

Processing of biodegradable blends of wheat gluten and modified polycaprolactone

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Different compositions of wheat gluten (65% and 75%) and polycaprolactone (PCL) were melt blended in a twin screw extruder. PCL was modified to incorporate a functional group that could interact with the functional groups on the protein. These samples were then injection moulded to obtain test samples whose tensile and flexural properties were obtained. Results indicate that a small amount of anhydride modified polycaprolactone in the blend improved the physical properties of these blends over those of simple mixtures of wheat gluten and polycaprolactone. These blends have a narrow window of processability. Up to 75% by weight of wheat gluten could be incorporated into the blends without adversely affecting the tensile properties. However, elongations decreased significantly at these levels of gluten. Weldline strengths ranged between 50 and 75% of the non-weldline strengths and decreased with increase in gluten content. Storage at high humidity and low temperature (freezer), or dry and elevated temperature conditions (oven), did not affect the physical properties of the blends. They could be re-ground and reused without any appreciable loss in properties. Dynamic mechanical spectroscopy was used to obtain information on the respective phases and the significance of G' and G'' as a function of temperature and frequency are discussed. Both G' and G'' for the compatible blends were an order of magnitude higher than blends containing simple mixtures. Morphology of the blends using an optical microscope indicate a two-phase system with PCL as the continuous phase and gluten as the dispersed phase. At such high gluten content the moulded samples absorbed around 40% by weight of water within 7 days. The mechanism of water uptake is discussed. Average oil absorption was less than 0.5% for a 20-day period. The samples were found to be biodegradable under aerobic conditions. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The use of low-cost natural polymers such as proteins and starch from crops can be considered beneficial to US agriculture. The utilisation of agricultural products in plastics application is considered by many as a possible future avenue for usage of surplus US farm products. In the seventies, the Japanese successfully demonstrated the usefulness of a variety of fermentation carbohydrate polymers as commodity plastic substitutes¹. However, agricultural products outside of food and animal feed areas have not received wide acceptance.

Because of the persistence of petrochemical-based plastic material lasting beyond its functional life, a major waste disposal problem is facing modern society. Research to alleviate pollution and litter problems include efforts to develop plastics that degrade more rapidly in the environment. Plastic formulations that degrade chemically as a result of exposure to sunlight have been developed². However, most of our waste is either stored in landfills or composted. For either of these two disposal techniques, biodegradation phenomena is more relevant. Most of the natural polymers are biodegradable. Similarly, aliphatic polyesters such as polycaprolactone (PCL), polylactic acid (PLA) and copolymers of poly(hydroxybutyrate-co-valerate) (PHBV) are also biodegradable. Therefore, the use of these materials as a substitute for non-biodegradable synthetic polymers can be considered to be environmentally

beneficial.

There is considerable interest in replacing some or all of the synthetic plastics by biodegradable polymers in many applications. While agricultural materials are abundantly available and cheap, their physical properties are the primary drawback as substitutes for plastics. The materials are hydrophillic, have very high viscosity, and are difficult to mould without the addition of high levels of plasticisers. Aliphatic polyesters such as PCL, PLA and PHBV on the other hand, are very expensive (costs are between \$2 and \$5/lb) and are not cost competitive with commodity plastics such as polystyrene and polyolefins. Blending of natural polymers with polyesters is a possibility. Several research groups^{3–15} have concentrated on the development of blends of natural polymers such as starch and synthetic polymers. The synthetic part of the blend may¹⁵ or may not be biodegradable^{8–14}, thus leading to fully or partially biodegradable materials.

Most natural polymers are hydrophillic and are not miscible with synthetic hydrophobic polymers. The poor interfacial adhesion in the blends of such polymers results in inferior mechanical properties. Compatibilisers have to be used to improve the properties. In non-reactive blending, the constituents are blended in the presence of preformed block or graft copolymers that act as compatibilisers. Alternately, two polymers with a functional group capable of reacting during the blending process can form a block or graft copolymers *in situ* which makes the blend more compatible and may improve the properties.

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Natural polymers such as proteins possess a highly complex structure. Amino acids, the monomeric units of proteins, are linked by a single peptide bond. Irrespective of the protein structure, the end groups of the protein molecule have an amine group at one end and a carboxyl group at the other. Hence, proteins may be considered to be functionalised polymers. Gluten is a mixture of several proteins in which gliadin, glutenin, globulin and albumin predominate. It is the largest protein fraction in wheat and represents about 8–15% of the dry weight of the grain. Polyesters such as PCL are hydroxyl terminated for stability and as such, cannot react with the amine or carboxyl group of proteins. Hence, these polyesters would have to be modified to introduce suitable functional groups capable of reacting to the amine or carboxyl group on the gluten.

Anhydride is a reactive functional group that can be incorporated in synthetic polymers by copolymerisation or grafting of compounds like maleic anhydride. References are available where maleic anhydride is used as a monomer grafted onto polypropylene, polyethylene and various other polymers^{16–18}. In a previous paper¹⁹, the grafting of maleic anhydride monomer to PCL was reported. This anhydride functional polyester can be used in reactive blending with proteins. Reaction of anhydride with amine is expected to occur under suitable conditions. The objective of this work is to report the various properties of blends of gluten and anhydride modified PCL. The gluten content was fixed at 65 and 75% by weight. A small percentage (2.5 wt%) of anhydride functionalised PCL was used as a compatibiliser. The tensile and flexural properties, water absorption, phase morphology using microscopy and dynamic mechanical spectroscopy, and biodegradability were evaluated.

MATERIALS AND METHODS

Materials

Polycaprolactone resin grades 787 and 767 (commercially available as TONE Polymer) were obtained from Union Carbide Chemicals and Plastics Co. Inc., Bound Brook, NJ. Maleic anhydride (99%) and Dicumyl peroxide (98%) were obtained from Aldrich Chemical Co. Gluten was donated by the Manildra Milling Corporation of Minnesota.

Grafting

The detailed procedure for grafting maleic anhydride onto a PCL backbone can be found elsewhere¹⁹. Briefly, maleic anhydride was grafted to the PCL backbone using dicumyl peroxide as the initiator. The grafting reaction was accomplished in an extruder. The graft content was determined using back titration²⁰. FTi.r. and n.m.r. were used to confirm the presence of grafted maleic anhydride on

the PCL backbone. Intrinsic viscosity and gel permeation chromatograph of the grafted material (PCL-MA) were also measured and compared to PCL. Only PCL-787 was modified using this technique.

Blend preparation

Blends were prepared continuously in an extruder. The extruder used in the blending was a laboratory-scale twin screw with co-rotating screws (Rheomex TW-100, Haake Instruments, Paramus, NJ). The barrel length to diameter ratio was 20:1 and the extruder was divided into three zones for temperature control. The materials were extruded through a capillary die. A torque meter attached to the extruder was used to monitor the torque continuously. Two blend compositions were prepared, one containing 65% gluten and the other containing 75% gluten by weight; the remaining materials were a mixture of PCL-MA and PCL. The samples were mixed in a Hobart mixer and fed into the extruder. The first zone temperature was set at 60°C, while the second and third were each held at 110°C. The die temperature was set at 90°C. Extrusion was carried out at a screw speed of 60 rpm. The resulting extrudate was in the form of a rope and had a smooth texture. The minimum residence time ranged from 30–45 s. The extruded samples were pelletised for further processing.

Moulding

Injection molding was accomplished in a 50-ton Boy injection moulding machine. The pelletised extrudate of the prepared blend was injection moulded to form ASTM D-638-68 Type I dog bone specimens approximately 3 mm thick. Tensile test specimens could be formed by injecting into the cavity from one end (single-gated) or both ends (double-gated). With double-gating, the test specimen had a weldline at the centre. A melt pressure transducer (PT 449 Industrial Sensors Inc., MA.) was flush mounted at the centre of the cavity to record the variation in cavity pressure with time. The mould temperature was maintained constant by a circulating water bath. For 65% gluten blend, the mould temperature was kept constant at 35°C, while for the 75% gluten blend the mould temperature was kept constant at 45°C. The various processing conditions used are summarised in Table 1.

Properties

For each processing condition, the samples were moulded using a standard dog bone-shaped mould as per the specifications of ASTM test method D638, and using a bar shaped mould for flexural test as per specification of ASTM test method D256. For tensile testing, the cross-head speed was 3 mm/min. For flexural testing, the cross-head speed was 9 mm/min. The definitions of the parameters are

Table 1 Processing conditions for gluten/PCL blends

Gluten (%)	Extrusion processing					Injection moulding			
	Pressure (MPa)	Torque (N-m)	Flow rate (g/s)	SME ^b (kJ/kg)	rpm	Temperature (°C)	Melt temp./mould temp.	rpm	IP/BP (bars)
65	18.5	50	1.13	278	60	60/110/110/90	110/45	80	160/50
75	22.1	55	1.25	277	60	60/110/110/90	110/45	80	145/80
65 ^a	11.2	33	2.99	69	60	60/110/110/90			
75 ^a	13.1	32	2.66	76	60	60/110/110/90			

^a Non-reactive blends

^b SME (Specific Mechanical Energy) = $\frac{\text{Torque (N-m)} \times \text{angular velocity (s}^{-1}\text{)}}{\text{throughput (kg/s)}}$

outlined in the above ASTM test methods. Stress is the measured force per unit cross-sectional area of the sample. Percentage elongation is the ratio of the change in the gauge length at any time to the original gauge length of the sample. The gauge length at any time was calculated from the time elapsed since the start of the test and the cross-head speed. Tensile and flexural moduli were determined from the initial linear portion of the stress-strain curve. Samples were conditioned at room temperature for 48 h before testing. In addition, the tensile strength of both blends were evaluated after storing in a freezer (-10°C) and in an oven (50°C) for a duration of 7 days. Test samples from storage studies were allowed to reach room temperature before testing.

Water and oil absorption

Tensile bars were used for water and oil absorption studies. The moulded strips of the blends were vacuum dried for one week at 50°C (below the melting temperature of PCL) and -90 kPa pressure, weighed, and immersed in water or oil at room temperature. The samples were then removed at specific intervals, gently blotted with tissue paper to remove the excess water on the surface, and the weight recorded. This process was repeated at several time intervals. For each condition, two samples were used to check the reproducibility of the results.

Leaching

Since PCL has a low melting temperature (63°C) there is a possibility that some of the polymer might leach out when used at temperatures above its melting point. The injection moulded samples were dried in a vacuum oven to a constant weight in order to remove any moisture. These dried samples were then kept in a constant temperature (65 , 70 , 75°C) water bath for 5, 10 and 15 min. The samples were taken out, blotted with paper, and the weight noted. It was then dried in a vacuum oven at 50°C and -90 kPa pressure to get a constant weight. The difference between the final dried weight and the initial dried weight was used to determine the percentage of material leached.

Dynamic mechanical analysis

Blend samples were molded into rectangular parallelepipeds of $2 \times 12 \times 50$ mm dimensions. A Rheometrics Mechanical Spectrometer (RMS-800) was used to evaluate the dynamic mechanical properties such as loss modulus (G''), storage modulus (G'), and loss tangent ($\tan \delta$). The samples were subjected to a sinusoidal strain in the torsion mode. The percentage strain and the frequency during temperature sweep were 0.1% and 1 rad/s, respectively. The temperature was increased at the rate of $10^{\circ}\text{C}/\text{min}$. Each sample was analysed in duplicate. In addition, a temperature/frequency sweep was done at a fixed strain of 0.1% with temperature starting from -50°C and ending at 50°C with a temperature ramp of 10°C . Time-temperature effect was superposed to obtain a master curve by shifting the different temperature values along the time or frequency axis.

Optical microscopy

The morphology of the blends was examined to study the effect of processing conditions and distribution of components using an optical microscope. Thin sections (~ 0.2 mm) of the samples were obtained at -70°C using a Leica cryomicrotome and transferred onto optical microscope slides. These sections were stained twice,

first with fast green solution followed by a wash with distilled water and a second staining with an iodine/KI solution. The sections were observed under the microscope at $40 \times$ magnification of the object.

Bio-degradation

ASTM test method D5209 that determines the degree and rate of aerobic biodegradability of polymeric material in the presence of municipal sludge was used. The degradability of the sample was measured by the rate and amount of carbon dioxide produced by enzymatic breakdown of the polymer and subsequent metabolising into carbon dioxide and water.

RESULTS AND DISCUSSION

Wheat gluten consists of two major forms of proteins: glutenin and gliadin. On a dry-matter basis gluten contains 75–85% protein; the remainder is carbohydrate and lipid embedded within the gluten protein matrix. Proteins have carboxyl functional groups on one end and an amine functional group on the other end. PCL on the other hand is hydroxyl terminated. PCL is a linear synthetic polyester with a hydroxyl group present at each end of the polymer chain because the polymerisation of ϵ -caprolactone is initiated with a diol. PCL is hydrophobic and incompatible with natural polymers such as gluten. The hydroxyl groups cannot react with any of the functional groups on protein. Hence, a functional group such as maleic anhydride, capable of reacting with the amino group, was introduced by free-radical grafting. FTi.r. and n.m.r. analysis have confirmed the grafting of maleic anhydride monomer on PCL backbone¹⁹. G.p.c. and intrinsic viscosity results also indicated that the molecular weight and the intrinsic viscosity of the PCL(787)-MA is close to the values for PCL-787, indicating minimum or no chain scission during the grafting process. Similarly, the tensile strength and percentage elongation of the grafted polymer is similar to the ungrafted PCL-787.

Processing

The torque, pressure, and energy values recorded during processing for the various blends are summarised in Table 1. It is observed that the values are much higher when a small percentage of PCL-MA is included in the blend. Note that when PCL-MA is included in the blend, the unmodified PCL is grade 767 while when there is no PCL-MA in the blend, PCL-787 is used. The viscosity of PCL-787 is eight times higher than the viscosity of PCL-767 at 100°C ²¹. Yet the torque required to extrude blends containing gluten/PCL-MA/PCL-767 are significantly higher (approximately 1.5 times) than that of gluten/PCL-787 for the similar ratio of natural to synthetic polymers. The specific mechanical energy (energy per unit mass) is five times higher for the reacted blends. Higher torque, pressures, and energy values are an indication of interaction or reaction between the anhydride group on the PCL to the amine group in the gluten. The processing temperature for gluten ranges between 90 and 120°C . At higher temperatures gluten tends to degrade. When PCL-MA is added to the gluten/PCL-787 blend, the viscosity of the blend increases significantly, thus increasing both the torque and pressure and making processing difficult. Similarly, as will be discussed later, injection moulding of gluten/PCL-MA/PCL-787 blends leads to imperfect parts.

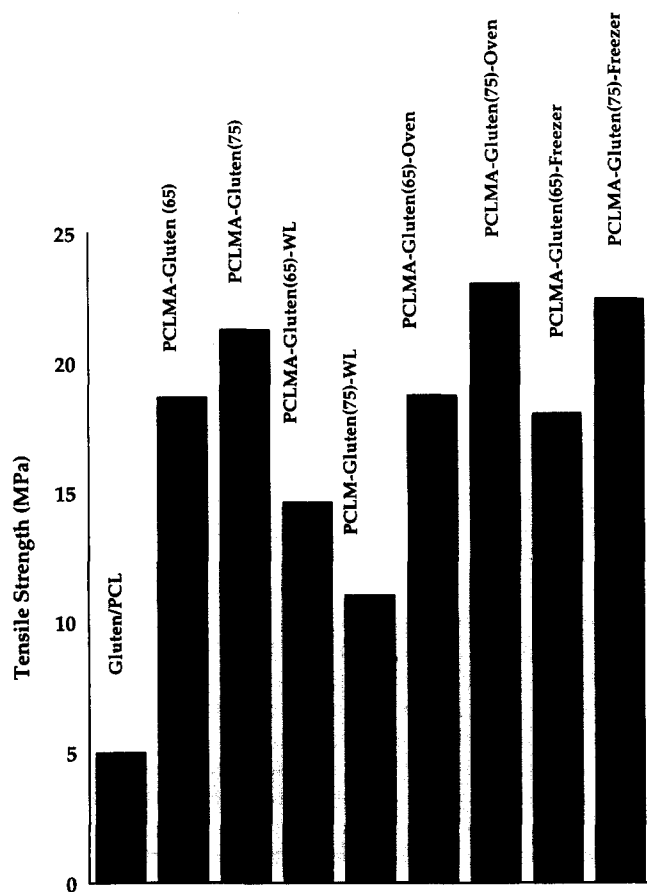


Figure 1 Tensile properties of blends

Tensile and flexural properties

Tensile strength of gluten-PCL blends are shown in Figure 1. When no compatibilisers (PCL-MA) are used, the tensile strength of the gluten (70)/PCL-787 (30) blend is approximately 5 MPa. The tensile strength of injection moulded PCL-787 is approximately 24 MPa. Addition of 2.5% PCL-MA improved the tensile strength of the blend significantly over simple mixtures (Figure 1). As mentioned before, when PCL-MA was added, PCL-787 was substituted

with PCL-767. A blend of gluten/PCL-MA/PCL-787 containing in excess of 60% weight of gluten was difficult to mould. The viscosity of the blend increased significantly and unless plasticisers were added, incomplete mould filling and jetting²² were observed at the maximum injection pressure (16.5 MPa) that was allowable with the machine, indicating that the flow rate was too low. Addition of plasticisers led to complete mould filling but resulted in materials with lower tensile strength and higher elongation. Increasing the mould temperature increased the degree of fill but still did not result in complete filling. Both the improvement in the tensile strength and increased viscosity of gluten/PCL blends containing compatibiliser over blends of simple mixtures would indicate the interaction between the anhydride group on the PCL and the amine group on gluten. The percentage elongation of the blends decreased drastically from 1000% for pure PCL to between 4 and 8% of blends containing 65 or 75% by weight of gluten.

The weldline properties of the blends are also shown in Figure 1. Weldlines are formed when two melt streams meet. These weldlines are always weaker in tension and flexural stress than samples without weldlines. Both the tensile strength and the percentage elongation of weldline samples decreased as compared to non-weldline ones. This decrease was higher for blends containing 75% by weight of gluten as compared to those containing 65% by weight of gluten. The average weldline tensile strength and percentage elongation for the blend containing 65% gluten were 80 and 75%, respectively, of that of the non-weldline samples. For the blend containing 75% gluten, the tensile strength and percentage elongation were 55 and 60%, respectively, of that of the non-weldline samples. The weldline strengths of gluten samples are lower than the weldline strengths of starch/synthetic polymer blends containing the same amount of natural polymers. The flexural strength of the blends follows the same trend as the tensile strength (Figure 2). The average weldline flexural strength for blends containing 65 and 75% gluten were 84 and 50% respectively.

The high viscosity of the melts can interfere with proper knitting at the weldline front. In addition, the inability of compressed air to escape completely leads to weak joints

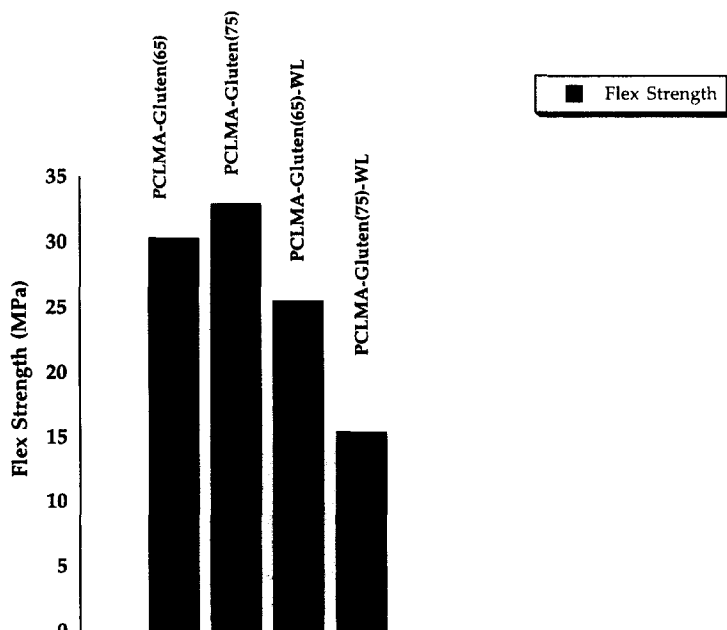


Figure 2 Flexural properties of blends

due to stress concentration. Generally, increased melt or mould temperature can improve weldline strength. However, the narrow processing temperature allowable for gluten makes it difficult to obtain improved weldline values for these blends. At temperatures higher than 120°C the gluten in the blend degraded with a pronounced burnt odour. Increasing the gluten content increased the tensile strength. Higher gluten content increased both the tensile and the flexural strength of the blends while the percentage elongation remained relatively unaffected.

The tensile strength of samples stored either in the freezer or in an oven did not vary from the freshly molded samples (Figure 1). Hygroscopic materials such as natural polymers absorb (or lose) moisture during storage and hence display significant variations in physical properties. No change in dimensions were observed after storing in the freezer or oven. Also, during injection moulding, the temperature gradient between the melt and the mould wall as well as the variation in density could lead to the development of thermal stresses. These stresses are reported to relax when annealed²³. The unusually small difference between the melt and the mould temperature probably led to minimal thermal stress development.

The effect of regrind on the properties of the blends are shown in Figure 3. The addition of regrind materials to the virgin polymer is important in the overall economics of the moulding process. Increasing the regrind content of both the 65 and 75% gluten blends from 20 to 100% gave essentially the same tensile strength as the original material. This is in sharp contrast to starch where between 25 and 35% regrind is permitted before a decrease in property is observed^{11,12}. Gluten is less susceptible to shear degradation than starch and hence the re-ground samples retain their properties.

Water and oil absorption

The water absorption for the two blends is shown in Figure 4. Samples from blends containing 75% gluten have a slightly higher equilibrium water uptake (40%) than those containing 65% gluten (32%). The higher gluten content samples also reached the equilibrium uptake faster (9 days) than those containing lower gluten content (14–17 days). There is a very sharp intake of water in the first few days. Approximately 70–80% of the equilibrium water uptake occurred in the first 3 days. Both samples showed significant mould growth during the duration of the experiment with

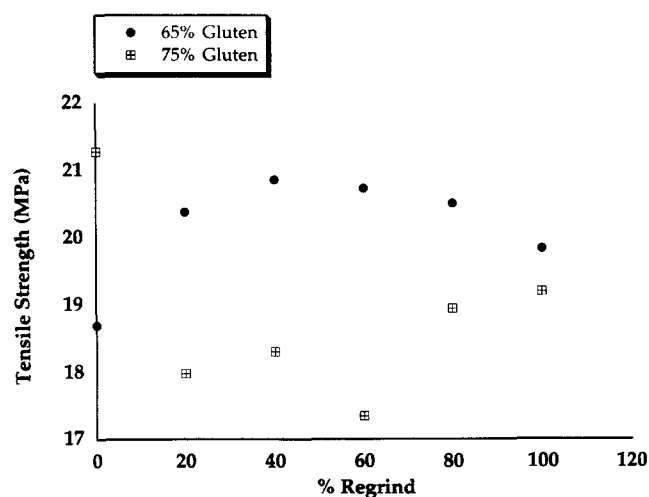


Figure 3 Tensile properties of blends as a function of percentage re-ground

most of the mould growth on the surface. When these samples were kept beyond the time required to reach equilibrium water uptake, a decrease in sample weight was observed indicating that some of the gluten from the surface was leaching out.

The equilibrium water uptake of the gluten blends are higher than blends containing starch and synthetic polymers and the time taken to reach equilibrium is faster than blends containing starch. Both starch and protein such as gluten, are biopolymers that have groups that can interact with water. The hydration of these biopolymers depends on the morphology and the molecular structure formed after processing. It is hypothesised that in starch, the hydroxyl group can interact with water while proteins which are composed of amino acids have not only the amino-group and the carboxyl-group, but also non-polar and ionic effects to interact with water. Carboxyl and amino groups are mainly responsible for binding with water. Gluten contains a large proportion of glutamic acid which has two carboxyl groups, one of which is free. During processing the protein molecule will be denatured due to the heat and stresses encountered in the processing equipment. Because of the unfolding of the protein molecule, it is speculated that these sites are exposed to the surface and hence have higher interaction with water. This leads to higher water absorption by gluten blends than by starch blends because gluten has more sites and stronger hydrophilic groups (glutamic acid residues) to interact with water.

The kinetics of solvent uptake for polymers can be described by the empirical relation given by

$$\frac{M(t)}{M_{\infty}} = kt^n \quad (1)$$

where $M(t)$ is the amount of water absorbed at time t , M_{∞} is the amount absorbed at long times, and k and n are constants. When the ratio of water uptake ($M(t)/M_{\infty}$) is proportional to $t^{0.5}$ then the mechanism is diffusion controlled. A logarithmic plot of the ratio of water to time gave slopes (n) that ranged between 0.5 and 0.6 for the blend containing 75% gluten, and between 0.76 and 0.96 for the blend containing 65% gluten. It appears that as the gluten content increases, the water uptake approaches diffusion controlled (or Fickian), while at lower gluten content the sorption mechanism is relaxation controlled. For $0.5 < n < 1$, the mechanism for penetrant transport is controlled both by diffusion and relaxation and is termed anomalous. Anomalous diffusion is complex and diffusion processes are affected by parameters such as history, orientation, and stress. The deviation from the Fickian process is speculated to be primarily due to the change in the polymer structure in response to the sorption of the penetrant molecules.

The diffusivity (D) can be calculated from the data for water uptake into a thin sheet using the solution to Fick's law (in one dimension). For a thin sheet of thickness L , and assuming a constant D and no swelling of the sample, the equation is given by²⁴

$$\frac{M(t)}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[\frac{-D(2n+1)^2 \pi^2}{L^2} t \right] \quad (2)$$

When the ratio is proportional to the square root of time, the diffusivity is given by²³

$$\frac{M(t)}{M_{\infty}} = \sqrt{\frac{16Dt}{\pi L^2}} \quad (3)$$

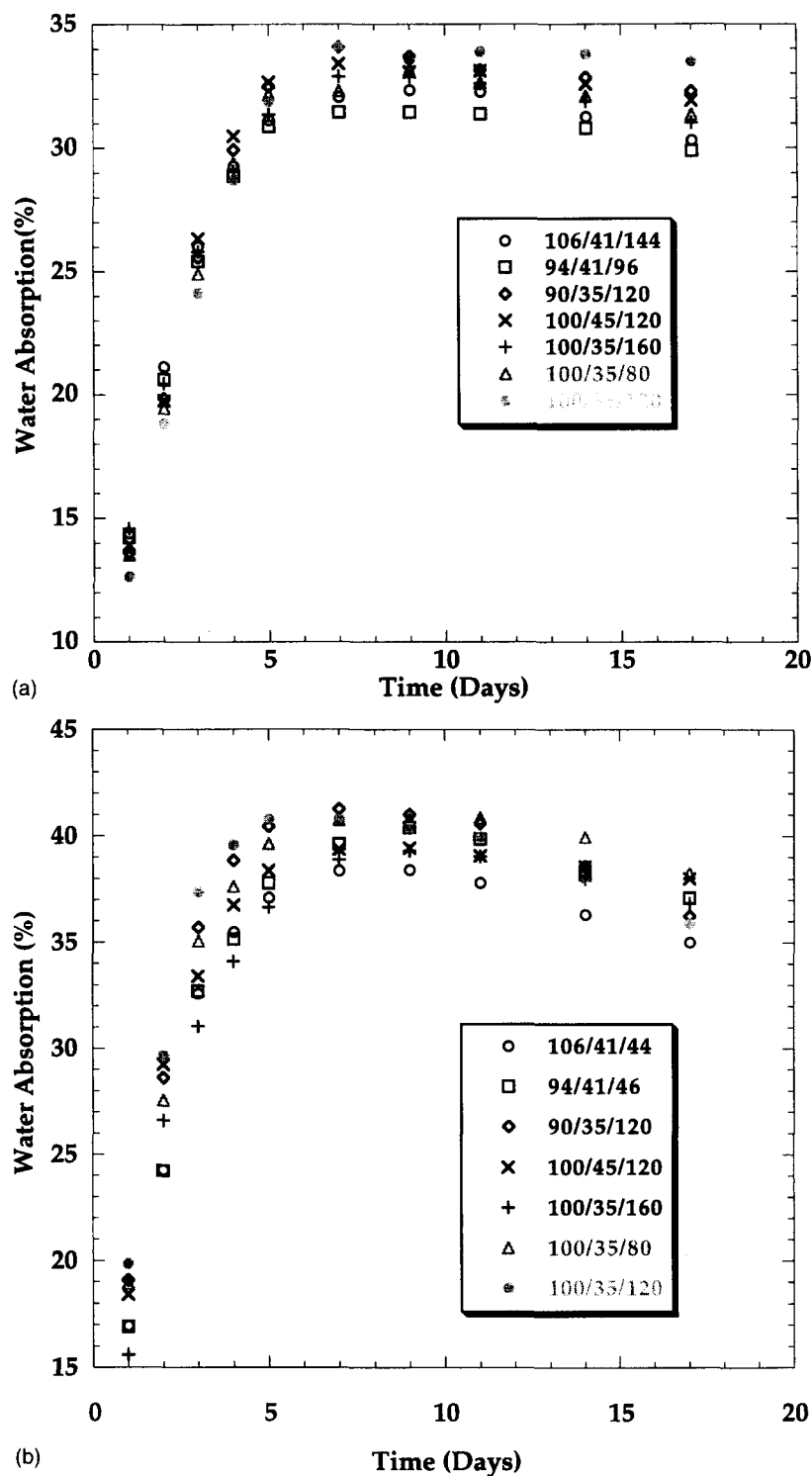


Figure 4 Water absorption of (a) 65% gluten blend and (b) 75% gluten blend as a function of processing conditions (barrel temperature (°C)/mould

The diffusivities for the 65% gluten blend were obtained using equation (2) and ranges between 6.5 and $9.2 \times 10^{-12} \text{ m}^2/\text{s}$, while that for the 75% blend and calculated using equation (3) ranges from 1.2 to $1.75 \times 10^{-12} \text{ m}^2/\text{s}$. It should be noted that the diffusion coefficient obtained is an average diffusivity over a range of concentrations that exist in the sample during the course of the experiments. The exact mechanism of diffusion is difficult to elucidate since the morphology is largely unknown. For blends existing in a co-continuous phase, connected pathways facilitate sorption of water molecules.

Oil absorption was less than 0.7% over a 20-day period. Under certain processing conditions (lower melt and mould

temperature), it was less than 0.25% over a 20-day period. The percentage of gluten did not influence the oil absorption.

Leaching

The results from the leaching experiment are summarised in Tables 2 and 3. Since PCL has a low melting point (63°C) there is a possibility that PCL might melt and diffuse during use at high temperature. Alternatively, gluten might also leach out because of its affinity to water. Three temperatures above the melting point of PCL were selected. In addition duplicate samples were immersed at three different times.

Table 2 Weight loss for 65% injection moulded gluten samples in hot water

Temperature (°C)	Initial weight (g)	Time in hot water (min)	Final dried weight (g)	Change in weight (%)
65	5.76	5	5.78	+0.35
	5.77	5	5.79	+0.35
	5.76	10	5.79	+0.52
	5.76	10	5.79	+0.52
	5.74	15	5.78	+0.70
	5.77	15	5.82	+0.87
70	5.77	5	5.78	+0.17
	5.77	5	5.77	+0.17
	5.77	10	5.78	+0.17
	5.77	10	5.78	+0.17
	5.77	15	5.78	+0.17
	5.76	15	5.77	+0.17
75	5.76	5	5.77	+0.17
	5.73	5	5.74	+0.17
	5.76	10	5.78	+0.34
	5.74	10	5.77	+0.51
	5.75	15	5.77	+0.34
	5.76	15	5.79	+0.51

Table 3 Weight loss for 75% injection moulded gluten samples in hot water

Temperature (°C)	Initial weight (g)	Time in hot water (min)	Final dried weight (g)	Change in weight (%)
65	5.80	5	5.73	-1.2
	5.79	5	5.73	-1.0
	5.79	10	5.72	-1.2
	5.77	10	5.70	-1.2
	5.79	15	5.72	-1.2
	5.75	15	5.68	-1.2
70	5.79	5	5.73	-1.0
	5.73	5	5.67	-1.0
	5.77	10	5.71	-1.0
	5.73	10	5.68	-0.87
	5.79	15	5.71	-1.4
	5.79	15	5.72	-1.2
75	5.79	5	5.72	-1.2
	5.80	5	5.73	-1.2
	5.81	10	5.72	-1.5
	5.79	10	5.72	-1.2
	5.78	15	5.71	-1.2
	5.80	15	5.73	-1.2

The samples containing 65% gluten did not indicate any loss in weight from the initial weight at each temperature. As seen from Table 2 it is observed that the samples had not dried out after 10 days in the oven. Drying for a longer duration did not seem to affect the final weight. The water in the beaker when visually examined did not indicate the presence of leached material unlike the case during the water absorption studies. The surface of the specimens also retained its gloss after the experiment.

The samples containing 75% gluten, on the other hand, indicated a small loss in weight at each temperature. The maximum weight loss was approximately 1.5%. Some leached material was observed in the water. It is not clear whether the loss was due to PCL leaching out because of the temperature exceeding its melting point or whether the gluten had leached out. The surface was rough and pale. Most of the loss in material would have happened from the surface. The samples tested were 3.5 mm thick and it is

unlikely that the entire sample had reached the melting temperature of PCL.

Dynamic mechanical analysis

Gluten is an amorphous polymer²⁵⁻²⁷. Both the gluten proteins, glutenin and gliadin, have glass transition curves similar to that of gluten²⁵⁻²⁷. The glass transition temperature (T_g) of gluten is a strong function of the plasticiser content. At water content of 2% the T_g is approximately 140°C while at water content of 16% the T_g drops to approximately 15°C. PCL is a semi-crystalline polymer with a $T_g \sim -50^\circ\text{C}$ and a melt temperature of 63°C. The temperature sweeps in the dynamic mechanical analysis (DMA) of PCL and the two blends are shown in Figure 5.

For both gluten compositions the temperature sweep showed two transition peaks: the first near -55°C which corresponds to the T_g of PCL and the second peak is around 66°C. The second peak is probably due to the melting peak of PCL. However, gluten has a T_g that is close to the second peak²⁶. It is possible that the T_g of gluten and the T_m of PCL overlap. A temperature sweep of pure gluten indicated a T_g of 80°C while a T_g of 70°C was obtained using a d.s.c.

It was impossible to continue the testing after the second transition as the magnitudes of G' and G'' dropped sharply below the sensitivity of the instrument. The magnitudes of G' and G'' are higher for the blends by an order of magnitude than for pure PCL (Figure 6). However, the blends have lower magnitudes of G' and G'' than pure gluten. Another interesting observation is that gluten/PCL blend without the compatibiliser has magnitudes of G' and G'' that are an order of magnitude below that of compatibilised blend (Figure 5). Also, note that the second peak in the temperature sweep plot for compatibilised blends occurs at a higher temperature than that of simple mixtures.

For the systems presented, the modulus decreases slowly with increased temperature. Near the glass transition region the value increases as the polymer becomes semi-rigid. After the material has undergone glass transition the G' becomes relatively independent of temperature due to the viscous flow of the material. Molecular weight does not affect the dynamic mechanical properties of polymeric materials below T_g as seen for PCL-767 and -787 which have molecular weights of 40 000 and 80 000 respectively. But for PCL-787 the slightly higher peak of $\tan \delta$ over PCL-767 is due to the entanglement of the polymer chain as the molecular weight increases. In the case of 65 and 75% gluten blends the magnitude of $\tan \delta$ is lower compared to that of the pure polymers. This indicates a measure of the rigidity of samples as the gluten content changes.

The frequency/temperature sweep for the blends and polymer were carried out at temperatures ranging from -40 to 50°C at a constant strain of 0.01%. The master curves were constructed by calculating the shift factor $a_T = \omega_s/\omega$ at the same G' value for different temperatures, where ω_s is the frequency from the reference curve (20°C) and ω is the frequency from any curve which has the same G' at the point ω_s . The time-temperature master curves are then obtained by shifting the values of G' along the x-axis. The corresponding shift factors (a_T) are given in Table 4. PCL-787 has the highest shift factor at all temperatures. At temperatures lower than the reference temperature, blends with 75% gluten have higher magnitudes of shift factors while at temperatures above the reference temperature, blends containing 65% gluten have a higher value. The range of shift factors is the highest for the blend containing 75% gluten (10^{-5} to 10^{12}) followed by PCL-787

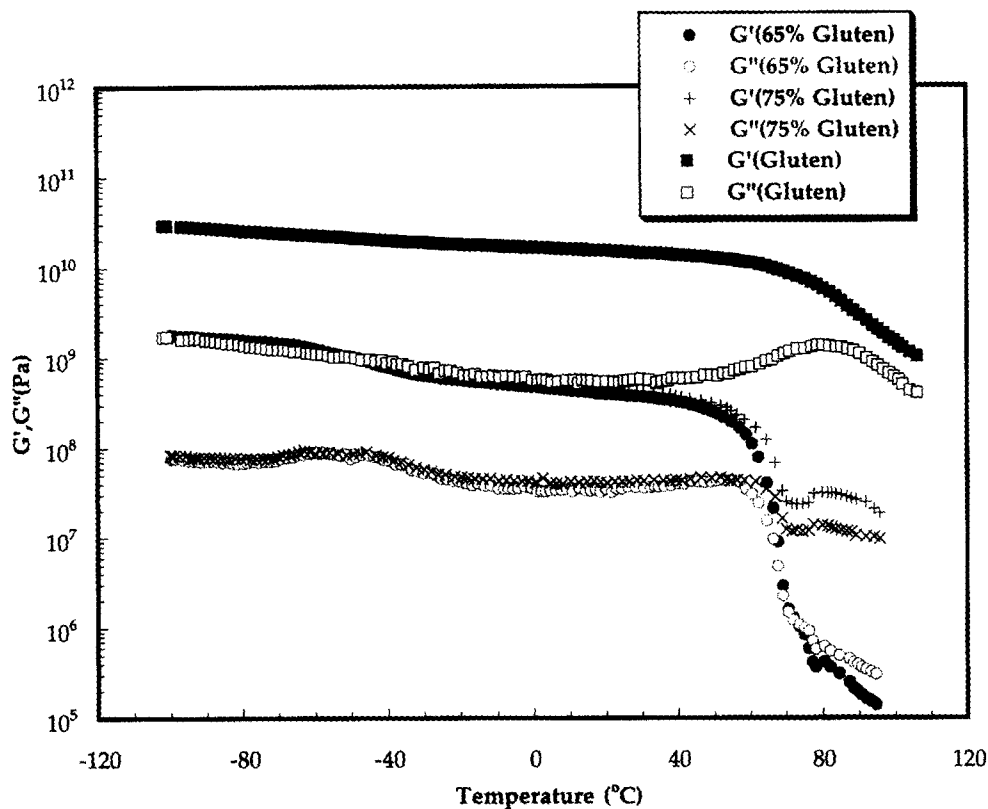


Figure 5 Dynamic mechanical analysis of PCL-787 and blends of PCL/PCL-MA/Gluten

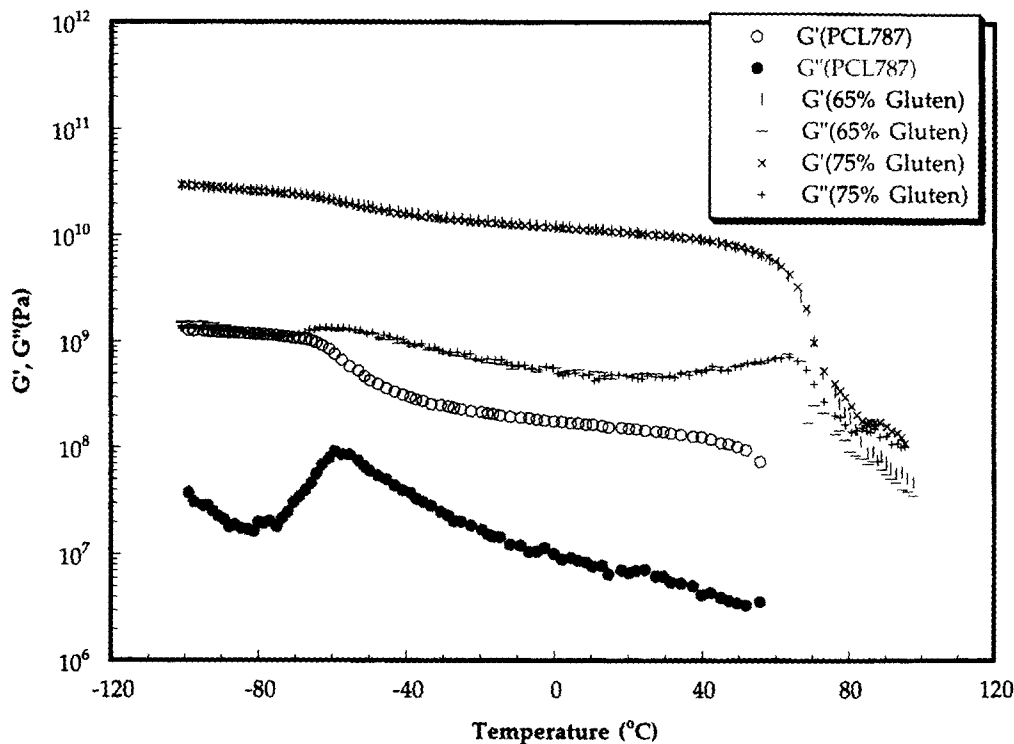


Figure 6 Dynamic mechanical analysis of gluten and blends of PCL/gluten

(10^{-3} to 10^{13}) and 65% gluten (10^{-4} to 10^{10}). At low frequencies the modulus is low, but it gradually increases as the frequency changes by decades.

Morphology

The morphology of the blends was studied by examining the batch mixed and extruded material with the help of

optical as well as scanning electron microscopes. Since the contrast between the phases of polymer and gluten were poor in the SEM graph, an optical microscope was used to probe into the different phases. A clear contrast is obtained after staining the samples and observing them under an optical microscope. After freezing under liquid nitrogen the samples were fractured in directions parallel (longitudinal)

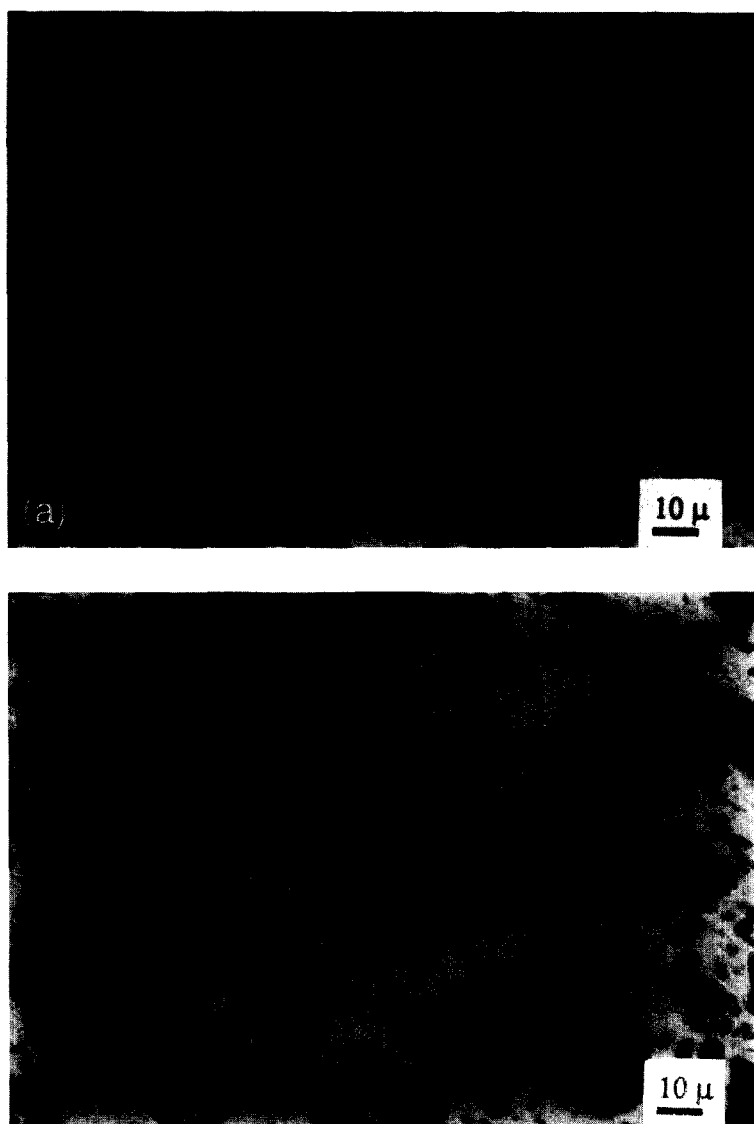


Figure 7 Optical micrograph of the blends of: (a) wheat gluten 65/PCL-g-MA 2.5/PCL-767 32.5; and (b) wheat gluten 75/PCL-g-MA 2.5/PCL-767 22.5

Table 4 Shift factors for PCL and blends of PCL/Gluten

Temperature (°C)	Shift factors		
	PCL-787	65% Gluten	75% Gluten
50		2.5×10^{-7}	6.3×10^{-7}
40	1.0×10^{-3}	2.5×10^{-4}	4.0×10^{-5}
30	1.0×10^{-2}	2.5×10^{-2}	1.0×10^{-2}
20	1.0	1.0	1.0
10	4.0×10^2	4	25
0	2.5×10^5	63	2.5×10^3
-10	6.4×10^7	6.3×10^2	2.5×10^5
-20	2.5×10^{10}	1.0×10^5	4.0×10^7
-30	2.5×10^{12}	2.5×10^7	1.0×10^{10}
-40	2.5×10^{13}	1.6×10^{10}	6.13×10^{12}

and perpendicular (transverse) to the direction of flow for optical microscopy. The representative areas of the sample were photographed and the dimensions were read directly from the photographs.

The optical micrographs of the blends obtained from extruder and batch mixer are shown in Figures 7, 8 and 9. The twin screw extruder gave more homogeneous and better dispersed blends when compared to the blends obtained using the batch mixer. The gluten aggregates are easily

identified due to the available contrast. In the figures, dark particles represent gluten aggregates. These figures show that the structure of gluten has mostly been destroyed and the derivatives are powders with a wide range of cluster sizes. These cluster sizes are small and fairly homogeneous in the case of twin screw extruded samples (Figure 7a, b and Figure 8a, b). Figure 8a and b show the optical micrograph of weldline samples obtained from the junction of the weldline in an injection moulded sample. In the case of batch mixed samples the poor mixing is visible from the size of the clusters (Figure 9c). It is also found that the gluten granules are not broken apart nor do they dissolve into the PCL melt, but they are well-dispersed within the PCL matrix. This indicates better mixing when using an extruder for blend preparation. From the microscopy data it is concluded that the improved mechanical properties of the blends are due to the chemical and physical interactions due to better dispersion of gluten aggregates in the modified PCL matrix.

Figure 9a and b show the optical micrographs of the blends of unmodified PCL with 65 and 75% gluten, respectively. The difference in tensile properties between the modified and unmodified polymer blends can easily be understood by comparing the morphological features. As

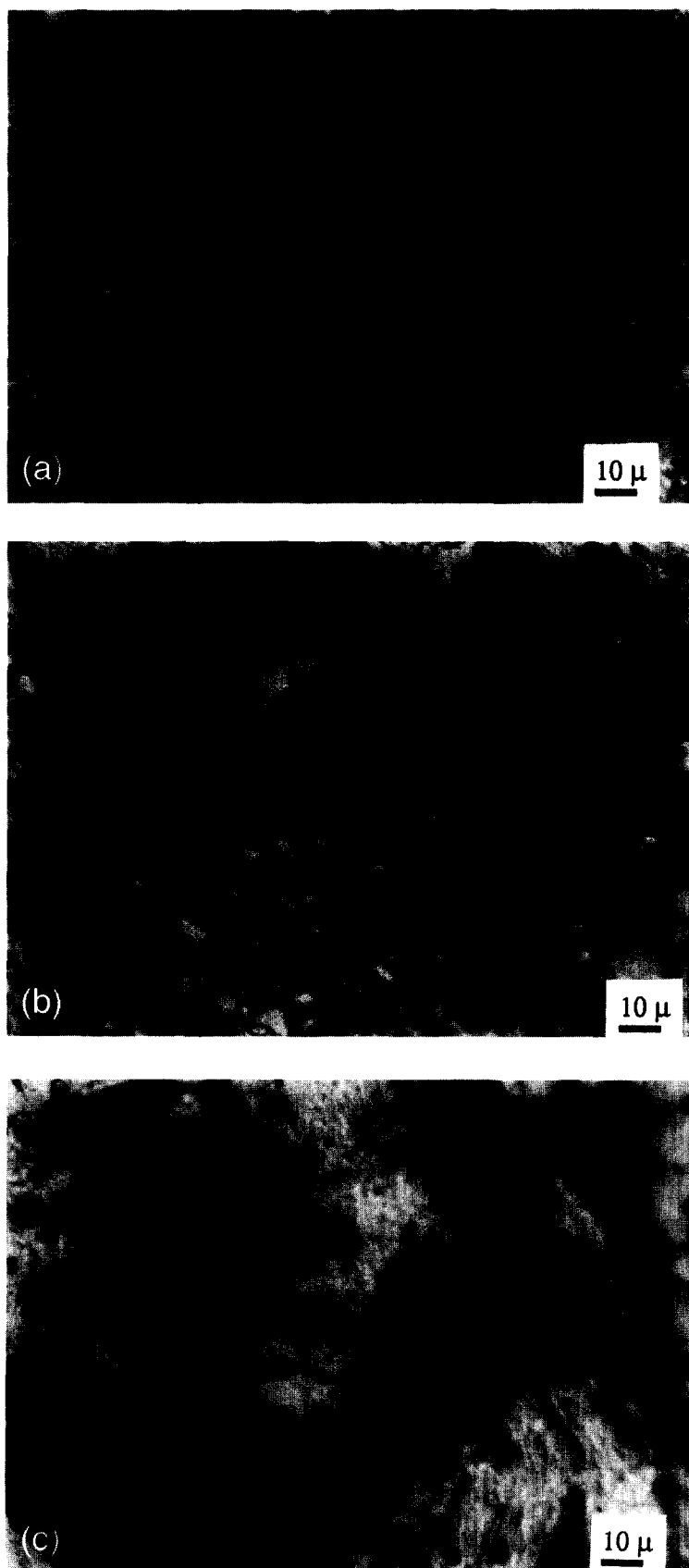


Figure 8 Optical micrograph of the blends of weldline samples: (a) wheat gluten 65/PCL-g-MA 2.5/PCL 32.5; (b) wheat gluten 75/PCL-g-MA 2.5/PCL 22.5; and (c) batch mixed sample of wheat gluten 70/PCL-g-MA 2.5/PCL 28.5

seen from the figures, when modified PCL is absent, large particles with no adhesion to the polymer matrix can be observed (*Figure 9*). By adding a small amount (2.5% modified polymer), a good homogeneity is achieved in the

blends (*Figure 7*). It is also found that very fine and homogeneous morphology increases the impact strength of the material. It is interesting to note that to reduce the production cost of the material, pure PCL can be added to

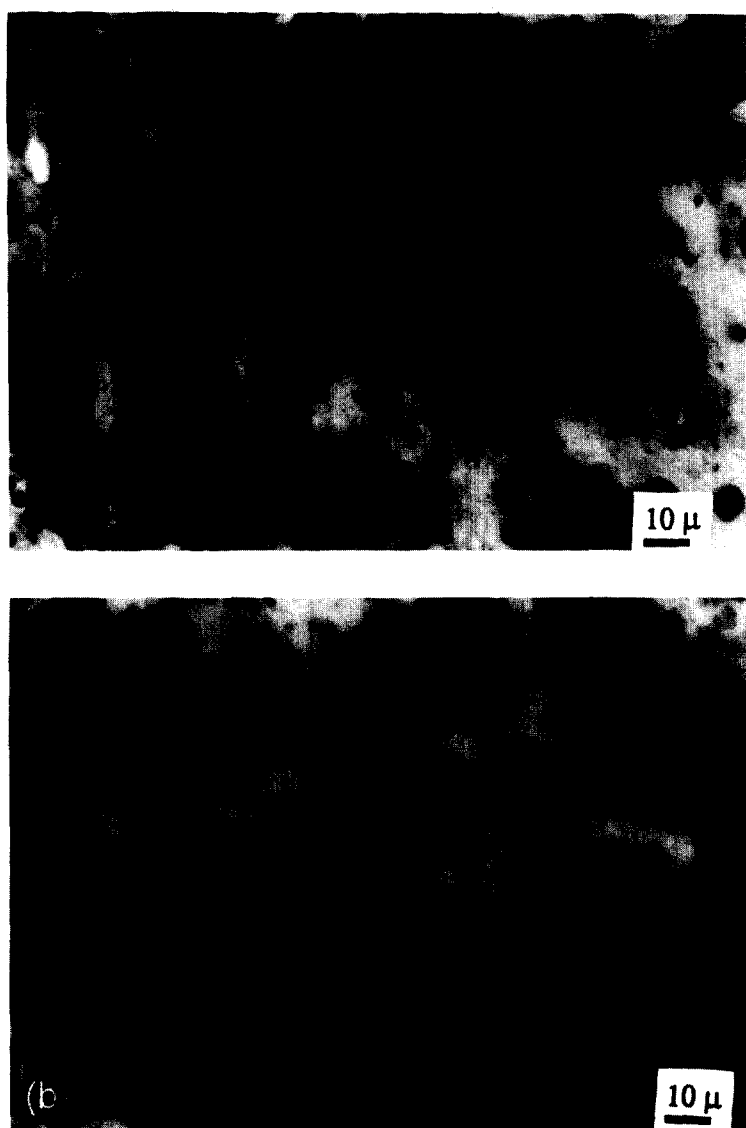


Figure 9 Optical micrograph of the blends of unmodified PCL with; (a) wheat gluten 65/PCL767 35; and (b) wheat gluten 75/PCL767 25

the blends to lower the proportion of modified PCL. To achieve this goal the amount of modified polymer in the blends was lowered to a minimum without compromising the desired properties. A blend of 2–5% modified polymer gave comparable tensile properties with a blend containing 25–30% modified polymer. This result is encouraging as the cost of the final product will be reduced considerably and the properties will remain unchanged.

Biodegradability

The degree and the rate of aerobic biodegradability determines the extent and time frame within which a plastic material in the environment may be eliminated. The degree of aerobic biodegradability is a function of carbon dioxide evolved, soluble organic carbon content, and the residual polymer weight.

Compression moulded samples (25.45 mm dia. and 3.3 mm thickness) were broken into smaller pieces and placed in the compost. Within a short period of time the samples displayed excellent growth of bacteria on the surface. The biodegradability of gluten/PCL blends was monitored against cellulose as a control. The carbon dioxide generated as a function of time is shown in *Figure 10*. The cellulose positive control had a total weight loss. All gluten

samples had good early bio-activity, but levelled off after 30 days. After a period of 10–20 days the activity picked up again. The replicates also showed different levels of activity. This is partly due to the difference in the size of the particles in the test leading to a different surface area. These samples would have degraded more, if they had been uniformly pressed into film or thinner sections. In addition, a blank sample (polyethylene) was inoculated to generate carbon dioxide to allow and correct for bacteria living on themselves. While cellulose samples lost 100% of their initial weights (completely biodegraded), gluten samples were reduced to 15% of their initial weights and PE samples showed an actual weight gain due to growth on the surface. PE consists of 78% carbon and does not biodegrade but merely offers a site for bacteria to grow and flourish. For cellulose, 70% of the carbon was converted to carbon dioxide while for gluten blends 41% was converted.

The gluten/PCL blend samples would have biodegraded more successfully if moulded in a thin film. Compared to the cellulose positive control, they did well even as thick as they were. The degradation showed that gluten/PCL samples would breakdown in composting or sewage treatment facilities even in thick cross-sections.

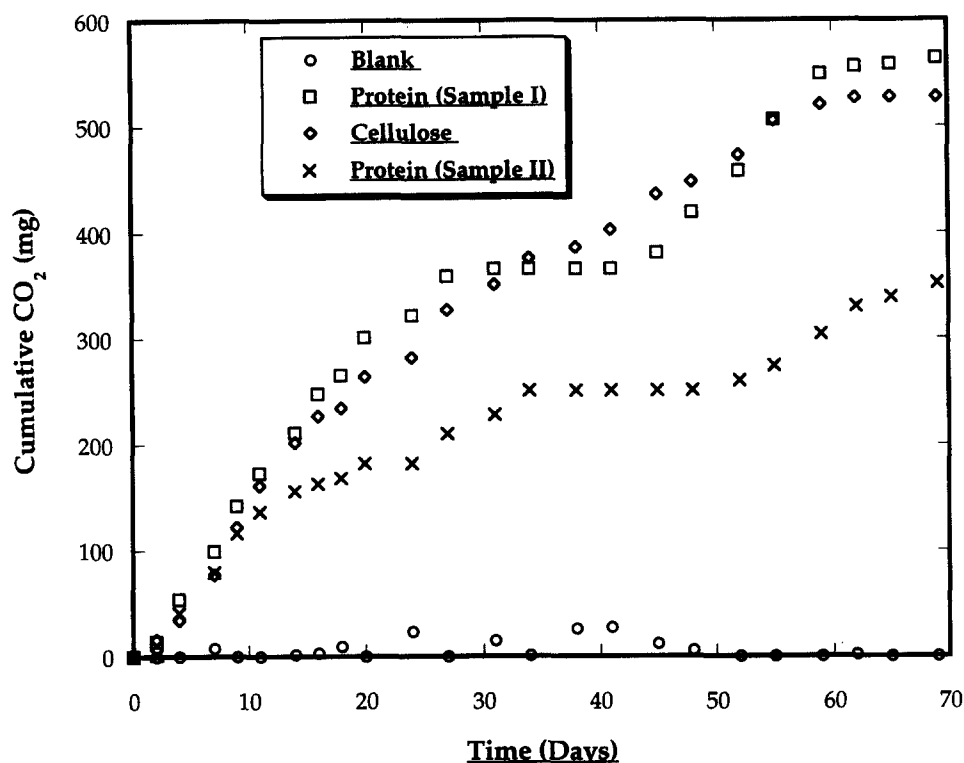


Figure 10 Aerobic biodegradation of blends in the presence of municipal sewage sludge

CONCLUSIONS

The processing parameters (pressure, torque and energy) of the blends are significantly increased by the addition of 2.5% by weight of anhydride modified PCL. Similarly, the properties are also enhanced by the addition of modified PCL. The tensile properties of blends containing 65 or 75 % gluten are comparable to those of pure PCL, although the percentage elongation is drastically reduced. The viscosity of the blends containing modified PCL is significantly higher than that of blends containing simple mixtures, as evidenced from the incomplete mould filling. These materials appear to display stable properties when stored under two extreme conditions (oven and freezer). Also, 100% re-ground blends have the same properties as the virgin blends indicating full recycling and reuse of these materials. This is an important consideration for process economics.

The equilibrium water content of the blends with 65 and 75% gluten were 32 and 40% respectively. These blends have a sharp uptake of water, i.e. most of the water was absorbed in the first 4 days. The water uptake of blends containing 75% gluten was diffusion controlled while it was anomalous for blends containing 65% gluten. Average oil absorption was less than 0.5% for a 20-day period and was unaffected by the gluten content in the blend.

Since PCL has a low melting temperature, the loss of material when used at temperatures near or above its melting point is a possibility. However, the 65% gluten blend, when immersed at temperatures as high as 75°C for 15 min, did not indicate any loss in weight. At higher gluten content a small amount of material was lost when immersed in water at temperatures above 65°C.

Dynamic mechanical analysis indicated that the modulus of blends containing a compatibiliser is higher than those in which the compatibiliser is absent. Similarly, the modulus is higher for the compatibilised blends than

those of pure PCL; however, both grades of PCL have similar moduli. Two transition peaks were observed for the blends. The first corresponds to the T_g of PCL while the second peak occurs at the T_m of PCL and the T_g of gluten. Also, the second peak occurred at a higher temperature for blends containing a compatibiliser over those containing simple mixtures. PCL-787 has higher shift factors than either blend compositions, indicating higher sensitivity to temperature.

Morphology of the blends indicate better mixing in an extruder than in a batch mixer. Also, when a small amount of modified PCL is added, a finer phase morphology is observed. In the blends, PCL is the continuous phase with gluten being the dispersed phase. The gluten/PCL/PCL-MA blends are biodegradable under aerobic conditions as seen from the ASTM test.

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