Gelatinized Starch/Biodegradable Polyester Blends: Processing, Morphology, and Properties

Katherine Dean, Long Yu, Stuart Bateman, Dong Yang Wu

CSIRO Manufacturing and Infrastructure Technology, 37 Graham Road, Highett, Victoria 3190, Australia

ABSTRACT: Blends of polycaprolactone (PCL)/gelatinized starch and polybutylene succinate adipate/gelatinized starch have been prepared in various ratios and their phase morphology and thermal/mechanical properties have been analyzed. For both the PCL/plasticized starch and polybutylene succinate adipate/plasticized starch blends the resistance to impact increased with increasing polyester content, and the tensile modulus reached a maximum at around 80 wt % polyester content. In blends containing up to 70 wt % polyester (as observed by scanning electron microscopy) a hierarchical dispersion of the gelatinized starch phase was observed (distinct domain sizes of those less than 5 μm and those greater than 15 μm) and in the blends containing 70–90 wt % polyester a more singular dispersed phase of gelatinized starch was observed within the polyester matrix. Dynamical mechanical analysis results showed some phase mixing was present in the PCL/gelatinized starch blends noted by the appearance of an additional tan δ peak located between the glass transition temperatures of the respective components and broadening of the low temperature transition corresponding to the T_g of the polyester (possibly the result of a starch-rich polyester phase) with some overlap with the low temperature β transition of the gelatinized starch itself. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 802–811, 2007

Key words: starch; blends; biopolymer; PCL; mechanical properties; Bionolle[TM]

INTRODUCTION

There is significant interest in the development of environmentally friendly biodegradable polymers, in particular natural biodegradable polymers from renewable resources. Natural biodegradable polymers (starches, proteins, and cellulose) are generally quite brittle, degrade relatively quickly (of the order of weeks-months depending on the environment in which they are held), and they are also hydrophilic in nature. Synthetic biodegradable polymers from petroleum-based products are generally not brittle, however they take significantly longer periods to degrade (up to years depending on the environment in which they are held) and are generally hydrophobic. A significant body of work has been undertaken on blends of starches and synthetic polyesters, with a focus on the compatibilization of the hydrophilic and hydrophobic components.[1–10]

A number of authors[2–10] have investigated the effects of blending ungelatinized starch with aliphatic biodegradable polyesters and thermoplastics. Park et al.[2] investigated a number of ungelatinized starch blends with thermoplastic polymers including a thermoplastic biodegradable polyester without the use of compatibilization. Scanning electron microscopy (SEM) of those samples indicated a decrease in interfacial adhesion and homogeneity with increasing starch content, which was reflected in the mechanical properties reported, where tensile strength and modulus both decreased with increasing starch content. Ratto et al.[3] also investigated a series of uncompatibilized starch/polyester blends and found that increasing the starch content led to a decrease in tensile strength and elongation as observed by Park et al.,[2] however a different trend was observed in the tensile modulus, where the modulus increased with increasing starch content. Bhattacharya and coworkers[4–7] investigated various aspects of ungelatinized starch/polyester blends. In those studies a small amount (around 5 wt %) of maleic anhydride grafted polyester was added to aid compatibilization and produced samples, which exhibited significant increases in tensile strength (increase of up to 24 MPa for the PBSA/starch blend) compared with the uncompatibilized blend of PBSA/starch. In all cases two glass transitions were observed; the lower subambient T_g corresponding to the polyester and the higher T_g (around 50–70°C) to the starch. Other researchers have also studied unplasticized starch/maleated PCL blends,[7] and other modifications of both the unplasticized starch and/or polyester component to improve compatibility.[9,10]

Matzinos et al.[11] investigated the properties of glycerol plasticized starch/PCL blends. For injection molded samples they observed an increase in modu-

Correspondence to: L. Yu (long.yu@csiro.au).

lus with increasing plasticized starch content (from 0 to 50 wt %) and a decrease in strength and elongation at both yield and break. Averous et al.[12,13] also studied the effects of composition on the mechanical and thermal properties of glycerol plasticized starch/PCL blends, observing very low compatibility between the polymeric systems but a significant reduction in moisture sensitivity compared with the pure plasticised starch itself. Averous et al.[12,13] also showed that the less viscous PCL migrated to the surface during injection molding in effect encapsulating the starch, potentially reducing water sorption.

Kim et al.[14] investigated both ungelatinized and gelatinized starch/PCL blends. In this case the starch was plasticized with either water or poly(ethylene glycol) in a Brabender mixer prior to final melt mixing with PCL. All samples were dried, molded by hot-pressing and specimens cut for tensile measurements. Kim et al.[14] did not vary the starch content of the samples, but rather investigated aspects such as the molecular weight of the poly(ethylene glycol), which was used and found that the correct choice of molecular weight for the poly(ethylene glycol) could maximize the mechanical properties and produce small domain sizes for the starch dispersed phases effectively stabilizing the starch/PCL interface. Rosa et al.[15] also investigated ungelatinized and gelatinized starch/PCL blends with the focus of their investigation on varying the ratios of the components and assessing what effect each had on the melt flow index, water absorption, and thermal properties. Rosa et al.[15] also found that starch increased the susceptibility of the material to absorb water and that the rupture of the starch granules during the gelatinization process further enhanced the materials susceptibility to water sorption. Light microscopy indicated that blends with gelatinized starch had better interfacial adhesion than those that were not. Bastioli et al.[16–18] have also studied PCL/starch blends quite extensively and in the early 90s patented the commercial product Mater-Bi[TM] a blend of de-structured (gelatinized) starch and PCL.

Dubois and Narayan[19] investigated gelatinized and ungelatinized starch blends with PCL. The authors[17] found conventional melt blending resulted in materials, with poor mechanical performance due to the lack of interfacial adhesion between the hydrophobic polyester and the hydrophilic starch. Compatibilization was undertaken via the grafting of PCL chains onto a polysaccharide backbone such as dextran, the compatibilized PCL/starch blends exhibited improved tensile properties and biodegraded more rapidly. Kim et al.[20] also investigated the effects of compatibilization in blends of gelatinized starch and PCL. PCL was modified using glycidyl methacrylate (GMA) and maleic anhydride. Reactive blends of PCL-g-GMA and starch showed well-dispersed starch domains in the matrix and better mechanical strength than the unmodified PCL/starch blend. However, the reaction between PCL-g-GMA and starch induced crosslinking during the reactive blending and this lowered the biodegradability of the blend during the composting test. The biodegradability was investigated by the weight loss and surface morphology change of the blend in the composting medium.[21]

Yu et al.[22,23] also investigated the effect of a compatibilizer (methylenediphenyl diisocyanate) distribution in 50 : 50 wt % blends of starch and PCL or PBSA and found significant improvement in interfacial bonding, which resulted in improved mechanical and thermal properties. They also reported possible evidence of grafting between the starch and polyester, which may have potentially effected the rate of degradation of these materials.[22,23]

Schwah and Averous[24] compared the morphology and properties of both glycerol gelatinized starch/PCL and glycerol gelatinized starch/PBSA blends, relating the interfacial compatibility of the various blends with their resulting morphologies and properties and found that PBSA was more compatible with starch than PCL and as a consequence exhibited a higher peel strength in a multi-laminate section.

This study outlines the different phase morphologies that are produced in melt blended starch/polyesters using a twin-screw extruder, with an emphasis on the starch phase being pregelatinized with water in the extruder prior to blending. The effects of varying the starch content and the relationships between the resulting morphologies and thermal and mechanical properties of these blends without the use of compatibilizers are also reported. There are a number of potential applications for these types of blends, such as improving the compatibility of multi-layered coextrusion (where the more water sensitive core consists of a starch/polyester blend) without the use of potentially toxic compatibilizing agents.

MATERIALS

Initially 85 wt % high amylose content starch (Penford, Australia) was combined with 15 wt % water (added dropwise to the starch in a high speed mixer). This mixture was then extruded at 170°C to form plasticized starch pellets. The gelatinized starch was then reextruded with varying percentages of either polybutylene succinate adipate (PBSA, Fig. 1,
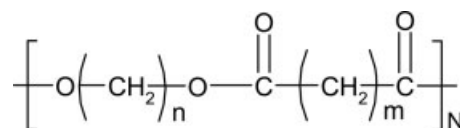
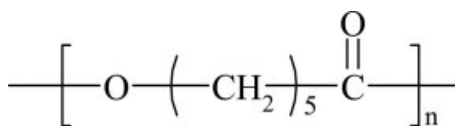**Figure 1** The structure of polybutylene succinate adipate (PBSA).

Figure 2 The structure of polycaprolactone (PCL).

Bionolle[TM] supplied by Showa Polymers, Japan) or polycaprolactone (PCL, Fig. 2, supplied by Solvay caprolactones, with a molecular weight of 50,000) and extruded at 160°C in both cases.

EXPERIMENTAL

A Theysohn corotating twin extruder with a barrel temperature of 160–170°C was used to process materials in this study. Down stream from the extruder, the molten strand of gelatinized starch and its corresponding blends were cooled in air and then pelletized. The samples were injection molded using a Battenfeld injection molder, with injection temperatures for the PBSA based blends being between 110 and 130°C and the injection temperatures for the PCL blends being between 80 and 90°C depending on the blend configuration. After extrusion all samples were conditioned at 50% relative humidity and 22.5°C for 14 days prior to characterization to allow samples to equilibriate.

The thermal properties of the blends were analyzed using two different methods. A Perkin–Elmer thermal gravimetic analyzer (TGA) was used to measure the weight loss of samples over a temperature range. Samples (>10 mg) were scanned from 50 to 600°C at a rate of 10°/min. A Pyris Diamond dynamical mechanical analyzer (DMA) was used to measure real modulus (E'), the loss modulus (E'') and tan δ (where tan δ = E''/E') using a three-point-bend configuration at 1 Hz over the temperature range from −100 to 100°C. The dimensions of the injection molded samples were

12.5 × 40 × 2 mm³. All scans were duplicated to ensure reproducibility.

Cryo-fracture surfaces were prepared by immersing samples in liquid nitrogen for 5 min followed by manual fracture. The samples were then immersed in water and placed in an ultrasonic bath for 40 min to partially dissolve the starch phase. The samples were mounted and carbon-coated in preparation for SEM imaging. A Leica Stereoscan 360FE SEM operating at 5 kV was used to image the fracture surfaces. Generally samples were magnified from 1000 to 3000 times.

The water absorption properties of the blends were studied by measuring the water uptake over time. Samples of dimensions 12.5 × 125 × 0.2 mm³ were equilibrated in the laboratory at 22.5°C and weighed prior to immersion in distilled water. The samples were periodically removed from the water, blotted on filter paper, and weighed to an accuracy of 0.0000 g. The values of percentage weight change were obtained from the average of three samples.

Tensile properties were evaluated in accordance to ASTM D 5938 on an Instron tensile testing apparatus (5565) utilizing a 30 kN load cell, 0.5 mm/min (modulus) 50 mm/min strain rate (tensile strength and elongation). An external extensometer was used for independent modulus measurements. The individual values provided were an average of 10 repeats. Impact properties were tested according to ASTM 256 on a Radmana ITR 2000 instrumented impact tester in Izod mode with impact strain rate 3.5 ± 0.2 m/s. The individual values provided were an average of 10 repeats.

RESULTS AND DISCUSSION

Figures 3 and 4 show the weight loss versus temperature as measured by TGA for the PBSA/starch blend and the PCL/starch blend, respectively. Three distinct regions can be seen in these figures, as discussed by
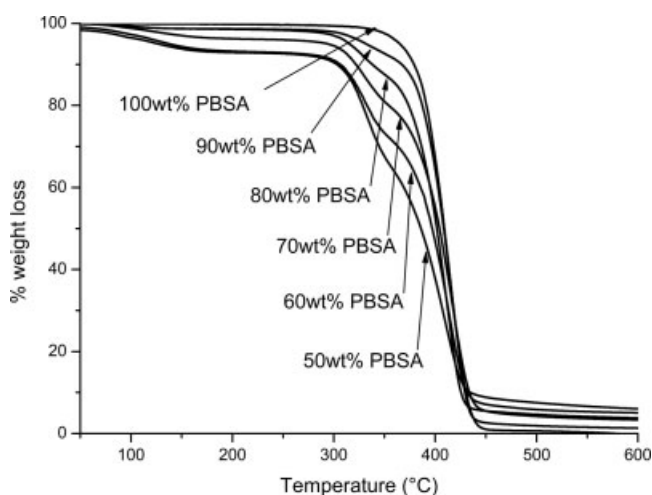

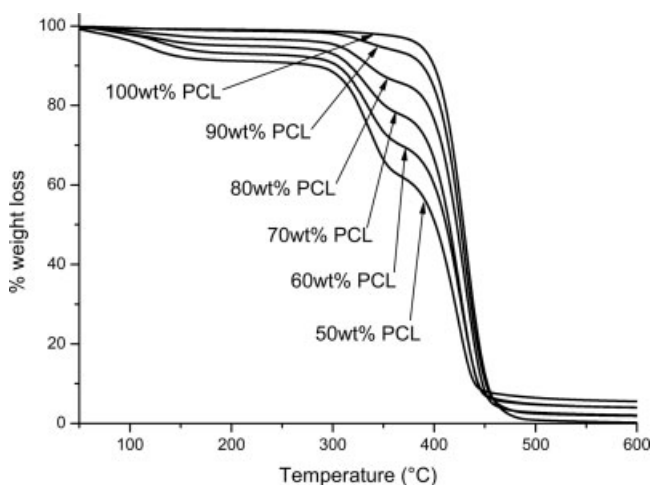**Figure 3** TGA scans of PBSA:starch blends.

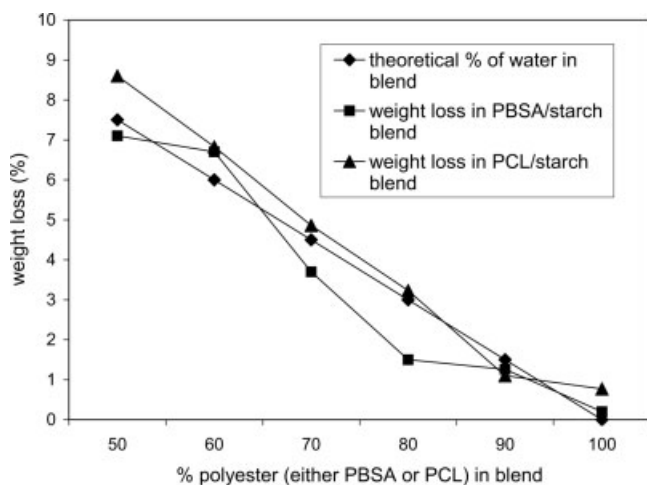**Figure 4** TGA scans of PCL:starch blends.

Figure 5 Theoretical water content compared with weight loss is respective blends after scanning up to 200°C as an indication of water level.

previous authors[23,24] the initial weight loss is generally due to loss of moisture (either free or bound)—Predominantly from the gelatinized starch (75–200°C); the second stage is the main degradation zone of both the starch and the polyester (predominantly due to depolymerization and the subsequent formation of low molecular weight unsaturated and aliphatic carbon species[25]) (300–400°C) and the final stage is generally carbonization (<400°C). The initial weight loss region shows a consistent trend of increased weight loss with increased gelatinized starch content as one may expect as the water content is directly proportional to the gelatinized starch content in the blend. Further analysis of the weight loss in these systems is illustrated in the proceeding figures. Figure 5 illustrates the theoretical water content as calculated from the original water content* of the samples prior to extrusion compared with the actual weight loss in the blends as they are heated up to 200°C. As discussed earlier in this article, the initial region of weight loss (up to 200°C) is primarily due to loss of moisture. Both blends show close correspondence to this theoretical value.

Figures 6 and 7 show the percentage weight loss at 200°C, 350°C and final weight loss at 600°C taken from the TGA scans for the respective PBSA/starch blend and the PCL/starch blend. The PBSA/starch blend showed an increase in weight loss with increasing starch content at both 200 and 350°C. This is due in part to the increased water content in the samples, which contained more starch. It also indicated the PBSA was potentially more thermally stable than the starch, which may be due to preferred tendency of

the starch to undergo thermally initiated hydrolysis compared with the PBSA.

The weight loss over the first 200°C for the PBSA/gelatinized starch blends increased with increasing gelatinized starch content, this may be expected as the starch is gelatinized with water and this weight loss would predominantly be water. After scanning up to 350°C the weight loss still increased with increasing amounts of gelatinized starch, although at 10 and 20 wt % starch this loss appeared to stabilize somewhat. After scanning to 600°C the neat PBSA sample was completely consumed, however, approximately 6 wt % of the original weight of the 50 : 50 wt % PBSA/starch remained, possibly because of carbonization of the starch as observed by other authors[26,27] at these kinds of temperatures. The PCL/gelatinized starch blends also showed similar trends in the TGA scan to the PBSA/gelatinized starch blends. The weight loss over the first 200°C for the PCL/gelatinized starch blends increased with increasing plasticized starch content. After scanning up to 350°C the weight loss still increased with increasing amounts of starch, although at 10 and 20 wt % starch this loss appeared to stabilize somewhat. After scanning to 600°C the neat PCL reached almost complete consumption, however, approximately 5.5 wt % of the original weight of the 50 : 50 wt % PCL/gelatinized starch remained, as in the PCL blends this residual weight was most likely due to the carbonization of the starch as suggested by previous authors.[26,27]

The DMA traces of tan δ for the PBSA/gelatinized starch blends (Fig. 8) show two clear glass transitions for the 50 : 50 and 60 : 40 PBSA/starch blends, indicating a phase separated system. The lower transition at around −38°C to −40°C, corresponds primarily to the T_g of the PBSA (with a small contribution from the β transition in gelatinized starch, which is generally found between −62°C and −54°C depending on the
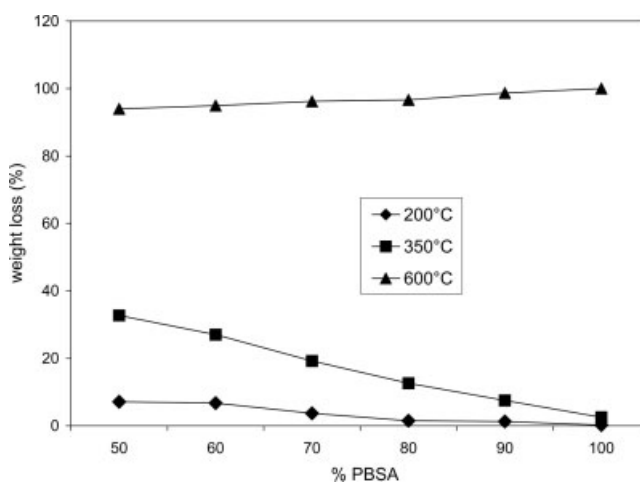

Figure 6 Percentage weight loss at different temperatures during the thermal scanning of PBSA/starch blends.

---

*Please note this does not include the original moisture content in the starch or the polyesters, the moisture contained in both of these is assumed to have driven off in the extrusion process.
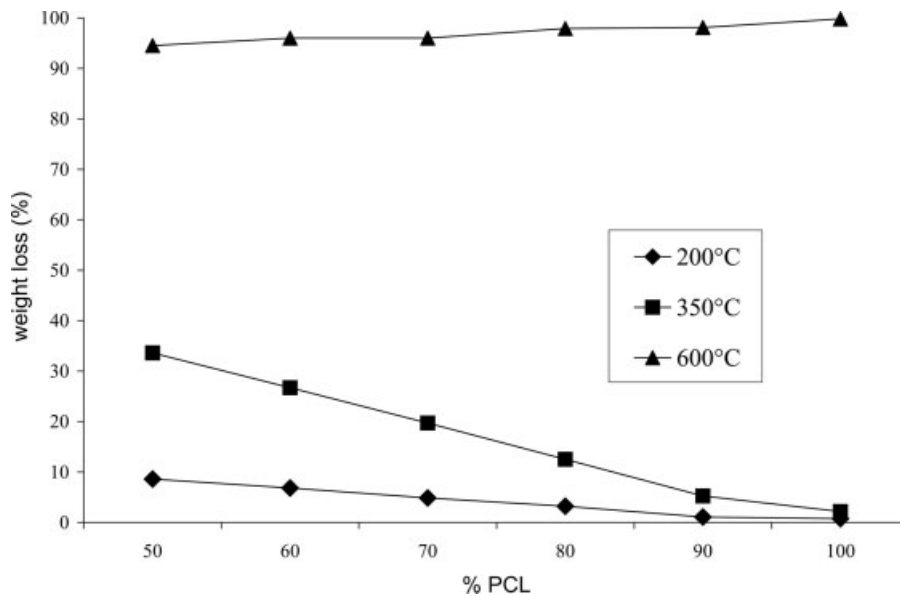
Figure 7 Percentage weight loss at different temperatures during the thermal scanning of PCL/starch blends.

plasticizer used[26]) and the higher transition at 50–60°C corresponds to the T_g of the gelatinized starch and are comparable to thermal transitions observed by other authors for blends of starches and polyesters.[6,12,28] As the amount of PBSA present in the blend was increased to 70 and 80 wt %, the higher temperature transition due to the starch became less visible. This transition may have also moved to a higher temperature due to restrictions in movement of the starch chains, either by the physical entanglement and/or encapsulation by the polyester, or the higher polyester content may affect the level of moisture in the starch and thus the level of plasticization. The low temperature transition due to the PBSA had a general downwards trend with increasing starch and water content (neat PBSA $T_g = -37.7°C$ compared with 50 : 50 wt % PBSA/gelatinized starch $T_g = -38.9°C$), this may be

because of a decrease in molecular weight of the polyester due to hydrolysis of the ester groups as suggested previously for the low molecular weight fraction in biodegradable polyesters or by the water acting as a plasticizer for the polyester.[29] The shift in the lower temperature transition was small, giving some indication that the variation in miscibility of the two polymers with varying starch content was minimal.

The DMA traces of tan δ for the PCL/gelatinized starch (Fig. 9) showed more interesting behavior. Similar to the 50 : 50 wt % starch/PBSA blends, two T_gs were also observed in this system; the lower at −56.4°C corresponding to PCL and the higher at 40.4°C corresponding to the gelatinized starch similar to behavior for gelatinized starch/PCL blends observed by previous authors.[12,28] As this blend was
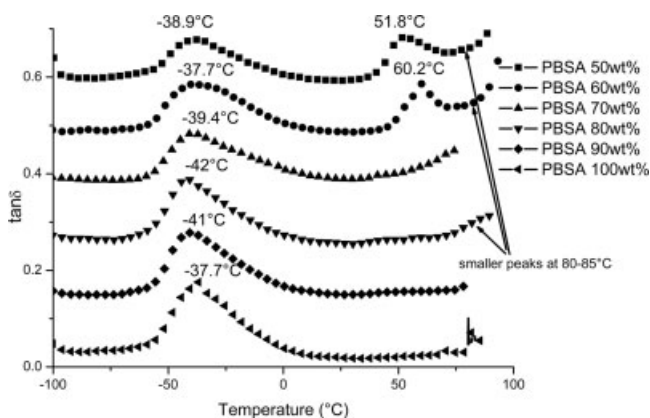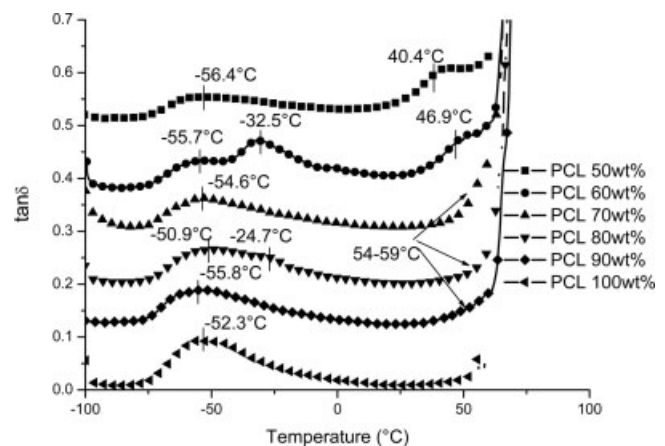

Figure 8 DMTA scans of starch/PBSA blends containing various amounts of PBSA (from 50 to 100 wt %) showing tan δ versus temperature (°C).

Figure 9 DMTA scans of PCL/starch blends containing various amounts of PCL (from 50 to 100 wt %) showing tan δ versus temperature (°C).
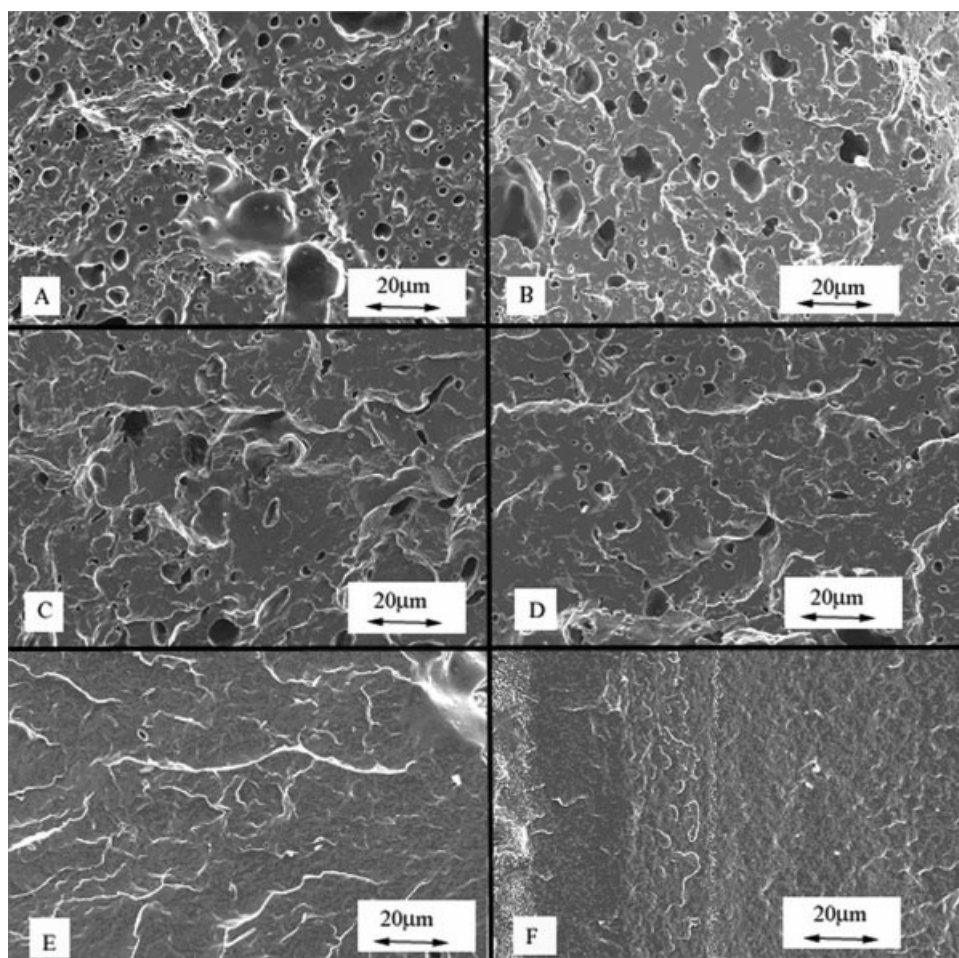
Figure 10 SEM imaging of different PBSA/starch blends: (A) 50 : 50 wt % PBSA/starch; (B) 60 : 40 wt % PBSA/starch; (C) 70 : 30 wt % PBSA/starch; (D) 80 : 20 wt % PBSA/starch; (E) 90 : 10 wt % PBSA/starch; and (F) 100 : 0 wt % PBSA/starch.

processed at a lower temperature the amount of water remaining in the material postextrusion as a plasticizer for starch is high, which may explain the lower T_g for the starch of 40.4°C compared with 51.8°C for the 50 : 50 wt % PBSA blend. The low temperature transition due to the PCL also showed a general downwards trend with increasing starch and water content (neat PCL $T_g = -52.3$°C compared with 50 : 50 wt % PCL gelatinized starch $T_g = -56.4$°C) possibly due to hydrolysis of the ester groups as suggested previously.[27] The lower temperature transition is very broad in all PCL/starch blends indicating some degree of miscibility or a more prominent β transition in the starch. Interestingly the 40 : 60 and 20 : 80 starch/PCL blends show clearly the presence of a third peak lying between the two expected. This third peak at −32°C and −24°C (for the 40 : 60 and 20 : 80 gelatinized starch/PCL blend, respectively), may correspond to a small miscible phase of starch/PCL. Miscibility may be due to hydrogen bonding between the hydroxyl groups of the starch and polyester, or ester exchange reactions between starch and polyester (greater concentration of ester groups in the PCL compared with

the PBSA) resulting in the formation of grafted PCL-starch structures.

A clearly hierarchical dispersion of the gelatinized starch phase was observed in the 50 : 50 wt %, 60 : 40 wt % and to a lesser extent in the 70 : 30 wt % PBSA/gelatinized starch blends [Fig. 10(A)–10(C), respectively]. In these cases the gelatinized starch phase was present in two different length scales (those less than 5 μm and those greater than 15 μm) As the amount of gelatinized starch in the blend was decreased to 20 and 10 wt % a more singular dispersed phase of gelatinized starch was observed within the polyester matrix [Fig. 10(D) and 10(E)]. Similar hierarchical structures were also visible in the 50 : 50 wt % and 60 : 40 wt % PCL/gelatinized starch blends [Fig. 11(A) and 11(B)], showing the starch phase again with two distinct length scales, those less than 5 μm and those greater than 15 μm. The larger starch phase in both high starch content PCL and PBSA blends exhibited a degree of continuity throughout the blend, but could not be classified as cocontinuous. The smaller scale starch phase in the 50 : 50 wt % PCL/gelatinized starch blend appeared more uniform than in the
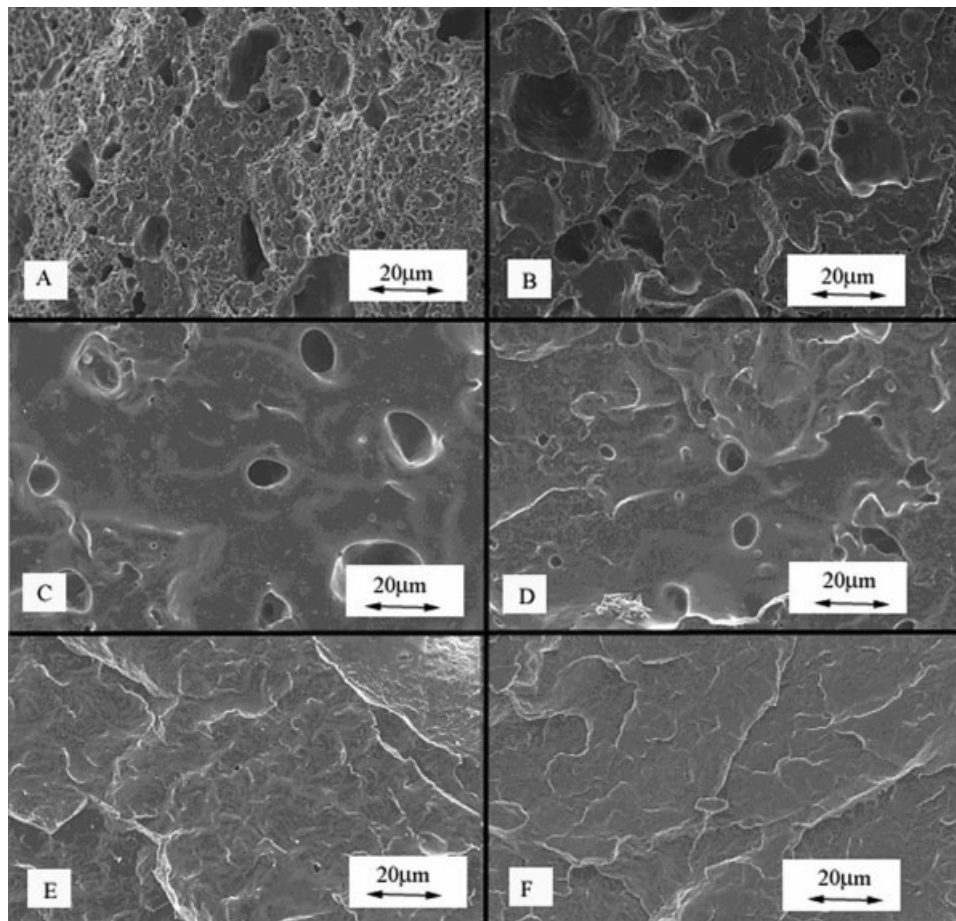
Figure 11 SEM imaging of different PCL/starch blends: (A) 50 : 50 wt % PCL/starch; (B) 60 : 40 wt % PCL/starch; (C) 70 : 30 wt % PCL/starch; (D) 80 : 20 wt % PCL/starch; (E) 90 : 10 wt % PCL/starch; and (F) 100 : 0 wt % PCL/starch.

50 : 50 wt % PBSA/gelatinized starch [compare Fig. 10(A) with Fig. 11(A)], exhibiting almost a cell type structure. Similar to the PBSA/gelatinized starch blend the PCL/gelatinized starch blend showed a more singular dispersed phase of gelatinized starch within the polyester matrix [Fig. 11(D) and 11(E)] as the amount of gelatinized starch in the blend was decreased to 20 wt % and 10 wt %, respectively.
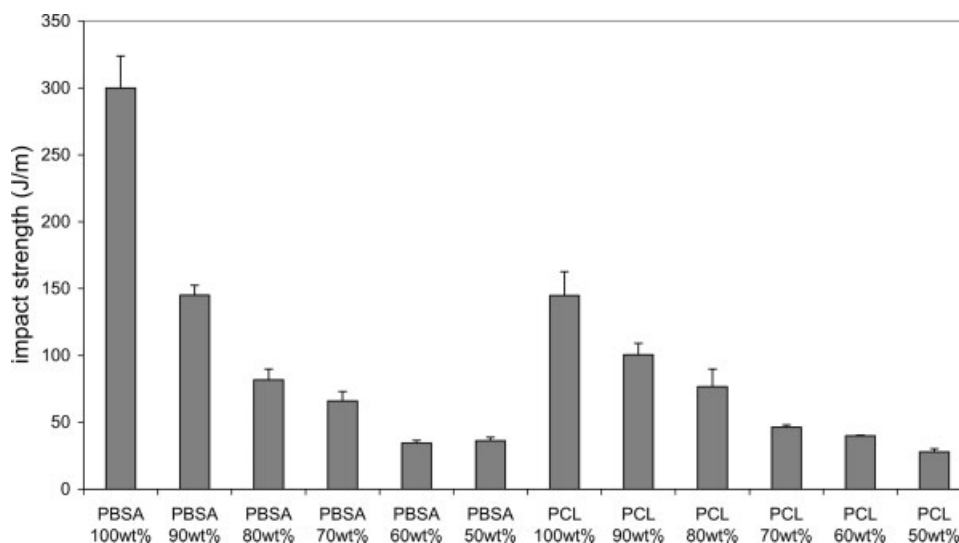

Figure 12 Notched impact strength (J/m) for various starch/PBSA and starch/PCL blends.
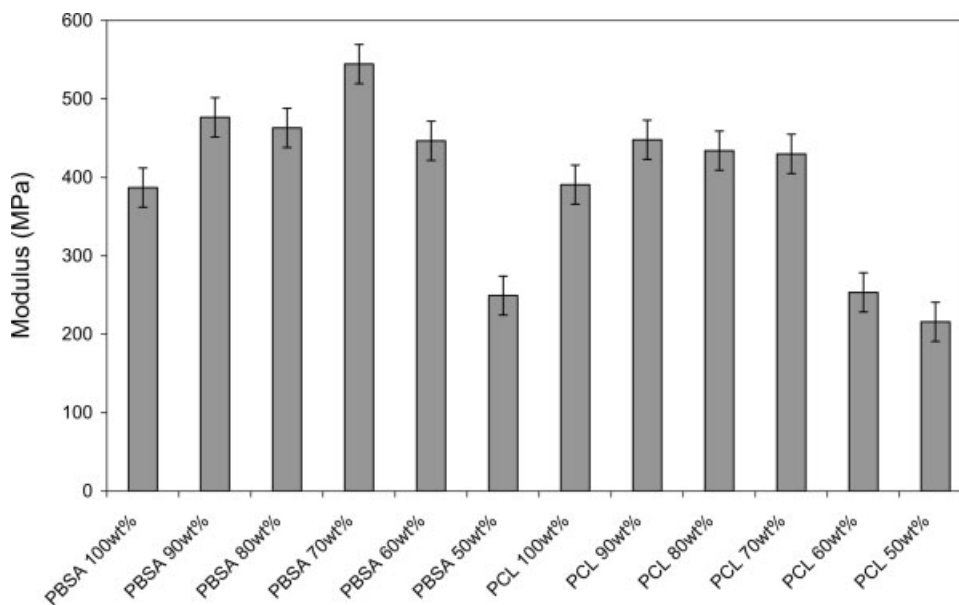
Figure 13 Tensile modulus (0.05 mm/min, extensometer used) for various PBSA/gelatinized starch and PCL/gelatinized starch blends.

An increase in impact strength corresponding to an increase in the polyester component was observed for both the PBSA/plasticized starch and the PCL/plasticized starch blends. Starch is inherently brittle and this type of impact strength behavior may be expected (Fig. 12).

Unlike the impact strength results, the modulus values reached a maximum at around 70 wt % PBSA for the PBSA/gelatinized starch blends and at approximately 70–80 wt % PCL for the PCL/gelatinized

starch blends (Fig. 13). This may be because of disappearance of the fine gelatinized starch phase (domain sizes of those around 5 μm) observed at higher starch content blends. In the blends containing a higher starch content (and thus higher water content) the water may have also acted as a plasticizer to the polyester reducing the modulus and increasing the elongation to break. The plasticizing effect of water from the gelatinized starch on the polyester phase is counterbalanced by the high modulus recorded for gelati-
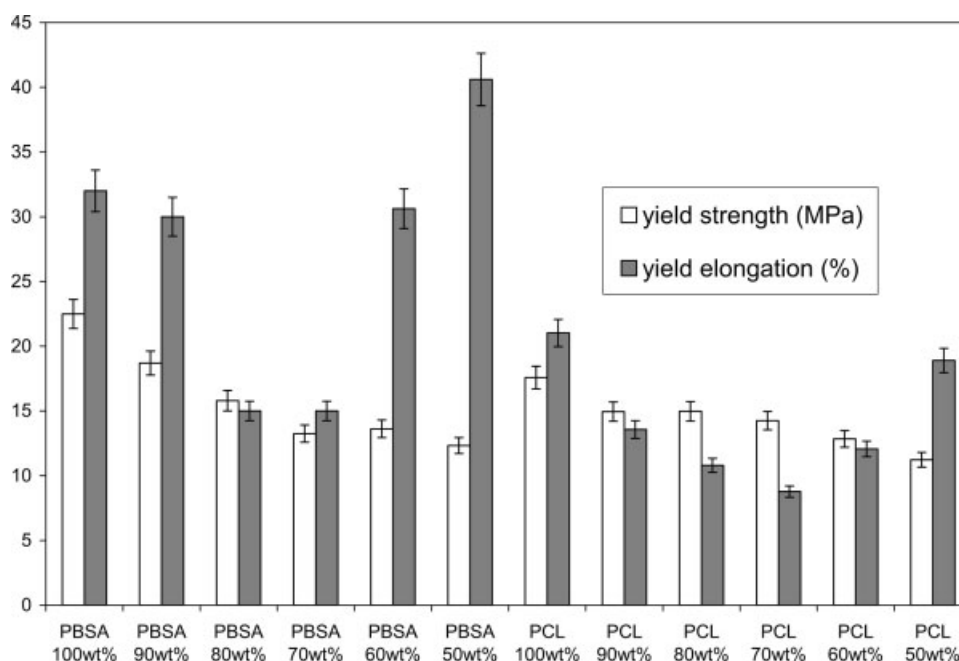

Figure 14 Tensile strength (MPa) and elongation at yield (%) for various starch/PBSA and starch/PCL blends.

nized starch itself (modulus of 2700–3000 MPa—Measured from a sheet extruded sample), hence the modulus of the blends reach a maximum value.

The yield strength increased with increasing polyester content with similar trends to those observed in the impact strength data, similar results were observed by Mani and Bhattacharya[6] with polyester blends containing ungelatinized starch (Fig. 14). The yield elongation showed a minima around 70–80 wt % polyester for both blends (Fig. 14). These minima in yield elongation may be explained by a number of mechanisms. Initially the neat polyesters have quite high elongations to break, as the gelatinized starch phase is increased the elongation of the blend decreases (because of the brittle nature of the starch itself). As the gelatinized starch content (and thus water content) is increased further the water could have had a plasticizing effect on the polyester phase leading to a recovery of the high elongation to break. The water gelatinized starch/polyester blends showed quite different mechanical behaviors to that reported for ungelatinized starch/polyester blends[2–10] giving further confirmation that the water present in the gelatinized starch phase has plasticized the polyester and played a major role in effecting the final properties of the blends.

With the exception of the 50 : 50 wt % blends, the PCL and PBSA blends exhibited similar weight increases due to water sorption. Although both the 50 : 50 wt % PBSA/gelatinized starch blend and the 50 : 50 wt % PCL/gelatinized starch blend clearly showed two different length scales of the starch phase (Figs. 10 and 11), the 50 : 50 wt % PCL/gelatinized starch blend appeared to have greater amount of finer structure. The finer starch phase (less than 5 μm) and
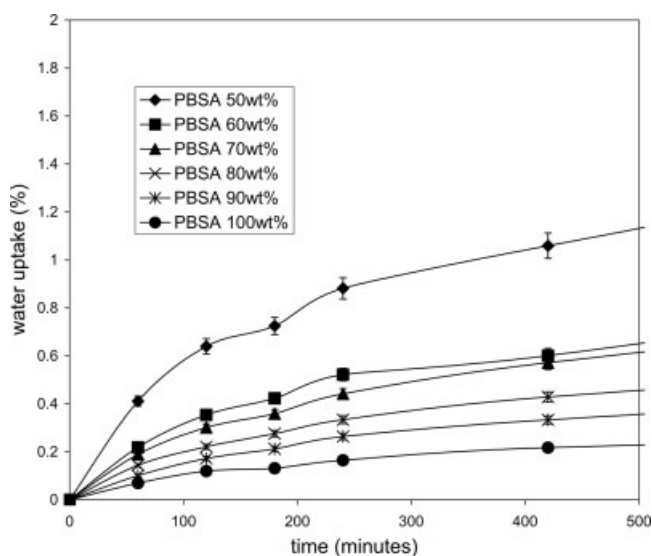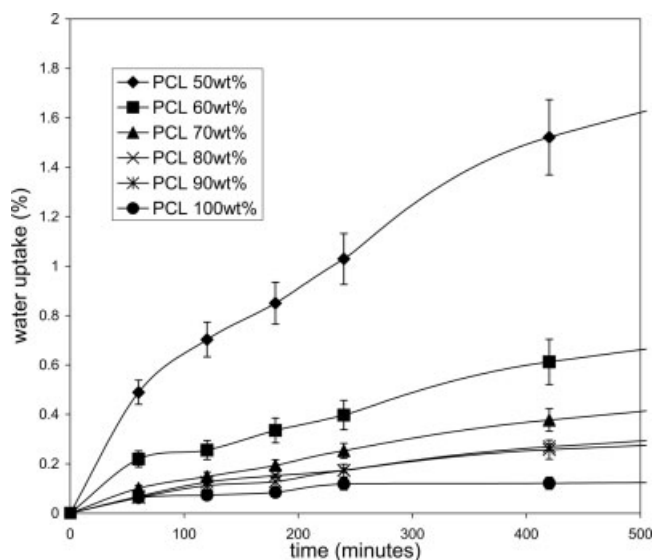

Figure 16 Water uptake at 18.5°C for the PCL/starch blends.

thus greater surface area of hydrophilic starch may have aided the sorption of water. The absorption of water in both blends was nonlinear, possibly due to a number of competing interactions occurring: the water being absorbed, water causing swelling and water partially dissolving the starch phase forming a larger surface area and thus more absorption of water.

CONCLUSIONS

Blends of PCL/gelatinized starch and PBSA/gelatinized starch have been prepared and their phase morphology and properties have been analyzed. For both the PCL/gelatinized starch and PBSA/gelatinized starch blends the resistance to impact increased with increasing polyester content. In blends containing up to 70 wt % polyester (as observed by SEM) a hierarchical dispersion of the gelatinized starch phase was observed (distinct domain sizes of those less than 5 μm and those greater than 15 μm) and in the blends containing 70–90 wt % polyester a more singular dispersed phase of gelatinized starch was observed within the polyester matrix. The modulus reached a maximum at around 70 wt % PBSA for the PBSA/gelatinized starch blends and at approximately 70–80 wt % PCL for the PCL/gelatinized starch blends, due to a balance between the high modulus of the gelatinized starch phase itself and the plasticizing effect of the water from the starch phase to the polyester (Figs. 15 and 16). The water sorption increased with starch content in all blends and was nonlinear due to competing absorption, swelling and dissolution (of the water soluble starch). Some miscibility was observed in the PCL-starch blends this was possibly due to hydrogen bonding between the hydroxyl groups of

Figure 15 Water uptake at 18.5°C for the PBSA/starch blends.

the starch and polyester, or ester exchange reactions between starch and polyester forming grafted PCL-starch structures.

References

1. Averous, L. J Macromol Sci Polym Rev 2004, 44, 231.
2. Park, H.-M.; Lee, S.-R.; Chowdhury, S. R.; Kang, T.-K.; Kim, H.-K.; Park, S.-H.; Ha, C.-S. J Appl Polym Sci 2002, 86, 2907.
3. Ratto, J. A.; Stenhouse, P. J.; Auerbach, M.; Mitchell, J.; Farrell, R. Polymer 1999, 40, 6777.
4. Sen, A.; Bhattacharya, M.; Stelson, K. A.; Voller, V. R. Mater Sci Eng A 2002, 338, 60.
5. Sen, A.; Bhattacharya, M. Polymer 2000, 41, 9177.
6. Mani, R.; Bhattacharya, M. Eur Polym J 2001, 37, 515.
7. John, J.; Mani, R.; Bhattacharya, M. J Polym Sci Part A: Polym Chem 2002, 40, 2003.
8. Wu, C.-S. Polym Degrad Stab 2003, 80, 127.
9. Koenig, M. F.; Huang, S. J. Polymer 1995, 36, 1877.
10. Kweon, D.-K.; Kawasaki, N.; Nakayama, A.; Aiba, S. J Appl Polym Sci 2004, 92, 1716.
11. Matzinos, P.; Tserki, V.; Kontoyiannis, A.; Panayiotou, C. Polym Degrad Stab 2002, 77, 17.
12. Averous, L.; Moro, L.; Dole, P.; Fringant, C. Polymer 2000, 41, 4157.
13. Belard, L.; Dole, P.; Averous, L. Aust J Chem 2005, 58, 457.
14. Kim, C.-H.; Choi, E.-J.; Park, J.-K. J Appl Polym Sci 2000, 77, 2049.
15. Rosa, D. S.; Guedes, C. G. F.; Pedroso, A. G.; Calil, M. R. Mater Sci Eng C 2004, 24, 663.
16. Bastioli, C.; Bellotti, V.; Del Tredici, G.; Lombi, R.; Montino, A.; Ponti, R.; Romano, G.; Tredici, G. D.; Bastiolo, C.; Monito, A.; Bastioli, K.; Bastioli, C.; Bellotti, V.; Montino, A. Eur. Pat. WO9219680-A (1992).
17. Bastioli, C.; Bellotti, V.; Del Giudice, L.; Gilli, G. J Environ Polym Degrad 1993, 1, 181.
18. Bastioli, C. Polym Degrad Stab 1998, 59, 263.
19. Dubois, P.; Narayan, R. Macromol Symp 2003, 197, 233.
20. Kim, C.-H.; Jung, K.-M.; Kim, J.-S.; Park, J.-K. J Polym Environ 2004, 12, 179.
21. Biresaw, G.; Carriere, C. J. J Polym Sci Part B: Polym Phys 2001, 39, 920.
22. Yu, L.; Liu, H.; Xie, F.; Dean, K. Int Polym Process 2005, 4, 1.
23. Yu, L.; Dean, K.; Yuan, Q.; Xie, F.; Liu, H. J Appl Polym Sci (in press).
24. Schwach, E.; Averous, L. Polym Int 2004, 53, 2115.
25. Soliman, A. A. A.; El-Shinnawy, N. A.; Mobarak, F. Thermochim Acta 1997, 296, 149.
26. Xu, Y. X.; Dzenis, Y.; Hanna, M. A. Ind Crops Prod 2005, 21, 361.
27. Zhang, X.; Golding, J.; Burgar, I. Polymer 2002, 43, 5791.
28. Averous, L.; Boquillon, N. Carbohydr Polym 2004, 56, 111.
29. Willett, J. L.; Doane, W. M. Polymer 2002, 43, 4413.