Mechanical Properties of Green Composites with Polycaprolactone and Wheat Gluten

V. L. Finkenstadt,[1] A. A. Mohamed,[2] G. Biresaw,[2] J. L. Willett[1]

[1]*Plant Polymer Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604*
[2]*Cereal Products and Food Science Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604*

ABSTRACT: Wheat gluten (WG) was incorporated into polycaprolactone (PCL) (up to 50% w/w) as a filler to form a biodegradable polymer composite. A microscopic examination showed a well-dispersed particle–matrix system. The composite was evaluated for its tensile properties. The tensile strength of the composite decreased linearly with increasing WG content from 20 (0% WG) to 6 MPa (50% WG). However, the reduction of the tensile strength did not fit the Nicolais–Narkis model, and this indicated that some adhesion between WG and PCL occurred. High elongation (>900%) was observed in PCL–WG composites with up to 20% WG; it decreased to 400% with 35% WG and finally to less than 100% with 40–50% WG. There was a particle-induced transition at a calculated critical volume of 0.3 corresponding to 30% WG by weight with respect to PCL. © 2008 Wiley Periodicals, Inc.* J Appl Polym Sci 110: 2218–2226, 2008

Key words: biodegradable; composites; extrusion; injection molding; mechanical properties

INTRODUCTION

Conventional plastics are produced from petroleum-based feedstocks and persist in the environment for years. Biodegradable polymers can be degraded in the environment by microorganisms, oxidation, and hydrolysis. Biodegradable polymers can be used for packaging materials, hygiene products, disposable consumer goods, and agricultural products. There are several challenges associated with replacing petroleum-based polymers with biodegradable or bio-based polymers.[1] The first is functionality; the polymer must have the appropriate physiochemical properties of its competitor. A second challenge is cost; the competition with inexpensive commodity plastics is difficult but can be won by the design of new material blends and when the demand for products using biodegradable polymers rises in the marketplace. The blending of a biobased polymeric material such as wheat gluten (WG) with a biodegradable polymer such as polycaprolactone (PCL) is one way of reducing costs and modifying material properties.

WG is a coproduct of starch production and is relatively inexpensive ($1.10/lb). WG is a heteropolymer that has two main groups of proteins: gliadin and glutenin.[2] It readily forms films via casting from ethanol/acetic acid solutions and can be plasticized and then heat-molded. Cast films rely on the disruption of chemical bonds, dispersion, solubilization of the protein, casting, and then drying of the film. Cast films have limited applications and are used mainly for coated materials such as paper, seeds, and food products. WG can also be processed by a thermomechanical treatment using plasticizers such as water and glycerol.[2] Upon heating, however, gluten undergoes crosslinking reactions that increase its viscosity and make extrusion problematic.[3] WG bioplastics can biodegrade in less than 50 days in soil.[4] WG is highly sensitive to water, which affects its mechanical and barrier properties.[2] To improve moisture resistance for use in packaging, WG has been blended with polymers such as poly(lactic acid),[5] adipic acid,[6] poly(vinyl alcohol),[7] and PCL.[8] In these studies, the polymer and gluten were compounded with thermal mixers and then compression- or injection-molded. In many cases, the polymers were used in small quantities (<10% w/w) with WG as the matrix polymer.

PCL is a linear synthetic polyester having the repeating structure $[-(CH_2)_5-COO-]_n$. PCL has a

---

glass-transition temperature (T_g) of approximately $-60°C$, melts around $120°C$, and exhibits high elongation. Typical uses for PCL include biomedical devices, films, and containers. PCL is readily degraded by microorganisms but is hydrophobic.[9] PCL is relatively expensive at $3.75/lb. PCL has been blended with WG,[8] starch,[10–15] corn zein,[16,17] wood flour/lignin,[18] and soy protein.[19] In general, PCL filled with starch, corn zein, or wood flour/lignin loses tensile strength in a linear fashion.[10–18] PCL has also been blended with cellulose fibers, which reinforce composites similarly to glass fibers.[20,21] Blends of WG (65–75% w/w) with maleic anhydride modified PCL by the use of a three-temperature-zone twin-screw extruder followed by injection molding resulted in increased tensile strength, which was attributed to increased adhesion between WG and modified PCL.[8]

In this study, polymer composite materials were made by pilot-scale extrusion processing and injection molding. PCL was used as the matrix polymer, with WG as the filler (0–50% w/w fill), and this reduced the cost of the final product. Other studies generally used WG as the primary matrix and PCL as a binder. This study sought to determine the amount of WG filler that could be added to PCL before an unacceptable loss of mechanical properties occurred. Both polymers were unmodified, and the composite was evaluated for its mechanical properties, including its tensile strength, modulus, and elongation, as a function of the blend composition. The data was analyzed with several polymer–particle models describing the level of interaction (or lack of interaction) between the two phases.

EXPERIMENTAL

Materials

WG, with a protein content of approximately 80% and residual moisture of 7% (w/w), was purchased from Sigma Chemical Co. (St. Louis, MO). PCL 787, with a T_g of $-60°C$, a melting temperature of $120°C$, and a molecular weight of 125 K, was obtained from Union Carbide. Both were used as supplied.

Extrusion and injection molding

PCL–WG composites were compounded with a Werner–Pfleiderer ZSK30 corotating twin-screw extruder (Coperion Corp., Ramsey, NJ). The barrel was composed of 14 sections with a length/diameter ratio of 44 : 1. The screw configuration is shown in Table I. The screw speed was 150 rpm. PCL was fed into barrel section 1 with a gravimetric feeder (model 3000, AccuRate, Inc., Whitewater, WI). After the melting of PCL, WG was fed into barrel section

TABLE I
ZSK30 Twin-Screw Design for the Extrusion Compounding of the PCL–WG Composites

Element type	Cumulative length (mm)
PCL	
Conveying 42/42 (5×)	210
Conveying 28/28 (4×)	322
Conveying 20/20	342
Kneading block 45/5/42	384
Kneading block 45/5/28	412
Conveying 28/28 (2×)	468
Kneading block 45/5/20	488
Kneading block 45/5/14 (2×)	516
Conveying 28/28	544
WG	
Conveying 42/42 (4×)	712
Conveying 28/28	740
Kneading block 45/5/42	782
Kneading block 45/5/28	810
Conveying 42/42	852
Conveying 28/28	880
Kneading block 45/5/28	908
Kneading block 45/5/20	928
Conveying 28/28 (2×)	984
Kneading block 45/5/20	1004
Kneading block 45/5/14	1018
Conveying 28/28 (2×)	1074
Kneading block 45/5/14 (2×)	1102
Conveying 28/28 (2×)	1158
Kneading block 45/5/14	1172
Kneading block 45/5/14 LH[a]	1186
Conveying 20/20 (5×)	1286
Conveying 14/14 (3×)	1328

[a] Left-handed screw element.

7 with a loss-in-weight feeder. Feed rates are shown in Table II. The barrel was heated with eight heating zones. The temperature profile was 88 (zone 1) and $127°C$ (zones 2–8). A die plate with 2 holes (4 mm in diameter each) was used. The melt temperature of the exudate at the die was approximately $100°C$ for neat PCL and increased with increasing WG content to a maximum value of $120°C$ at 75% WG. The residence time was approximately 2.5 min for all blends. The die pressure, torque, and feed rate were allowed to stabilize between formulations before the sample was collected. Strands were pelletized with a laboratory pelletizer (Killion Extruders, Inc., Cedar Grove, NJ).

An ACT75B injection molder (Cincinnati Milacron, Batavia, OH) was used to injection-mold ASTM D 638-99 type I tensile bars (Master Precision Mold, Greenville, MI). Latex gloves were used to handle freshly molded samples, which were stored in clean ziplock bags after cooling. Injection-molding conditions for each sample are summarized in Table III. For an increased WG level, the barrel temperatures had to be adjusted upward and the cooling time had to be increased to help forward material while the feed section was still being cooled. Packing pressures were inverted for samples because of extreme flash-

TABLE II
Feed Rates for the PCL–WG Composites

PCL : WG	PCL (g/min)	WG (g/min)	Total feed rate (g/min)	Actual WG (%)
100 : 0	74.1	0.0	74.1	0
90 : 10	67.1	7.0	74.1	9.4
80 : 20	60.2	15.1	75.3	20.1
70 : 30	52.8	28.0	80.8	34.7
60 : 40	45.0	32.0	77.0	41.6
50 : 50	37.6	37.1	74.8	49.6
25 : 75	22.5	64.4	86.9	74.1

ing characteristics. Because of the decreasing density of the feeds, pressure was applied to the feed throat to help forward material. The cooling time was 35–45 s, and the maximum injection pressure was 14,000 psi. The mold temperature was 45°C.

Scanning electron microscopy (SEM)

SEM of freeze-fractured and stretched PCL–WG composites was conducted on a JEOL (Peabody, MA) 6400V scanning electron microscope with an accelerating voltage of 10 kV after gold coating with an SPI (West Chester, PA) sputter coater. Care was taken not to heat the sample area of the PCL–WG fracture surface above the melting point of PCL in either the sputter coater or SEM instrument.

Thermal properties

The tan δ peaks were determined with a TA Instruments (Wilmington, DE) ARES LS2 controlled strain rheometer. Rectangular torsion bars were obtained from injection-molded dog bones through the cutting out of the middle section (12.7 mm × 3.15 mm) of the injection-molded sample. The samples were placed in a forced-air oven with a refrigeration unit capable of cooling to low temperatures. The samples were then heated at 2°C/min up to 60°C to remove any internal stresses from injection molding with a constant 1 rad/s frequency and 0.05% strain. They were then cooled at 5°C/min down to −70°C with a 5-min isothermal hold and heated again up to 90°C

or until the sample response was below the transducer sensitivity.

Mechanical properties

Mechanical property measurements were performed with a mechanical property testing machine (model 4201, Instron Corp., Norwood, MA). The thickness of the individual tensile bars was measured before testing and was 3 mm on average. The gauge length was 40 mm, and the strain rate was 50 mm/min. All samples were conditioned for at least 48 h at standard room temperature and humidity (23°C and 50% relative humidity). Each test was repeated at least five times, and average values were used in data analyses.

RESULTS AND DISCUSSION

Processing

The specific mechanical energy (SME) was determined from torque and angular velocity measurements during extrusion. The net mechanical energy input to the screws was divided by the extrudate flow rate. SME for the PCL–WG composites is shown in Figure 1. The total feed rate ranged from 74 to 87 g/min (Table II). SME for 100% PCL was 1150 J/g. For PCL–WG composites, SME decreased as the weight fraction of WG increased. At 50% WG, SME was around 840 J/g. At 75% WG, SME was 675 J/g. The reduction in SME is typical upon the reduction of the PCL feed rate when a polymer is compounded with rigid particulate fillers. Pressure at the die increased in a linear fashion as the WG content increased (Fig. 1). This was not unexpected as WG filled the PCL matrix and the viscosity of the melt increased. The temperature at the die (product temperature) increased from 83 (0% WG) to 115°C (75% WG). In comparison, twin-screw processing of PCL–lignin (or wood flour) was conducted at 160°C with the screw speed set at 200 rpm and a feed rate of approximately 83 g/min.[17] Although 75% WG could be extruded, it was not possible to injection-

TABLE III
Injection-Molding Conditions for the Plasticized PCL–WG Composites

| PCL : WG	Barrel zone 1/barrel zone 2/barrel zone 3/nozzle (°C)	Cooling time (s)	Shot size (in.)	First and second packing pressures (kpsi/s)	Velocity 1 (in./s)/velocity 2 (in./s)/switch point (in.)
100 : 0	77/104/127/127	35	3.0	4/2, 12/8	1/0.5/1.0
90 : 10	77/104/127/127	35	3.0	4/2, 12/8	1/0.5/1.0
80 : 20	77/104/127/127	35	2.9	4/2, 12/8	1/0.5/1.0
70 : 30	77/113/127/127	35	2.9	4/2, 12/8	1/0.5/1.0
60 : 40	77/113/138/138	45	3.3	4/2, 14/8	2/1/1.0
50 : 50	77/113/138/138	45	3.0	4/2, 14/8	2/1/1.0
25 : 75	77/113/149/149	45	3.0	4/2, 14/8	9/4/1.0
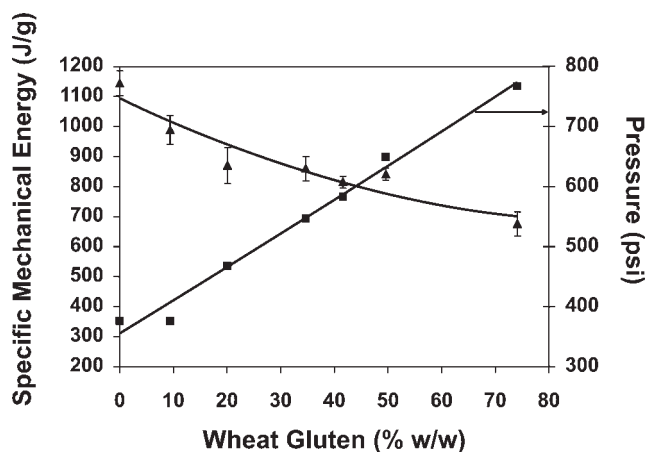
Figure 1 SME and pressure during the compounding of PCL–WG composites.

mold samples that could be tested. An analysis of the tensile properties of PCL–WG was conducted for a WG range of 0–50% (w/w) fill.

Microscopic evaluation

Freeze-fractured surfaces of PCL–WG composites are shown in Figure 2. The particle size of WG was between 1 and 100 μm, with the larger particles being more prevalent in higher fill amounts as the protein aggregates. PCL was the matrix polymer and appeared continuous up to 20% fill [Fig. 2(a–c)]. Larger aggregates of WG weakened the composite, and particle pullout from the PCL matrix occurred frequently [Fig. 2(d–f)]. At 75% fill, the PCL matrix was discontinuous, and this made it impossible to injection-mold samples [Fig. 2(g)].

Thermal properties

T_gs were obtained from rheometry, and T_g for PCL was −50°C. The addition of WG (up to 50% fill) lowered T_g to approximately −54°C. Figure 3 shows PCL (0% WG) and PCL–WG at 50% fill. A complete analysis of the thermal properties is the subject of another article.[22]

Mechanical properties

In polymer blends, the addition of a rigid filler significantly reduces the ductility of the polymer, which is measured as the strain percentage in a stress–strain curve. The stress–strain behavior of the PCL–WG composites shows that up to 20% WG can be incorporated without loss of ductility (Fig. 4). The yield strength decreased as the WG content increased. The onset of yielding also decreased from 50% strain for pure PCL to 1% strain for 50% WG. PCL and PCL–WG composites with up to 20% fill

did not break during testing. After the yield point, the stress dropped to the draw strength and remained constant. The samples stretched, whitened, and exhibited a behavior known as necking, in which the cross-sectional area of the test sample is drawn out and becomes thinner and thinner. Necking is an uneven process in which a portion of the sample will deform and stretch while the rest of the sample remains unchanged (at least visually). The necking began in the middle of the test sample and progressed toward the grips. It was followed by a period of strain hardening in which the stress increased (Fig. 4). When the necking reached the grips, the sample could no longer be held and slipped out. Similar stress–strain behavior was noted for PCL–starch composites, although the necking phenomenon did not occur above 20% fill.[14] At a high WG content (35–50%), PCL composites broke under strain, and the onset of whitening/cracking was more pronounced in the early stages of strain. Figure 5 shows representative SEM images of the stretched PCL–WG composites. At 20% WG, at which strain hardening occurred after yielding and drawing, the PCL–WG composite showed void formation around WG particles, with the PCL stretching throughout the sample [Fig. 5(a)]. At 35% WG, at which no strain hardening took place, voids formed around WG particles, and the PCL matrix failure appeared to start near the particles [Fig. 5(b)]. This indicated that the critical concentration of WG was located between 20 and 35% (w/w). At 50% WG, there was little yield, and the composite broke very quickly. Some void formation was evident, but no stretching of the PCL matrix was observed [Fig. 5(c)].

The tensile strength and yield stress of the PCL–WG composites decreased linearly with increasing WG content [Fig. 6(a)]. PCL filled with other agricultural materials (starch, zein, and wood flour/lignin) showed similar reductions in tensile strength as the filler amount increased.[11,12,15,17,18] The tensile strength of PCL–WG was higher than the yield stress at lower fill amounts because the PCL exhibited drawing and strain-hardening phenomena. This behavior was also exhibited by PCL–starch composites.[15] At higher WG amounts, the composite yielded and then fractured very quickly. Stiffness (modulus) also increased as WG was added [Fig. 6(b)]. The elastic modulus is related to the hard domain of the composite (i.e., WG). Examining Figure 6(b), we found that the modulus increased slightly up to 20% filler but showed a significant increase above 35% WG. In comparison, the modulus of PCL–zein composites did not increase over 25% filler because of the addition of glycerol as a plasticizer.[17] Elongation values for PCL–WG also showed a significant change when the WG content was above 20%
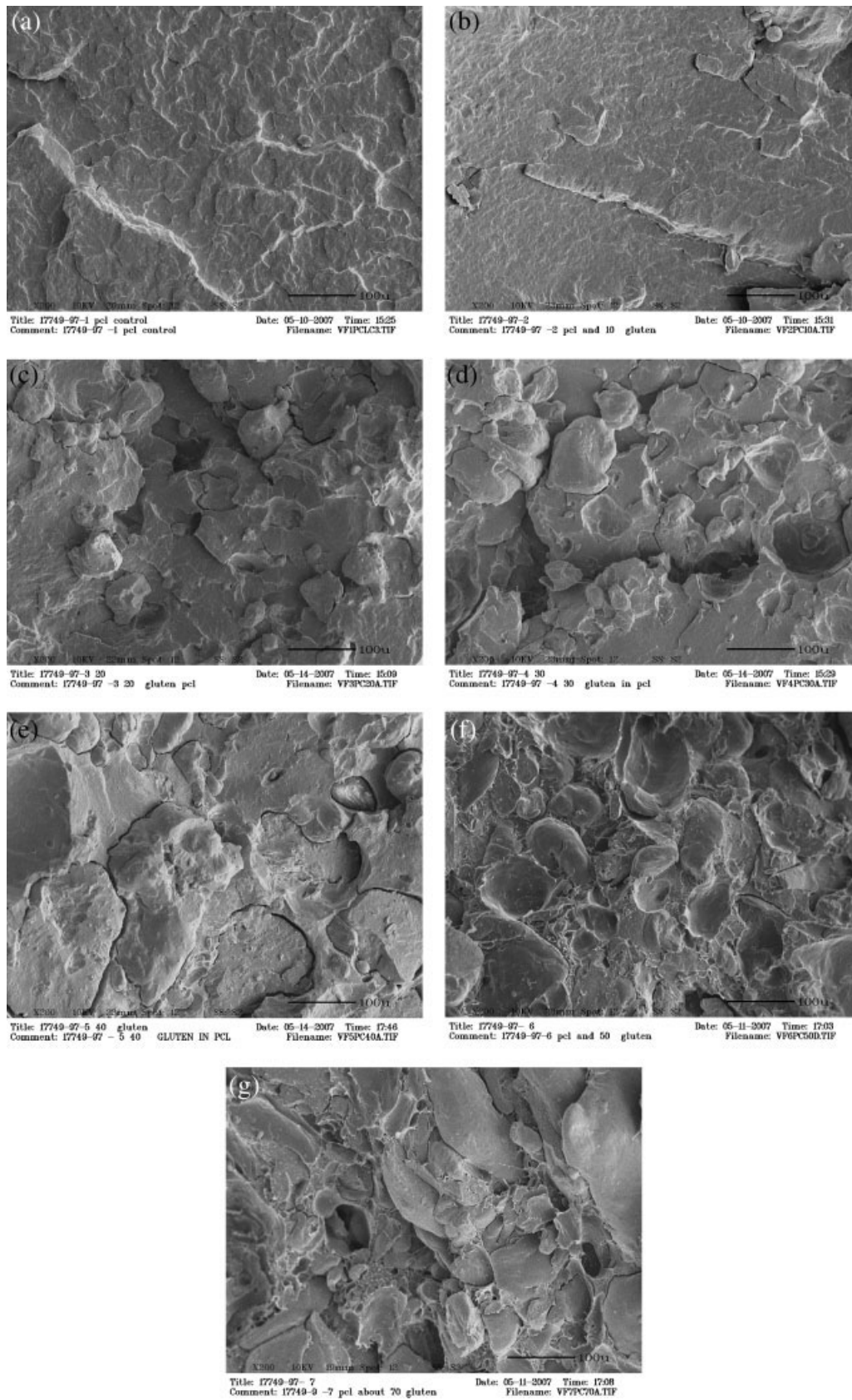
Figure 2 SEM photomicrographs of freeze-fractured surfaces of PCL–WG composites: (a) 100% PCL, (b) 9% gluten, (c) 20% gluten, (d) 35% gluten, (e) 42% gluten, (f) 50% gluten, and (g) 74% gluten. The original magnification was 200×.
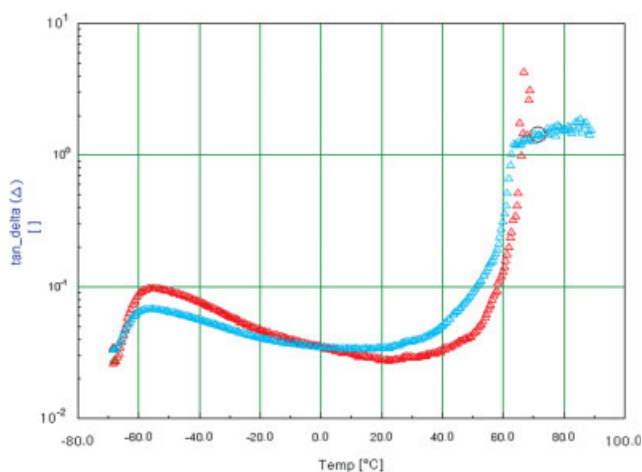
Figure 3 Thermal properties of the PCL–WG composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fill [Fig. 6(c)]. Up to 20% WG, the elongation of the PCL–WG composites was greater than 900%. At 35% WG and higher, the elongation decreased dramatically to less than 100%. In all cases, the elongation values of pure PCL were in agreement with previous results.[15,17] In contrast, the elongation behavior for other PCL composites was linear because the filler content was limited to two data points, 25 and 50% (w/w).[15,17] PCL–lignin composites retained high elongation (>500%) with up to 40% lignin.[18] For PCL/wood flour composites, the elongation decreased dramatically at 20% fill, similarly to PCL–WG.[18] Thermoplastic and native sago starch could be incorporated into PCL up to 60% fill, with the tensile strength and elongation decreasing in a linear fashion.[11,12] However, gelatinized and nongelatinized corn starch showed a radical drop between 25 and 50% fill, and this was similar to the elongation behavior of PCL–WG.[15]
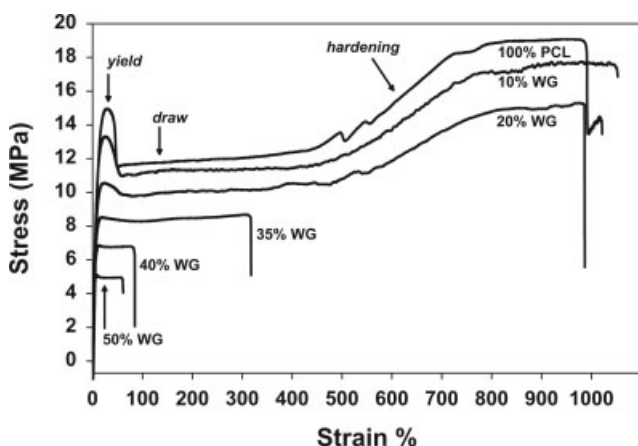

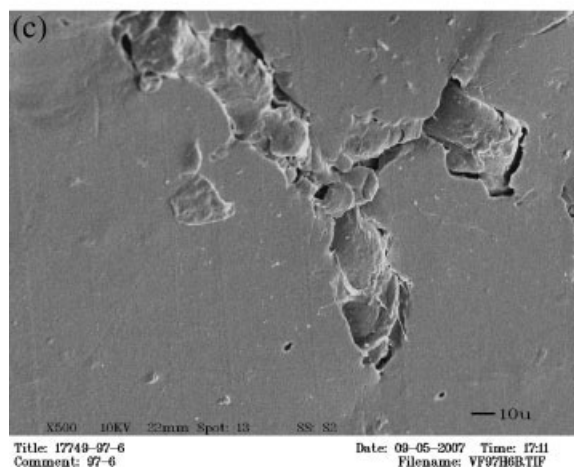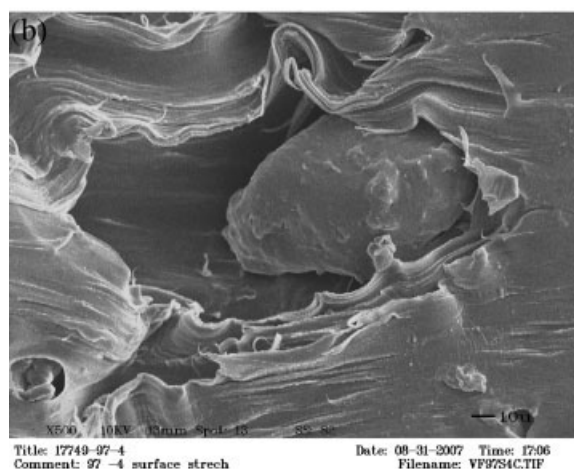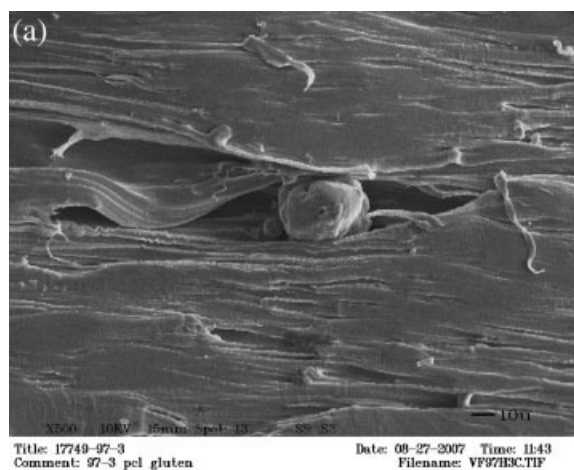**Figure 4** Stress–strain curves for the PCL–WG composites.

Figure 5 SEM photomicrographs of the stretched PCL–WG composites: (a) 20% gluten, (b) 35% gluten, and (c) 50% gluten. The original magnification was 500×.

Analysis of the mechanical properties of PCL–WG

The Nicolais–Narkis (N–N) model was used to evaluate the adhesion between the PCL matrix and WG filler with tensile data. According to the N–N model, the loss of yield strength for polymer composites (σ)
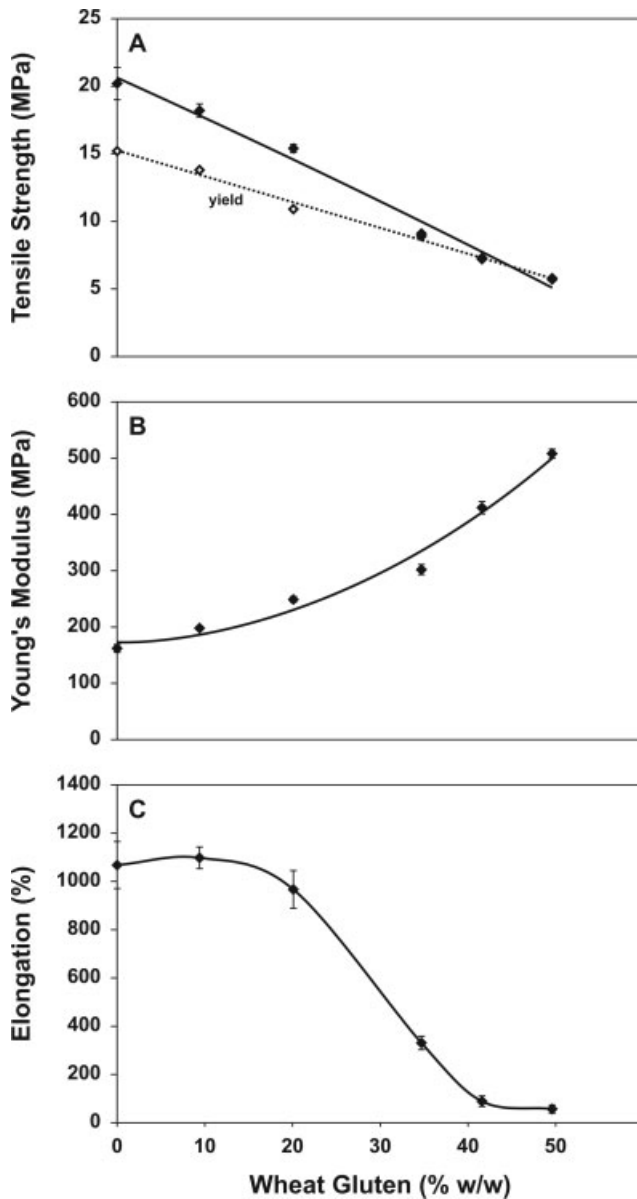
Figure 6 Tensile properties of the PCL–WG composites with respect to the weight fraction of WG: (a) tensile strength (closed symbols) and yield strength (open symbols), (b) Young's modulus, and (c) elongation.

with a uniformly distributed, rigid, spherical filler is given by[23]

$$\sigma = \sigma_o \left[1 - 1.21 V_{wg}^{2/3} \right]$$

where V_{wg} is the volume fraction of WG and σ_o is the yield strength of pure PCL. V_{wg} was calculated as follows (ASTM D 3171: ''Standard Test Method for Constituent Content of Composite Materials''):

$$V_{wg} = \frac{\rho_{pcl} W_{wg}}{\rho_{wg} W_{pcl} + \rho_{pcl} W_{wg}}$$

where ρ_{wg} and ρ_{pcl} are the densities of WG (1.16 g/mL) and PCL (1.15 g/mL) and W_{wg} and W_{pcl} are the weight fractions of WG and PCL, respectively. In this case, the yield strength was used instead of the ultimate tensile strength because adhesion effects were exhibited during debonding that occurred at or before yielding. Figure 7(a) compares the experimen-
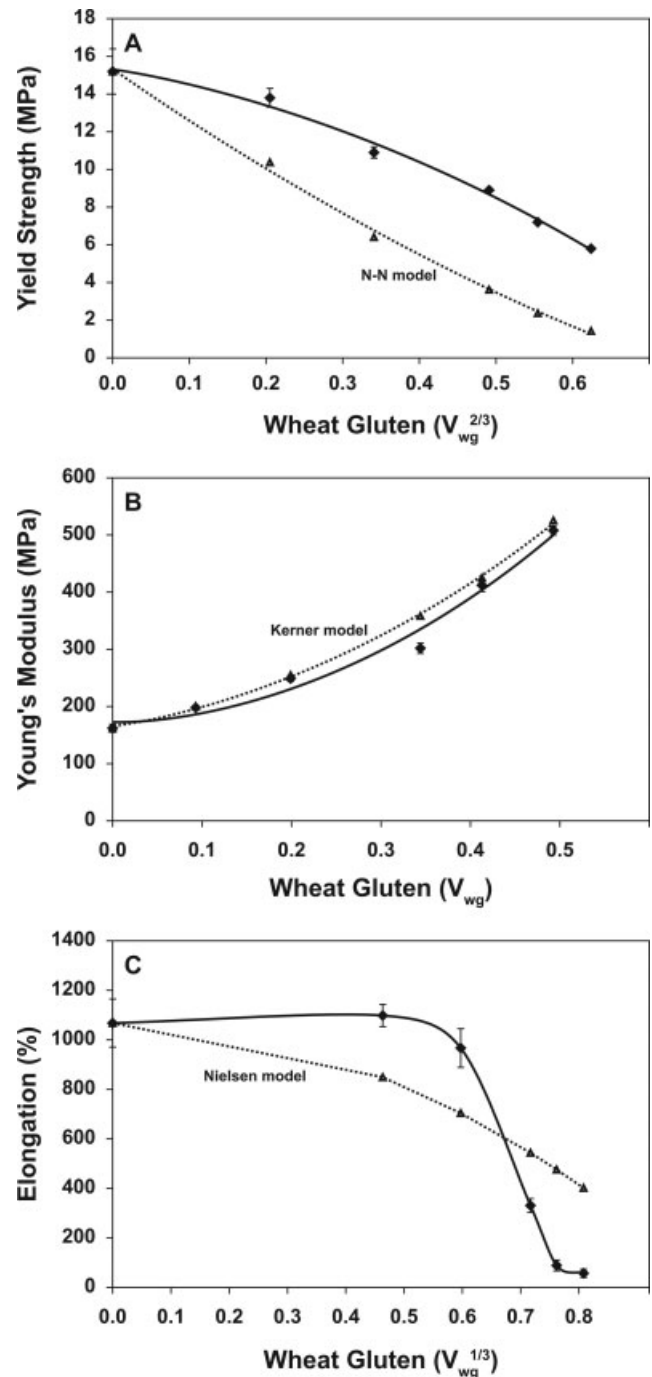

Figure 7 (a) N–N model for the yield strength of the PCL–WG composites, (b) Kerner model for the modulus of the PCL–WG composites, and (c) Nielsen model for the elongation of the PCL–WG composites. The models are shown with open symbols and dotted lines.

tal yield strength of the PCL–WG composites and the yield strength predicted by the N–N model versus $(V_{wg})^{2/3}$. The N–N model assumed no adhesion between the particles and matrix, and this resulted in a linear decrease in the yield strength with increasing filler content due to the decrease in the load-bearing surface area of the polymer matrix. The comparison showed that the experimental yield strength was higher than predicted for all volume fractions. This outcome was an indication of some degree of adhesion between the PCL matrix and the WG particles. If complete adhesion had been present in PCL–WG, the stress would have been transferred from the PCL matrix to the WG particles, so no reduction in the load bearing surface area would have occurred.

The elastic modulus (E) for systems with fillers that are more rigid than the polymer matrix may also be modeled with a simplified Kerner equation:[24]

$$E = E_0\left(1 + \frac{2.31V_{wg}}{1 - V_{wg}}\right)$$

where 2.31 incorporates the Poisson ratio [taken to be equal to that of polyethylene (0.43)] and E_0 is the elastic modulus of PCL. Figure 7(b) shows the actual and predicted moduli for PCL–WG composites plotted against V_{wg}. The Kerner equation provided a good fit to the PCL–WG data, and this indicated that the modulus of WG was higher than that of PCL because the Kerner model assumes that the elastic modulus of the filler is much larger than the elastic modulus of the polymer matrix.

In modeling elongation (ε) for a particle-filled system in which there is complete adhesion, the Nielsen equation predicts a loss of elongation with increasing filler content[24]

$$\varepsilon = \varepsilon_0\left(1 - V_{wg}^{1/3}\right)$$

where ε_0 is the elongation of PCL. This model assumes that the particles do not elongate so the polymer between the particles undergoes greater stress than the bulk polymer. A polymer that strain-hardens, such as PCL, is able to sustain loads larger than the draw stress.[25] A polymer filled with a non-bonded, non-load-bearing filler such as WG is able to support the load without fracturing, even though the cross-sectional area is reduced between the particles. However, as the polymer cross-sectional area is reduced and the filler content is increased, a critical volume of filler will be obtained, and the strain-hardening strength of the polymer will not be enough to support the stress. The critical volume of filler for the transition from ductile behavior to quasibrittle fracture (V_{wg}^*) is described by[25]

$$V_{wg}^* = 1.33\left(1 - \frac{\sigma_d}{\sigma_o}\right)^{3/2}$$

where σ_d is the draw stress of PCL and 1.33 includes the geometric term for spherical particles. For PCL–WG composites, the critical volume fraction was calculated to be approximately 0.30. According to the experimental data, the critical volume fraction of PCL–WG composites occurred between 0.20 and 0.35, at which PCL lost its ability to strain-harden (Fig. 4). When a material does not strain-harden, loss of ductility will occur with small additions of a filler. The Nielsen model does not fit the experimental data [Fig. 7(c)] because it considers only the filler content and elongation at break and does not consider strain-hardening behavior. For PCL–WG, there was a particle-induced transition from an even distribution of stress in the propagating neck at 20% (w/w) WG to fracture without propagation at 35% (w/w) WG.

CONCLUSIONS

WG was incorporated into PCL (up to 50 wt %) as a filler to form a biodegradable polymer composite. An examination by microscopy showed a well-dispersed particle–matrix system at high levels of fill. As expected, the tensile strength of the composite decreased linearly with increasing WG content from 20 to 6 MPa, and this indicated that WG acted as a nonreinforcing filler with PCL. However, the measured tensile data did not fit the N–N model for nonadherence of particle-filled plastics, and this indicated that some adhesion between WG and PCL occurred. High elongation (>900%) was observed until 35% filler and finally was less than 100% at 50% WG. There was a particle-induced transition at a calculated critical volume of 0.3 corresponding to 30% WG by weight with respect to PCL. The next phase of this work will be to investigate cocontinuous, biphasic PCL–WG composites.

References

1. Gross, R. A.; Katra, B. Science 2002, 297, 803.
2. Jerez, A.; Partal, P.; Martinez, I.; Gallegos, C.; Guerrero, A. Biochem Eng J 2005, 26, 131.
3. Morel, M. H.; Redl, A.; Guilbert, S. Biomacromolecules 2002, 3, 488.
4. Domenek, S.; Feuilloley, P.; Gratraud, J.; Morel, M. H.; Guilbert, S. Chemosphere 2004, 54, 551.
5. Mohamed, A. A.; Gordon, S. H.; Carriere, C. J.; Kim, S. H. J Food Qual 2006, 29, 266.

6. Lim, S. W.; Jung, I. K.; Lee, K. H.; Jin, B. S. Eur Polym J 1999, 35, 1975.
7. Zhang, X. Q.; Burgar, I.; Lourbakos, E.; Beh, H. Polymer 2004, 45, 3305.
8. John, J.; Tang, J.; Bhattacharya, M. Polymer 1998, 39, 2883.
9. Goldberg, D. J Polym Environ 1995, 3, 61.
10. Pranamuda, H.; Tokiwa, Y.; Tanak, H. J Polym Environ 1996, 4, 1.
11. Odusanya, O. S.; Ishiaku, U. S.; Azemi, B. M. Polym Sci Eng 2000, 40, 1298.
12. Ishiaku, U. S.; Pang, K. W.; Lee, W. S.; Mohd Ishak, Z. A. Eur Polym J 2002, 38, 393.
13. Biresaw, G.; Carriere, C. J. Polym Prepr (Am Chem Soc Div Polym Chem) 2000, 41, 64.
14. Biresaw, G.; Carriere, C. J. J Polym Sci Part B: Polym Phys 2001, 39, 920.
15. Rosa, D. S.; Guedes, C. G. F.; Pedreso, A. G. Polim Cienc Tecnol 2004, 14, 181.
16. Wu, Q. X.; Yoshino, T.; Sakabe, H.; Zhang, H. K.; Isobe, S. Polymer 2003, 44, 3909.
17. Corradini, E.; Mattoso, L. H. C.; Guedes, C. G. F.; Rosa, D. S. Polym Adv Technol 2004, 15, 340.
18. Nitz, H.; Semke, H.; Landers, R.; Mulhaupt, R. J Appl Polym Sci 2001, 81, 1972.
19. Mungara, P.; Chang, T.; Zhu, J.; Jane, J. J Polym Environ 2002, 10, 31.
20. Shibata, M.; Yosomiya, R.; Ohta, N.; Sakamoto, A.; Takeishi, H. Polym Polym Compos 2003, 11, 359.
21. Kunioka, M.; Inuzuka, Y.; Ninomiya, F.; Funabashi, M. Macromol Biosci 2006, 6, 517.
22. Mohamed, A. A.; Finkenstadt, V. L.; Gordon, S. H.; Biresaw, G.; Palmquist, D. L.; Rayas-Duarte, P. Polym Degrad Stab, to appear.
23. Nicolais, L.; Narkis, M. J Appl Polym Sci 1971, 15, 469.
24. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites, 2nd ed.; Marcel Decker: New York, 1994.
25. Bazhenov, S.; Li, J. X.; Hiltner, A.; Baer, E. J Appl Polym Sci 1994, 52, 243.