim of this work was to study high-starch blends, compositions in which CAP had a higher percentage than starch were not investigated.

2.2. Differential scanning calorimetry (DSC)

Thermal analysis of the materials has been done using a Perkin Elmer DSC(Pyris1) equipped with a liquid nitrogen cooling accessory. The DSC was calibrated using indium. For each measurement, a sample weight of about 8 mg was placed in an aluminium pan and heated from 15 °C to 150 °C (10 °C/min) then quenched to 15 °C (20 °C/min) and heated again to 150 °C (10 °C/min). The melting points, the heat of fusion (the melting heat) and the degree of crystallinity were determined after two scan cycles by taking the average of the two values.

2.3. Dynamic mechanical & thermal properties

Dynamic Mechanical & Thermal Properties(DMTA) measurements were made using Rheometrics Solids Analyser, Model RSAII, in the rectangular torsional mode at 2°C/min and 1Hz (heating rate and frequency). The dimensions of specimens were 50.0 × 5.0 × 1.0 mm

Table 1. Blend Compositions (%) by weight

Blend codes	PCL	Starch	CAP	Blend codes	PCL	Starch	CAP
PCL	100	0	0	B-10	40	30	30
CAP	0	0	100	B-11	40	0	60
B-1	20	80	0	B-12	60	40	0
B-2	20	70	10	B-13	60	30	10
B-3	20	60	20	B-14	60	20	20
B-4	20	50	30	B-15	60	0	40
B-5	20	40	40	B-16	80	20	0
B-6	20	0	80	B-17	80	15	5
B-7	40	60	0	B-18	80	10	10
B-8	40	50	10	B-19	80	0	20
B-9	40	40	20				

2.4. Mechanical Properties

Tensile tests were made using an Instron, Model 5564 using dumb-bell shaped specimens in accordance to the recommended ASTM standard method (D638) [5]. The deformation rate employed was 10mm/min at 25°C. Prior to the tensile tests, samples were adjusted at $50 \pm 5\%$ relative humidity for 72 h at room temperature in a closed chamber with hydrated calcium nitrate solution (in accord with American Society for Testing and Materials Standard E104).

3. Results & discussion

3.1. Thermal analysis properties

Due to the low melting point of PCL, It is difficult to process it by traditional techniques for thermoplastic polymers. For example, films produced using blowing technique are sticky during processing [6]. We can overcome this difficulty by blending it with starch and CAP. The melt temperature of starch is about 230 °C [6], so it helps to overcome PCL stickiness problems during extrusion when processed at high temperatures. For PCL, the recorded values of melting temperature (T_m) were 55.7 °C, 57.8 °C, 59.9 °C. These give mean equals to 57.8°C and a standard deviation $S = 1.69$. To determine the confidence limits (error or uncertainty), we use the student's t-test parameters $t_{2,0.05,2}$ with 95% confidence, such that $T = \text{mean} \pm t_{2,0.05,2} \times S/(n)^{1/2}$ where n is the number of measurements (n=3 in this case and $t_{2,0.05,2} = 4.3$).

Table 2. Thermal analysis data for the different blends

Code	T_m	$\Delta H_x(\text{J/g})$	$X_c\%$	Code	T_m	$\Delta H_x(\text{J/g})$	$X_c\%$
PCL	57.8±4	59.4	43.7	B-10	53.3±4	20.3	14.9
B-1	57.1±4	17.8	13.0	B-11	-----	-----	-----
B-2	55.9±4	17.6	12.9	B-12	57.7±4	37.3	27.4
B-3	54.3±4	16.7	12.3	B-13	56.9±4	36.8	27.1
B-4	-----	-----	-----	B-14	56.5±4	35.5	26.1
B-5	-----	-----	-----	B-15	55.3±4	33.6	24.7
B-6	-----	-----	-----	B-16	57.8±4	47.5	34.9
CAP	-----	-----	-----	B-17	57.7± 4	46.9	34.5
B-7	57.5±4	28.2	20.8	B-18	56.9±4	46.3	34.1
B-8	56.3±4	26.0	19.1	B-19	55.6±4	44.4	32.6
B-9	54.7±4	23.2	17.0				

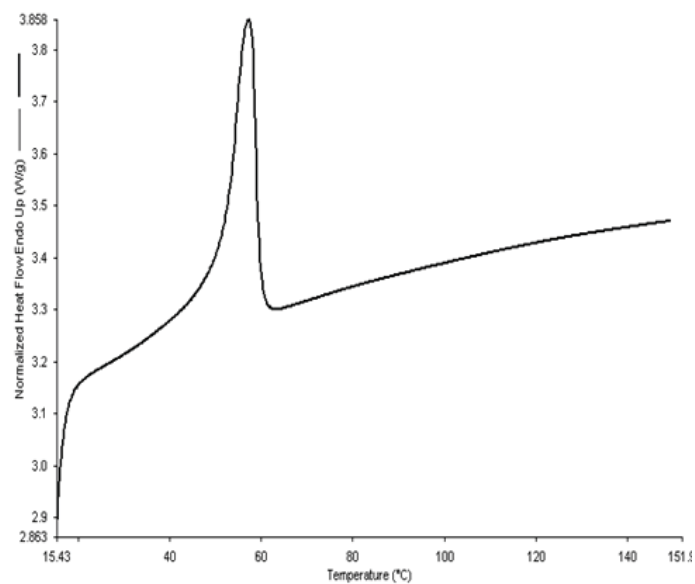
Crystallinity percentage ($X_c\%$) was calculated as a ratio of $\Delta H_x / \Delta H_m$ where ΔH_x is the fusion enthalpy of PCL in the blend and ΔH_m for the hypothetical perfect crystal of PCL ($\Delta H_m = 136 \text{ J/g}$) [7].

The main thermal parameters, melting temperature (T_m), and percentage of crystallinity ($X_c\%$) for the different samples tested are recorded in Table 2. The melt temperatures (shown in Table 2) of all the PCL/Starch blends were nearly similar to the melting temperature of pure PCL indicating a phase separation which normally found in non-miscible polymers. Similar results were also indicated by other researchers [8]. It was found that the melt temperature T_m decreased with increasing of CAP content. This is may be due to the amorphous nature of CAP which decrease the crystallinity content of PCL and lower the melting temperatures. Figures 1 and 2 show the DSC thermograms for pure PCL and pure CAP and some blends after the second heating scan which shows typical outputs obtained with these mixtures. Figure 1a for pure PCL shows a single melting endotherm which indicates that the PCL sample is a semi-crystalline polymer. Figure 1b represents that CAP does not undergo a melting phase transition, and the thermogram is characteristic of an amorphous polymer with a high T_g (102.8°C). The peaks of some blends could not be determined due to the high content of amorphous CAP compared to PCL content.

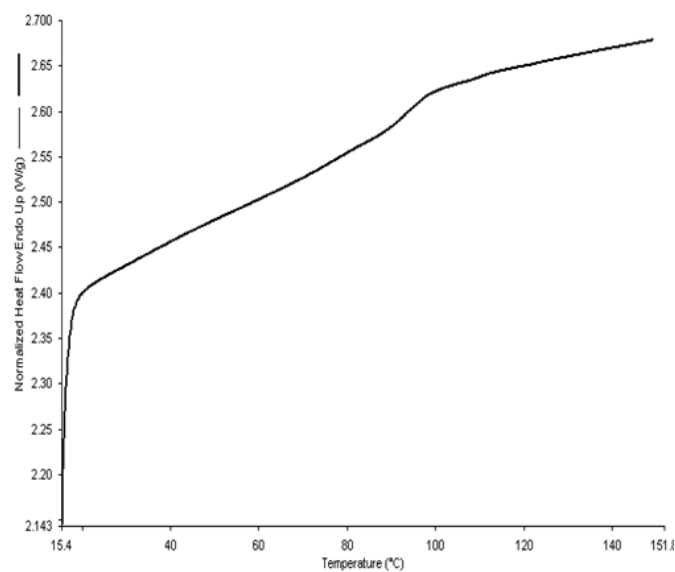
The noticeable decrease in the melting point of all blends which contained CAP indicated that no phase separation occurred in those blends and CAP may act as a compatibilizer which lowers the melting temperatures, the melt viscosity and makes them easier to be processed. It will be useful in practice to study the compatibility between the components of these blends because it may control physical properties of such blends which affect their end use. Dynamic Mechanical Thermal Analysis (DMTA) was used to evaluate the compatibility between different components.

3.2. Dynamic Mechanical Thermal Properties

The glass transition temperatures for different composites with different CAP contents are shown in Table 3. There is a slight difference between T_g values of PCL/Starch blends and the PCL glass transition temperature indicating a phase separation found in all non-miscible polymers. Other researchers found same results [8]. On the other hand, there is a big difference between T_g values of PCL/Starch/CAP blends and the PCL glass transition temperature which indicates that no phase separation occurs in such blends. The presence of other components in the blend has a great effect on the primary nucleation of the crystallizing component [9]. The effect of the other polymers on the nucleation of the crystallizing component depends on the chemical properties of the polymer, its miscibility, its ability to crystallize and blend composition. When the polymers are miscible, the energy barrier to form a critical nucleus in the blend is greater than that of the homopolymer [10]. Therefore, the nucleation activity of heterogeneous nuclei in the blend decreases with increasing the concentration of the other components. The results of crystallinity percentage of PCL indicated that the crystallization of PCL-starch-CAP blends decreased by the addition of CAP. This is may be due to the amorphous nature of CAP as the CAP prohibited the movements of the polymer segments. The melting temperature and crystallinity percentage depressions are associated with miscibility [11]. These results suggested that the PCL/starch/CAP blends are partially miscible. Glass transition temperatures of all PCL/Starch blends values were nearly around PCL glass transition temperature which means that starch did not affect PCL glass transition temperature. On blending PCL/Starch with CAP, there was a change in the glass transition temperatures values which indicates that CAP acts as a compatibilizer between PCL and starch due to the existence of hydroxyl groups (in starch and CAP) and ester carbonyls (in PCL and CAP) [12].



(a)



(b)

Figure 1.DSC curves for: (a) PCL (b) CAP

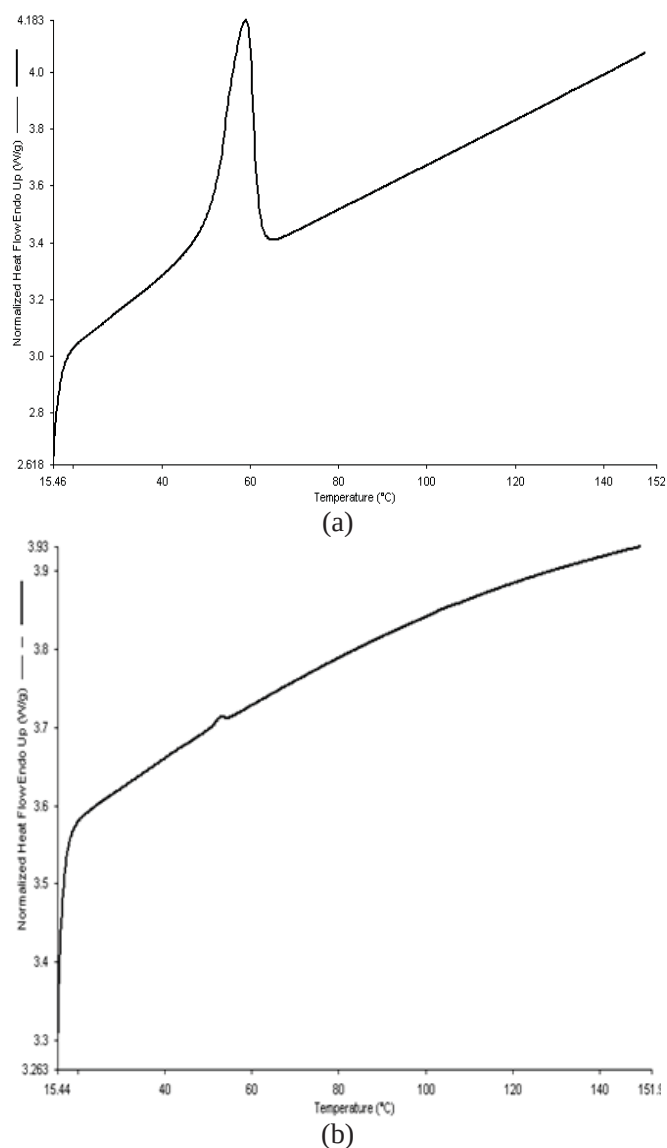


Figure 2. DSC curves for: (a) B13(b) B4

There is an interaction between PCL, CAP, and starch. This interaction binds them more strongly with each other than PCL/Starch blends components which give these blends better mechanical properties than PCL/Starch blends and can be used in some packaging and domestic applications such as plastic bags, trays, wash bottles, cutlery, flower pots and foodstorage.

Table 3.Glass-transitions temperatures

Blend	T _g	Blend	T _g
PCL	-53.9±4	B-10	-11.4±4
B-1	-53.5±4	B-11	-5.5±4
B-2	-22.3±4	B-12	-53.8±4
B-3	-12.3±4	B-13	-29±4
B-4	-9.4±4	B-14	-21.4±4
B-5	-7.9±4	B-15	-15.4±4
B-6	-1.4±4	B-16	-53.9±4
B-7	-53.7±4	B-17	-44.1±4
B-8	-25±4	B-18	-36.3±4
B-9	-15.9±4	B-19	-28.5±4

3.3. Mechanical Properties

Tensile strength at yield (σ_y), at break (σ_b) and elongation at break (ϵ_b) were calculated from stress-strain curves (Figure 3 as an example). By comparing the results obtained for binary blends of PCL/starch with the tensile properties data for PCL/starch/CAP blends, increases are noticed as well as significant increases in the elongation at break. In PCL/starch composites, the mechanical incompatibility of the two phases was great and increased with the starch content. As the starch content increased, the tensile strength and elongation at break of blends decreased. This decrease for the binary blends of polycaprolactone and starch could be due to the phase separation between the hydrophobic PCL and the hydrophilic starch. The higher the degree of phase separation, the lower the mechanical properties of the resulting blends [13-15]. It is suggested that CAP improved the compatibility and the interfacial adhesion between polycaprolactone and starch [16-18]. Mechanical properties of polymer blends depend on chain stiffness of the individual polymers and the intermolecular forces [19]. The mechanical properties of PCL/starch/CAP composites represented the polymer chains interactions during blending. Yield stress determines the maximum stress that could be borne without permanent deformation in the consideration of materials for packaging [19]. It was found that the tensile yield strengths of most PCL/Starch/CAP blends were higher than yield tensile strength of pure PCL itself. This is may be due to the existence of an interaction between these blend components. The values of tensile yield strength and tensile strength at break are quite high compared with non biodegradable material such as low-density polyethylene (LDPE) [2]. LDPE used in different applications such as trays and for general purpose containers such as those used in food storage. Many of these products require flexibility such as plastic bags, tubing and dispensing bottles. Most of these applications can be made by using these different blend compositions of PCL/Starch/CAP with consideration of their physical properties.

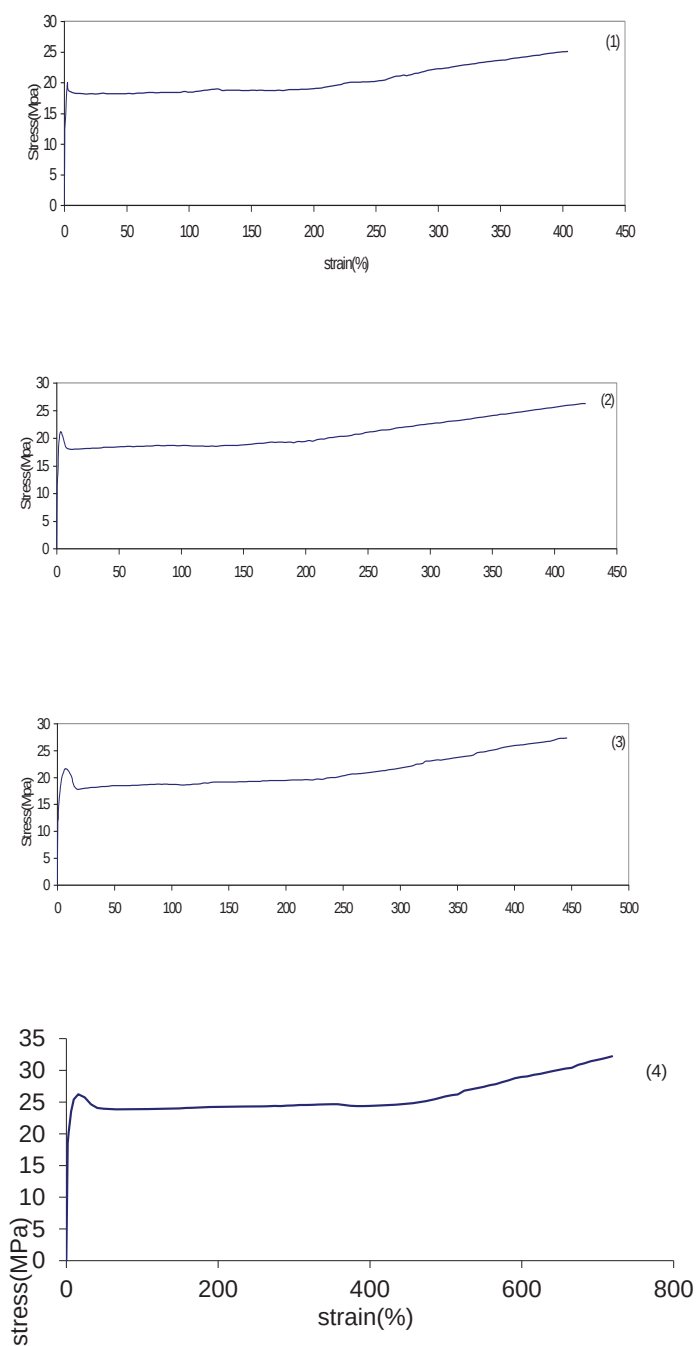


Figure 3. Stress-Strain curves of: (1) B 12 (2) B 13 (3) B 14 (4) B 15

4. Conclusion

A significant decrease in mechanical properties was noted at a starch high content with PCL; this is may be due to incompatibility between PCL and starch which has been reported by other workers. On blending CAP with starch and PCL, there was an improvement in most mechanical and thermal properties even at a high content of starch; this may be due to CAP acting as a compatibilizer between PCL and starch which prevents the phase separation between the components of the blends. The mechanical properties of the blends were enhanced by adding CAP, which could induce the best intermolecular adhesion between PCL and starch and govern the interaction between the components of such blends.

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