

Properties and Morphology of Poly(lactic acid)/Soy Protein Isolate Blends

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ABSTRACT: Poly(lactic acid) (PLA)/soy protein isolate (SPI) blends with and without modifier were melt compounded in a intensive mixer. Tensile strength of PLA/SPI simple blends decreased more than pure PLA because the dispersed SPI granules acted as the stress concentration; tensile strength was improved by loading of sodium bisulfite (NaHSO₃). At 0.5 wt % NaHSO₃ loading, the blend gave 43.9 MPa of tensile strength. Blends containing both methylene diphenyl diisocyanate (MDI) and NaHSO₃ displayed a significant improvement in tensile strength, which increased by 38% at 4 wt % MDI, compared with the PLA/SPI/NaHSO₃ blend. The scanning electron mi-

croscopic observation demonstrated that incorporating NaHSO₃ and MDI improved compatibility between PLA and SPI. The differential scanning calorimetry indicated that SPI induced and accelerated cold crystallization of PLA in the blends, which was also affected by the presence of NaHSO₃ and MDI. The PLA/SPI blend containing both NaHSO₃ and MDI displayed higher water resistance than the PLA/SPI/NaHSO₃ blend. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 754–759, 2009

Key words: poly(lactic acid); soy protein; thermal blending; morphology; compatibility

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester that can be degraded by simple hydrolysis of the ester bond.¹ In addition to its biodegradability and biocompatibility, the PLA performance is comparable (e.g., mechanical strength and thermal plasticity) with that of petroleum-based plastics. PLA has attracted attention for its applicability in biomedical devices and biodegradable plastics.

Soy protein isolate (SPI), a commercially available, natural biopolymer, has potential for engineering applications. Plastics made from unmodified soy proteins are highly hydrophilic, which results in poor mechanical properties. Processing these plastics is difficult because SPI have strong intra- and intermolecular interactions. Many efforts have been made to improve processibility, flexibility, and stretchability of SPI polymers by modifying SPI with different plasticizers^{2–4} or blending SPI with other polyesters of hydrophobic nature, such as poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride),⁵ polycaprolactone,⁶ and PLA.⁷

However, PLA and SPI were thermodynamically immiscible and their interfacial adhesion was very weak, resulting in poor mechanical properties. For plastics made from two incompatible materials, the interfacial modification plays an important role in controlling both the segregation scale and solid-state adhesion between the components.⁸ Compatibility was necessary to improve interfacial strength between PLA and SPI. Sodium bisulfite (NaHSO₃) can efficiently break disulfite bonds in SPI subunits by fractionating soy protein into a glycinin-rich and a β -conglycinin-rich fraction, which improves flexibility and processibility of SPI. Methylene diphenyl diisocyanate (MDI) was highly reactive, forming urethane linkages⁹ with both hydroxyl and carboxyl groups. The effect of MDI (as a compatibilizer for the SPI/PLA blend¹⁰ or SP/PCL blend⁶) on tensile strength has been investigated. The main objective of this study was to improve compatibility between PLA and SPI through the loading of NaHSO₃ and MDI. Mechanical and thermal properties as well as water absorption of different PLA/SPI blends were evaluated.

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EXPERIMENTAL

Materials

The PLA (grade 2002D) with molecular weight of 120 kDa used in the experimental work was a

commercially available product from Natureworks, Inc. (Minnetonka, MN). Protein samples were isolated from defatted soy flour using the acidic precipitation method. Defatted soy flour was the product of Cargill (Cedar Rapids, IA) and used for preparation of SPI. Sodium bisulfite in solid form was the product of Fisher Chemicals (Fisher Scientific, Houston, TX). Polymeric MDI (Rubinate 1840) was obtained from ICI polyurethanes (Geismar, LA).

The SPI was extracted from the defatted soy flour by isoelectric point precipitation at pH 4.2. The precipitation was freeze dried (freeze-dryer, model 6211-0495, The Virtis Co., Inc., Gardiner, NY), and then milled (Cyclone Sample Mill, UDY Corp., Fort Collins, CO) into powder. The SPI contained more than 90% protein on a moisture-free basis.

Preparation of blends

PLA/SPI blends with or without NaHSO_3 were mixed by melt blending using an intensive mixer (Rheomix600, HB Instruments Inc., Paramus, NJ) at a rotation speed of $140 \times g$ at 175°C for 4 min. As to the preparation of PLA/SPI blends containing both NaHSO_3 and MDI, MDI and SPI were first mixed in a blender (International MFG, Co., NE) for 20 min at room temperature, and then the mixture, PLA, and NaHSO_3 were melt blended using the same blending conditions as the PLA/SPI blends. All the melt blends were ground into powder with about 1 mm particle size using a Model 4 Laboratory Mill (Thomas-Wiley Co., PA) and then were dried in a vacuum drying oven (Model 285A, Fisher Scientific, Co., PA) for 4 h before being compression molded into tensile bars.

The PLA/SPI simple blends, PLA/SPI blends containing only NaHSO_3 , and PLA/SPI blends containing both NaHSO_3 and MDI were abbreviated as SPI-X, NaHSO_3 -Y, and MDI-Z, respectively. X, Y, and Z denoted SPI, NaHSO_3 , and MDI weight percentage of PLA/SPI blends, respectively.

Mechanical property tests and morphology

Blends from the mixer were ground into powders then compression molded into tensile bars according to ASTM Method D 638-91 with a Carver hot press (Model 3889, Auto "M", Carver Inc., Wabash, IN) at 165°C and 5 MPa for 12 min (preheated for 7 min, pressed for 5 min). Molded specimens were cooled for 8 min before removal from the mold and then preconditioned at 50% relative humidity and 25°C for 48 h before testing. Tensile strength, elongation at break, and Young's modulus were determined with an Instron testing system (model 4465, Canton, MA) according to ASTM D 638-91 with a crosshead speed of 5 mm/min and 25-mm gauge length. Six

tensile bars were prepared for each treatment. Microstructures of the fractured samples after tensile testing were observed using a Hitachi S-3500N scanning electron microscope (SEM) (Hitachi Science Systems, Ltd., Ibaraki, Japan) at an accelerated voltage of 5 kV.

Differential scanning calorimetry

Thermal characteristics of PLA/SPI blends were determined by differential scanning calorimetry (DSC) (PerkinElmer Pyris 1, Norwalk, CT) from 20°C to 180°C at a scanning rate of $10^\circ\text{C}/\text{min}$ under protection of nitrogen flow. Peak temperatures and enthalpies at glass transition, crystallization, and melting were recorded. All results were obtained from the second DSC scan to eliminate different thermal history effects.

Water absorption

Rectangular samples (with length of 20 mm, width of 3 mm, thickness of 2 mm) were used for water absorption evaluation. Specimens were dried at 50°C for 24 h and cooled to room temperature. Dried specimens were submerged in distilled water at 25°C for a designated period, removed from the water, blotted with tissue paper to remove excess surface water, and weighed. Water absorption was calculated on a dry basis. Each measurement was replicated three times.

RESULTS AND DISCUSSION

SEM observation

The SEM experiment was used to observe phase morphology of PLA/SPI blends. There was a distinct interface between PLA and SPI for the uncompatibilized PLA/SPI blend; the dispersed SPI phase particles were large and nonuniform due to the inherent immiscibility [Fig 1(a)]. Notably, blends containing NaHSO_3 showed a significant change in morphology [Fig. 1(b-d)]. It exhibited much smaller (although still a few large) individual SPI particles at 0.05% NaHSO_3 loading. Moreover, the interface between PLA and SPI for the blend containing 0.5% NaHSO_3 was indistinct; although, a few smaller SPI agglomerates were observed. Degree of agglomeration of the SPI particles increased significantly at a high NaHSO_3 loading level, such as 3 wt %. Many functional groups such as the hydroxyl group in the SPI chains become active because of breakage of the disulfide bond of SPI induced by the presence of NaHSO_3 . We argue that hydrogen bonding might be formed between active hydroxyl groups and carboxyl groups of PLA chains, which could contribute

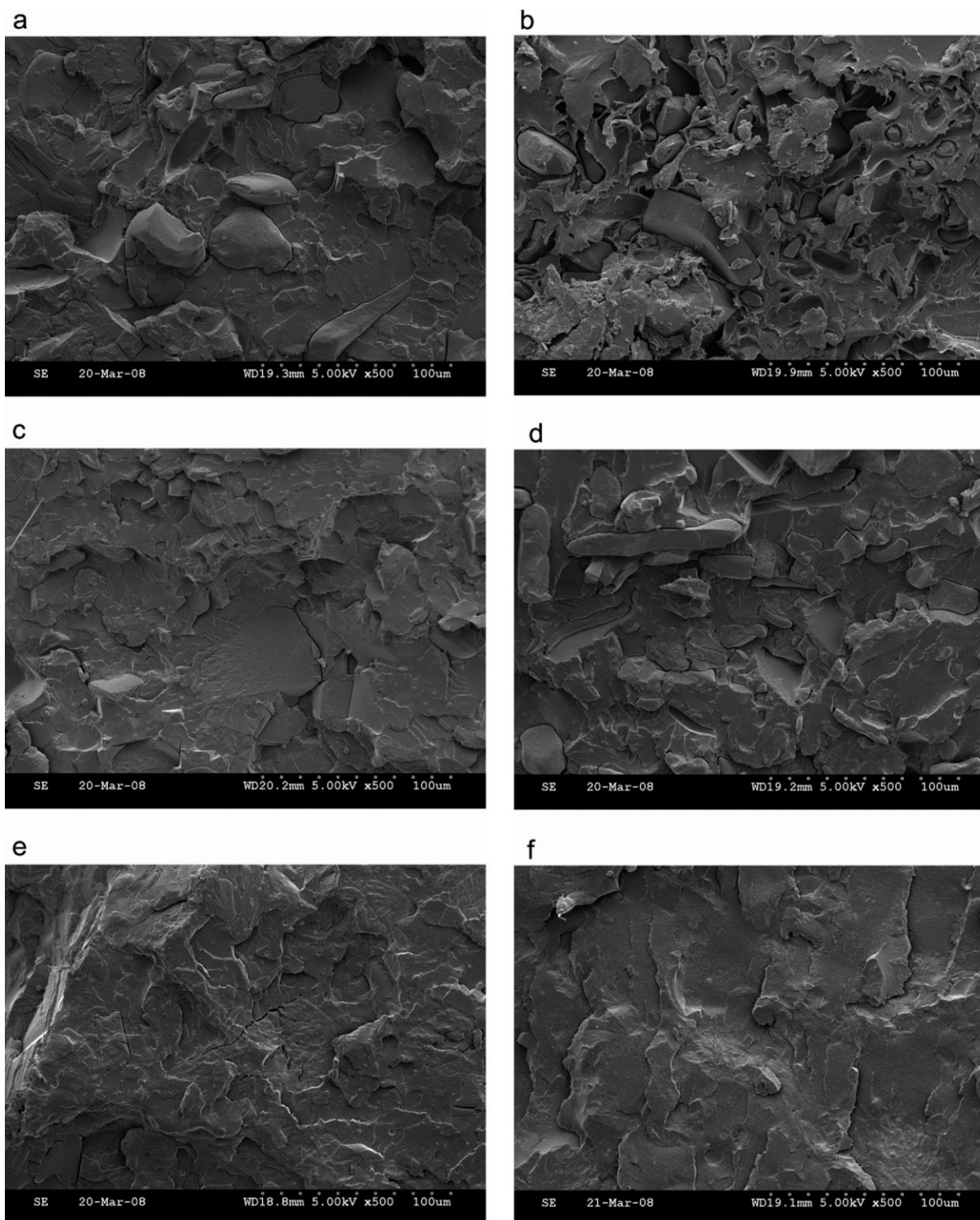


Figure 1 SEM micrographs of the tensile-fractured surface of different PLA/SPI (75/25) blends. (a) SPI-25; (b) NaHSO₃-0.1, (c) NaHSO₃-0.5, (d) NaHSO₃-3, (e) MDI-0.5, (f) MDI-4.

to improved compatibility between PLA and SPI. However, SPI particles tended to aggregate because breakage of the disulfide also resulted in stronger intermolecular charge–charge interactions between SPI. The blend containing both NaHSO₃ and MDI

displayed more uniform morphology [Fig. 1(e,f)]. Block or graft copolymers of PLA and SPI formed through urethane linkages in the presence of the reactive MDI. Those copolymers carrying the neighboring SPI chains readily diffused into the PLA

TABLE I
Mechanical Properties of Raw PLA and Different PLA/SPI Blends

Sample	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Neat PLA	64.6 ± 4.6	4.94 ± 0.24	1731 ± 102
SPI-10	42.8 ± 2.0	3.61 ± 0.52	1654 ± 133
SPI-25	33.3 ± 2.9	2.27 ± 0.18	1852 ± 115
SPI-40	24.6 ± 2.0	1.62 ± 0.06	1960 ± 101
NaHSO ₃ -0.1	30.02 ± 1.01	2.05 ± 0.07	1914 ± 105
NaHSO ₃ -0.25	42.15 ± 1.90	3.27 ± 0.21	2040 ± 41
NaHSO ₃ -0.5	43.87 ± 2.11	3.13 ± 0.18	2104 ± 178
NaHSO ₃ -1	26.11 ± 1.57	2.25 ± 0.13	1539 ± 97
NaHSO ₃ -3	24.26 ± 2.01	2.27 ± 0.2	1550 ± 170
MDI-0.25	43.1 ± 3.2	3.57 ± 0.20	1956 ± 99
MDI-0.5	58.1 ± 4.2 (48.9 ± 3.3)	3.39 ± 0.18 (3.53 ± 0.13)	2137 ± 91 (1988 ± 101)
MDI-1	55.6 ± 2.2	3.35 ± 0.33	2011 ± 148
MDI-2	55.3 ± 1.8	4.46 ± 0.21	1949 ± 80
MDI-4	60.4 ± 4.0	3.4 ± 0.20	2162 ± 92

matrix, which resulted in thicker interface between PLA and SPI and the concentration of gradient of each component at the interface decreased. Therefore, the interface of the blend containing both NaHSO₃ and MDI was hardly distinguished.

Mechanical properties

Mechanical performance data measured for PLA/SPI blends were compared with those measured for the pure PLA matrix (Table I). As expected, tensile strength and elongation at break of the PLA/SPI blends decreased linearly with increasing SPI content because dispersed SPI granules acted as stress concentration. Tensile strength of the blend containing 25% SPI decreased to 33.3 MPa, compared with 64.6 MPa for pure PLA. Mechanical properties of the PLA/SPI blends were improved after loading of NaHSO₃ (Table I). Maximum tensile strength was obtained at 0.5% NaHSO₃ loading; higher NaHSO₃ levels resulted in poor mechanical properties. Such phenomena were related to interfacial adhesion as affected by the NaHSO₃ content. Interfacial adhesion between PLA and SPI was improved at 0.5 wt % NaHSO₃ and below; at these levels, stress transferred effectively between the PLA and SPI phases. However, agglomerates of dispersed SPI particles [Fig. 1(d)] acted as the stress concentration, often inducing cracks and resulting in low strength. For the blend containing MDI in the presence of 0.5 wt % NaHSO₃, as described previously, the urethane linkage formed among three components (MDI, PLA, and SPI) led to stronger interfacial adhesion between PLA and SPI. Consequently, the blend displayed significant improvement in the tensile strength (Table I) compared with the blend containing only 0.5 wt % NaHSO₃. At 4 wt % MDI, tensile strength was about 60.4 MPa, which was 38% more

than that of the blend containing 0.5 wt % NaHSO₃ and slightly lower than that of pure PLA. It was well known that both PLA and SPI were rigid polymers and showed brittleness without proper plasticization, all SPI/PLA blends exhibited, as expected, low elongation at break and low tensile toughness, which were both unaffected by the compatibilizer.

Thermal properties

The DSC thermograms of pure PLA, SPI, and their blends are shown in Figure 2, and results are listed in Table II. There was no exothermic peak in the DSC curve for SPI specimens. Small molecules, such as water, in the protein system acted as plasticizers and reduced protein exothermic temperatures.^{11,12} No crystallization and melting peak was detected in the annealed raw PLA as a control, which was

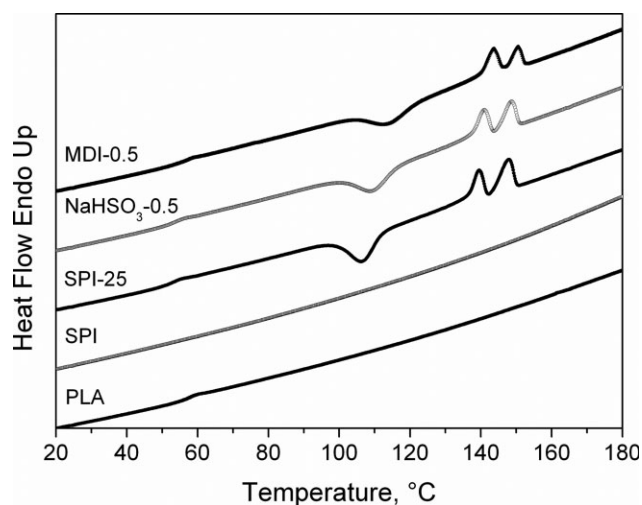


Figure 2 DSC thermograms of PLA, SPI, and different PLA/SPI (75/25) blends.

TABLE II
Thermal Properties of Pure PLA and Various PLA/SPI (75/25) Blends
Determined by DSC

Sample	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)
Neat PLA	56.5				
SPI-25	52.0	106.5	25.4	139.59	147.79
NaHSO ₃ -0.5	52.8	109.4	21.7	140.96	148.65
MDI-0.5	55.5	113.6	17.3	143.54	150.54

probably caused because the incorporation of D-mers into the L-chain disturbs its stereoregularity and lowers its ability to crystallize. When the D content is greater than 15%, a polymer, fully amorphous and noncrystallizable under heat treatment, was obtained.¹³ However, an obvious crystallization peak and double-melting peaks appeared in the DSC curves for all PLA/SPI blends. Such behavior indicated that SPI acted as a heterogeneous nucleating agent for the PLA matrix, and this induced and accelerated crystallization of PLA. The bimodal melting behavior might be contributed to the simultaneous occurrence of melting-reorganization and recrystallization-remelting of the lamellae originally formed during the crystallization process.^{14,15} The control PLA/SPI simple blend displayed a glass transition temperature (T_g) of 52.0°C and a cold crystallization temperature (T_{cc}) of 106.5°C. After loading of 0.5 wt % NaHSO₃, the glass transition temperature and cold crystallization temperature of the blend shifted to 52.8°C and 109.4°C, respectively. Such behaviors were caused by restricted slippage and mobility of the PLA macromolecular segment because interactions between PLA and SPI increased in the presence of NaHSO₃. Slippage and mobility of the PLA chain were further restricted by formation of urethane linkage in the presence of NaHSO₃ and

MDI; T_g and T_{cc} of the blends consequently increased to 55.5°C and 113.4°C, respectively.

Water absorption

Water absorption by all specimens increased quickly during the first few days and then leveled off (Fig. 3). SPI is a hydrophilic polymer because of its polar groups (e.g., hydroxyl, amino, and carboxyl groups) and ionic groups.⁵ As expected, water absorption of PLA/SPI simple blends significantly increased with increasing SPI content (data not shown). Regardless whether modifier was added, all specimens showed similar water absorption around 12 wt %, which depended on SPI loading content. However, water absorption rate was different; SPI-25 > NaHSO₃-0.5 > MDI-0.5. Such phenomena were related to microstructure of the blends. For the PLA/SPI blends containing NaHSO₃, intermolecular disulfite bonds were broken in the presence of NaHSO₃,¹⁶ which caused the hydrophobic group to be unsheltered and thus increased surface hydrophobicity of the blends. Water penetration was hindered, which resulted in a slow penetration rate. Water penetration rate of the PLA/SPI/NaSO₃ blends might be further lowered by incorporating MDI because of the formation of urethane linkages, which make the microstructure of the blend more compact.

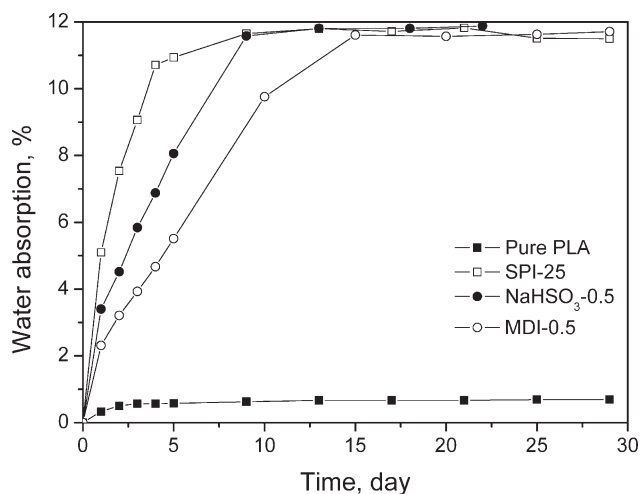


Figure 3 Water absorption versus time for (a) Neat PLA and different PLA/SPI (75/25) blends, (b) SPI-25, (c) NaHSO₃-0.5, and (d) MDI-0.5.

CONCLUSION

Compatibility between PLA and SPI is improved by incorporating NaHSO₃ alone or NaHSO₃/MDI. Particularly, a co-continuous phase is obtained for PLA/SPI blends containing both NaHSO₃ and MDI. Compared with the PLA/SPI simple blend, tensile strength of PLA/SPI/NaHSO₃ and PLA/SPI/NaSO₃/MDI blends is increased by 32% and 81%, respectively. Incorporating SPI and MDI affects the water absorption rate of blends but has no influence on ultimate water absorption, which depends on SPI content.

References

1. Garlotta, D. J. *Polym Environ* 2001, 9, 63.
2. Mo, X.; Sun, S. X. *J. Polym Environ* 2000, 8, 161.
3. Nanda, P. K.; Rao, K. K.; Kar, R. K.; Nayak, P. L. *J. Therm Anal Cal* 2007, 89, 935.

4. Mo, X.; Sun, X. *JAACS* 2002, 79, 197.
5. Zhong, Z.; Sun, X. *J. Appl Polym Sci* 2003, 88, 407.
6. Mungara, P.; Chang, T.; Zhu, J.; Jane., J. *J Polym Environ* 2002, 10, 31.
7. Zhang, J.; Jiang, L.; Zhou, L.; Jane, J.; Mungara, P. *Biomacromolecules* 2006, 7, 1551.
8. Huneault, A.; Li, H. *Polymer* 2007, 48, 270.
9. Dieteroch, D.; Grigat, E.; Hahn, W. Oertel, G., Ed. *Polyurethane Handbook*. Hanser: New York, 1985; p 7.
10. Wang, H.; Sun, X.; Seib, P. J. *Appl Polym Sci* 2001, 82, 1761.
11. Mo, X.; Sun, X. *J. Appl Polym Sci* 1999, 73, 2595.
12. Sun, X. *JAACS* 1999, 76, 117.
13. Pluta, M.; Galeski, A. *Biomacromolecules* 2007, 8, 1836.
14. Holdsworth, P. J.; Turner-Jones, A. *Polymer* 1971, 12, 195.
15. Mano, Jf; Wang, Y. M.; Viana, J. C.; Denchev, Z.; Oliveira, M. J. *Macromol Mater Eng* 2004, 289, 910.
16. Abtahi, S.; Aminlari, M. *J. Agric Food Chem* 1997, 45, 4768.