Biodegradable Blends of Poly(L-lactide) and Starch

M. Kozlowski,[1,2] R. Masirek,[1] E. Piorkowska,[1] M. Gazicki-Lipman[2]

[1]*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90 363 Lodz, Poland*
[2]*Institute for Materials Science and Engineering, Technical University of Lodz, 90 924 Lodz, Poland*

Received 26 April 2006; accepted 1 September 2006
DOI 10.1002/app.26088
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends of poly(L-lactide) (PLA), containing from 5, 15, or 25 wt % potato starch, unmodified or hydrophobized in methane plasma, were prepared and studied. To enhance the drawability of the blends, the plasticization of PLA with 10 wt % poly (ethylene glycol) (PEG) was also employed. The thermal and mechanical properties of the blends with amorphous and crystalline matrices were investigated. The hydrophobization of starch did not improve the ultimate properties of the blends, which were generally worse than those of neat PLA, because of the separation of the starch grains from the polymer matrix during tensile drawing. The separation also occurred in blends with a PEG-plasticized matrix containing 15 wt % modified starch, which fractured earlier than PLA plasticized with PEG. Nevertheless, the elongation at break of the plasticized blends reached 1.3, which was considerably more than that of blends with corresponding starch contents without a plasticizer (ca. 0.05). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 269–277, 2007

Key words: biodegradable blends; mechanical properties; thermal properties

INTRODUCTION

Polylactide, a biodegradable polymer that can be produced from renewable resources, has recently drawn increasing attention. Though expensive in the past, polylactide has become more competitive because of recent developments in polymerization technology.[1]

The chiral center in the structure allows the enantiomeric composition of polylactide to be varied. Although both poly(D-lactide) and poly(L-lactide) (PLA) are crystallizable polymers, dimers of different chiralities lower the ability of the polymer chain to crystallize. Slowly crystallizing polylactides can be quenched to the glassy state and cold-crystallized during subsequent heating above the glass-transition temperature (T_g). Spherulites in cold-crystallized samples are smaller than those in samples crystallized via cooling from the melt.[2] However, beyond a certain concentration of the minor comonomer, crystallization does not occur.[3]

Amorphous polylactide is rigid and brittle under ambient conditions, having an elastic modulus of about 3 GPa and a low ability for plastic deformation; the glass transition of polylactide is in the range of 50–60°C. To modify the properties, polylactide has been blended with a number of polymers, including polycaprolactone,[4] poly(vinyl acetate),[5] poly(methyl methacrylate),[6] poly(hydroxy butyrate),[7] and poly (ethylene oxide).[8] Citrate esters,[9,10] triacetine,[10] and poly(ethylene glycol) (PEG)[11–14] and recently poly (propylene glycol)[15] have been found to be efficient plasticizers for polylactide. The resulting plasticized materials have been improved with respect to deformation and resilience.

The crystallization of polylactide and polylactide plasticized with PEG lowers the drawability. However, PEG-plasticized polylactide after crystallization still retains some ability for plastic deformation.[14]

Polylactide has also been blended with starch.[16,17] Starch, itself biodegradable, is an attractive blend component for polylactide because it offers advantages in terms of cost. Starch is blended with other biodegradable polymers and also with nonbiodegradable polymers to lower the cost of the final product and to enhance the biodegradable characteristics. Known examples include blends of poly(ε-caprolactone) and poly(3-hydroxybutyrate-3-hydroxyvalerate) with starch[18] and blends of poly(vinyl alcohol) with starch.[19]

Blending polylactide with thermoplastic starch, plasticized with glycerol,[17] results in a decrease in the modulus of elasticity. Polylactide-rich blends, with 30 wt % starch or less, exhibit lower tensile strength and decreased elongation in comparison with neat polylactide. Gelatinization improves the interfacial adhesion between the starch and polylactide and polylactide blends. Although the mechanical properties of polylactide with gelatinized starch are superior to those for polylactide blends with pure starch,[16] they are worse than those of neat polylactide. Softening the resulting material, which reduces the modulus of elas-

This article is dedicated to the memory of Professor Marian Kryszewski.

Correspondence to: E. Piorkowska (epiorkow@bilbo.cbmm.lodz.pl).

©2007 Wiley Periodicals, Inc.
WILEY InterScience® DISCOVER SOMETHING GREAT

ticity and lowers the tensile strength, only slightly increases the elongation at break.[16]

In this article, we report studies concerning the blending of polylactide with starch. Our strategy was to plasticize the polylactide matrix rather than the starch. To improve the properties of the resulting blends, we plasticized polylactide with PEG. Unmodified starch and starch hydrophobized in low plasma process (long used to modify polymer surfaces[20–22]), were utilized in the study. The hydrophobization was expected to prevent water absorption and possible PEG absorption by starch and to modify the properties of the starch–polylactide interface. Also, the modification of starch in methane (CH_4) plasma was found to reduce a tendency of starch to agglomerate.[23] Blends with an amorphous polylactide matrix or a crystalline polylactide matrix, without a plasticizer or plasticized with PEG, were studied.

EXPERIMENTAL

We used PLA, manufactured by Cargill–Dow, Inc. (Minnetonka, MN), with a D-lactide content of 4.1% and a residual lactide content of 0.1%. The weight-average molecular weight (M_w) and weight-average molecular weight/number-average molecular weight (M_w/M_n) ratio, determined by size exclusion chromatography (SEC) in methylene chloride, were 126 kg/mol and 1.48, respectively. PEG with a nominal M_w value of 600 g/mol, purchased from Loba Chemie (Vienna, Austria), was applied to plasticize PLA; M_w and M_w/M_n, determined by matrix-assisted laser desorption/ionization time-of-flight, were equal to 578 g/mol and 1.08, respectively, whereas the melting temperature was 20°C during heating at 10 K/min in a differential scanning calorimetry (DSC) apparatus.[14,15]

Potato starch with a moisture content of 20 wt %, a density of 1.55 g/ccm, and a grain size as below 100 μm was produced by Przedsiebiorstwo Przemyslu Ziemniaczanego (Lubon, Poland).

The plasma processing of starch grains was carried out with the help of a rotary radio frequency (RF) plasma reactor. CH_4 was used as a working medium, and its flow rate was controlled with the help of an MKS (Methven, MA) 1179 AX mass flow controller. A starch modification cycle began with the setting of the flow of CH_4, then the rotation of the tubular element with a selected rpm value was introduced, and finally an RF glow discharge was generated in the reactor. Powdered starch in this reactor was stirred very efficiently, and this enabled effective plasma surface modification of the grains. A detailed description of the equipment and method has been reported elsewhere.[23]

Before blending, PLA and PEG were vacuum-dried at 100°C for 4 h. The starch was dried for 48 h at 85°C. Melt blends containing 5, 15, or 25 wt % starch in the PLA matrix were prepared with a Brabender (Duisburg, Germany) mixer operating at 190°C for 20 min at 60 rpm under a flow of dry, gaseous nitrogen. The materials with unmodified starch are called PLA/S5, PLA/S15, and PLA/S25, whereas those with modified starch are called PLA/SM5, PLA/SM15, and PLA/SM25; the numbers indicate the starch content. Neat PLA was also processed in the same way to obtain a reference material.

Blends of starch and plasticized PLA were prepared by two-step blending under the same conditions and with the same equipment. First, PLA was blended with 10 wt % PEG, and the resulting blend, PLA/PEG, was mixed in the second step with 15 wt % plasma-modified starch to obtain a ternary blend, PLA/PEG/SM15. The modified starch content was selected on the basis of preliminary research. PLA/PEG blends were also prepared for comparison.

All the blends and samples prepared from them were stored in a dry atmosphere in a desiccator.

The molecular weight of neat PLA before and after processing and the molecular weight of PLA in the blends were determined. SEC traces were recorded with an Agilent (Santa Clara, CA) series 1100 isocratic pump, a degasser, an autosampler thermostatic box for the columns, and a set of TSKgel columns (G 2000 H_{XL} and G 6400 H_{XL}) at 25°C. An Optilab rEX interferometric refractometer and a MALLS Dawn Eos laser photometer (Wyatt Technology Corp., Santa Barbara, CA) were applied as detectors. Methylene chloride was used as the eluent at a flow rate of 0.8 mL/min. M_n and M_w/M_n were calculated from the experimental traces with the Astra program (version 4.90.07) from Wyatt Technology. The PEG used in the study was also measured. In addition, PEG and a suspension of starch in methylene chloride were prepared, filtered, and tested.

To characterize the obtained materials, DSC was carried out with a TA Instruments (New Castle, DE) 2920 differential scanning calorimeter. The specimens were heated and cooled at the rate of 10 K/min to determine the thermal conditions for the preparation of the amorphous and crystalline samples for mechanical tests. Thermogravimetric studies were conducted with a TA Instruments Universal V2.6D thermogravimetric analyzer at the rate of 20 K/min. The crystallization of the blends was studied in thin films, about 20 μm thick, which were compression-molded between microscopic glass slides. The films were heated to 180°C and after approximately 3 min cooled to the crystallization temperature in a Linkam (Waterfield, UK) THMS 600 hot stage (equipped with a TMS92 control unit) mounted in a light microscope.

Entirely amorphous films (0.3–0.4 mm thick) of neat PLA and blend films with amorphous matrices, referred to as amorphous materials, were prepared by compression molding at 180°C for 3 min in a hydrau-

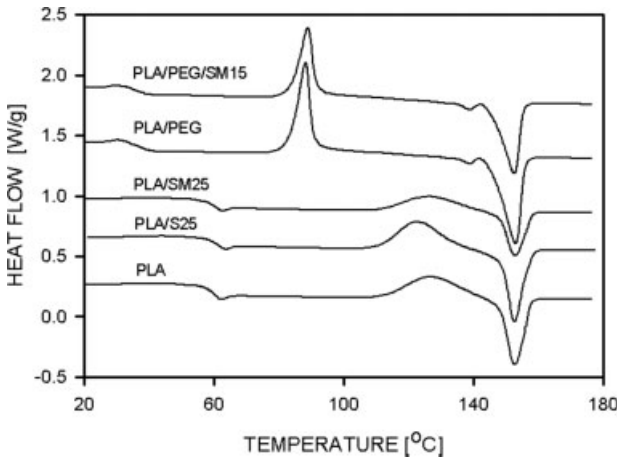

Figure 1 Exemplary DSC heating thermograms recorded for amorphous neat PLA and for PLA/S25, PLA/SM25, PLA/PEG, and PLA/PEG/SM15 blends with an amorphous matrix. The thermograms have been shifted vertically.

lic hot press followed by quenching between thick metal blocks kept at room temperature. Some of the amorphous films were cold-crystallized between two metal blocks equipped with heaters and Pt resistance thermometers connected to a temperature controller, which enabled either heating or cooling of both blocks at the same programmed constant rate or holding a steady temperature with an accuracy of 0.2 K. The thermal treatment of the films was elaborated on the basis of preliminary DSC measurements. The films were heated at the rate of 10 K/min from room temperature to a selected final temperature: 135°C for PLA, PLA/S, and PLA/SM and 120°C for PLA/PEG and PLA/PEG/SM blends. After the final temperature was reached, the films were quenched to room temperature. As the crystallization in PLA and blends of PLA with starch was not completed during heating,

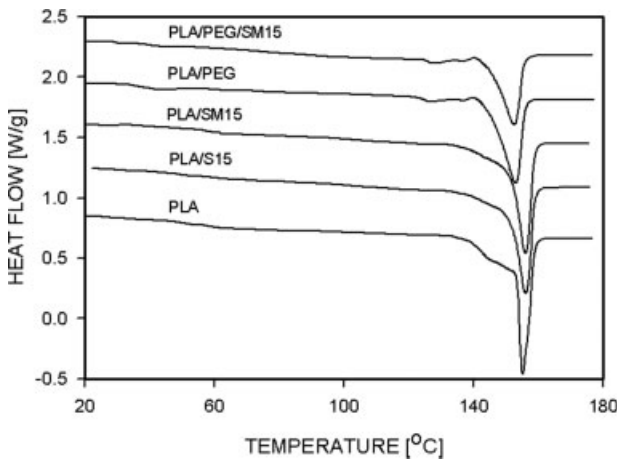

Figure 2 Exemplary DSC heating thermograms recorded for crystallized neat PLA and for PLA/S15, PLA/SM15, PLA/PEG, and PLA/PEG/SM15 blends with a crystallized matrix. The thermograms have been shifted vertically.

the PLA and blends were annealed additionally for 75 min at 130°C.

The amorphous and semicrystalline films were characterized by a DSC technique at the heating rate of 10 K/min.

Oar-shaped specimens, with a 9.53-mm gauge length and a width of 3.18 mm, were cut from the freshly prepared films for tensile tests, which were carried out a day after. The PLA/PEG blend was also tested 1 week and 1 month after the film preparation. The tensile tests were performed on an Instron (High

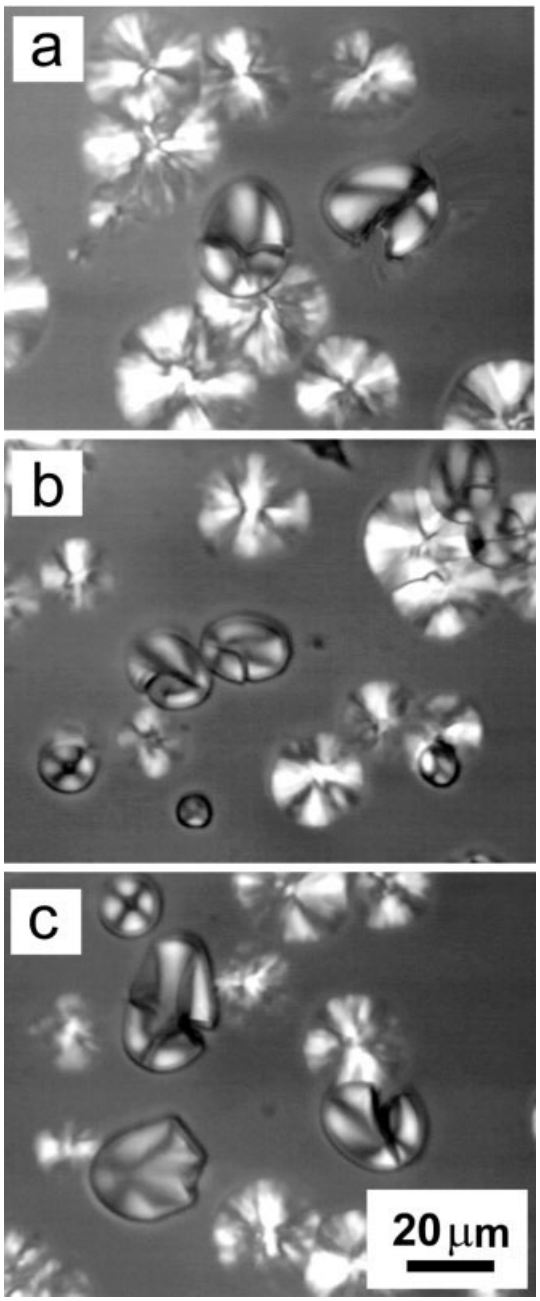

Figure 3 Polarized light micrographs of isothermal crystallization from the melt of (a) PLA/S5 at 116°C, (b) PLA/SM5 at 116°C, and (c) PLA/PEG/SM15 at 112°C.

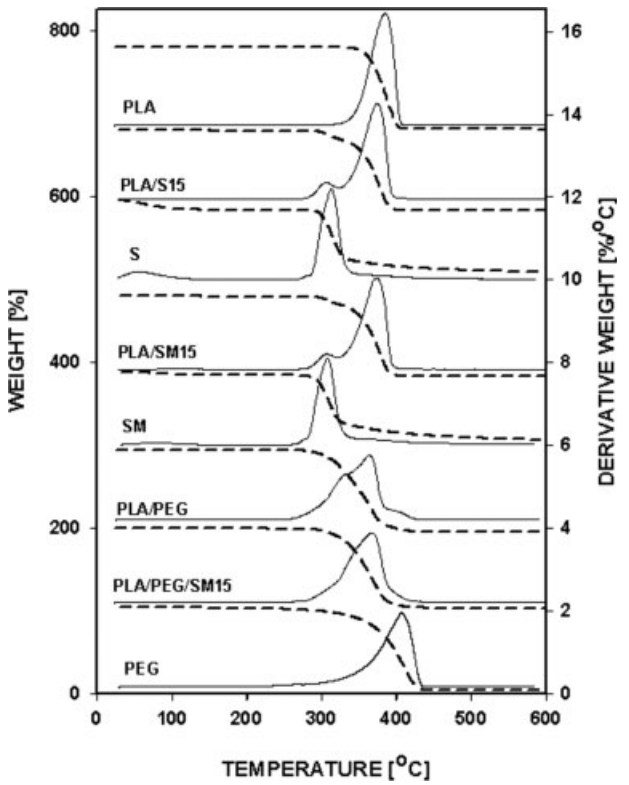

Figure 4 Exemplary TGA thermograms for neat PLA, PEG, PLA/PEG blends, unmodified starch (S), and modified starch (SM) and for PLA/S15, PLA/SM15, and PLA/PEG/SM15 blends recorded during heating in a nitrogen atmosphere. The thermograms have been shifted vertically.

Wycombe, UK) 5582 tensile testing machine in a temperature chamber with circulating air at 25°C at a rate of 0.5 mm/min. At least three specimens of each material were tested.

The gauge region of the deformed samples was examined under a polarized light microscope with crossed polarizers rotated by 45° with respect to the drawing direction. The fracture surfaces of all the materials were sputtered with gold and studied under a JEOL (Tokyo, Japan) 5500LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Processing reduced M_w of the neat PLA from 126 to 106 kg/mol, whereas the polydispersity was less affected; it changed only from 1.48 to 1.43. Starch and PEG did not affect significantly the molecular weight of PLA. On the molecular weight distributions recorded for the blends, small separate peaks or shoulders on the slopes of the main peaks appeared in the range of 100–10,000 g/mol. They originated mainly from PEG and from fractions of starch grains dissolved in methylene chloride, as concluded from a comparison with SEC traces of PEG and a filtered suspension of the starch. M_w determined for PLA in the blends with starch varied from 102 to 107 kg/mol, whereas M_w/M_n was within the range of 1.28–1.82.

Exemplary heating thermograms of the samples of films prepared for a tensile test are shown in Figures 1 and 2. The samples of amorphous films, without a plasticizer, heated in a DSC apparatus exhibited T_g around 56–57°C, whereas T_g of the plasticized materials was about 36°C. All amorphous films cold-crystallized upon heating and melted at a higher temperature. The crystallization peak temperatures of PLA, PLA/S25, and PLA/SM25 were in the range of 122–127°C, whereas the melting peak temperatures were about 152–153°C. PLA/PEG and PLA/PEG/SM15 crystallized at lower temperatures, 88–89°C, and melted at 153°C. An additional, small melting peak was observed for both blends at 139°C. The melting enthalpy corresponded always to the crystallization enthalpy, indicating that no crystallinity developed in these materials during quenching to room temperature after the compression molding. The crystalline films exhibited no cold crystallization, only melting with melting peaks at 155–157°C for PLA and PLA/starch and at 152–153°C for PLA/PEG and PLA/PEG/SM15. On the thermograms of the latter, additional, low melting peaks were observed at temperatures lower than those of the main peaks. For PLA and

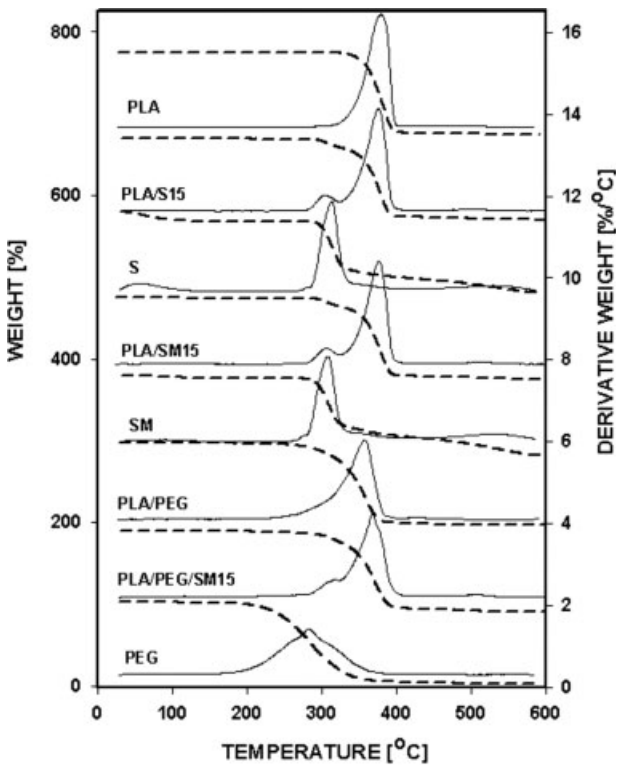

Figure 5 Exemplary TGA thermograms for neat PLA, PEG, PLA/PEG blends, unmodified starch (S), and modified starch (SM) and for PLA/S15, PLA/SM15, and PLA/PEG/SM15 blends recorded during heating in an air atmosphere. The thermograms have been shifted vertically.

TABLE I
Stress at Break (σ_B) and Strain at Break (ε_B) During the Tensile Drawing of Amorphous and Cold-Crystallized PLA and PLA-Based Blends with Starch

	Amorphous		Cold-crystallized	
Composition	ε_B (m/m)	σ_B (MPa)	ε_B (m/m)	σ_B (MPa)
PLA	0.092 ± 0.025	42.2 ± 2.2	0.037 ± 0.004	45.2 ± 3.2
PLA/S5	0.064 ± 0.015	37.5 ± 1.3	0.022 ± 0.003	29.9 ± 4.5
PLA/S15	0.051 ± 0.005	35.1 ± 3.1	0.027 ± 0.005	35.1 ± 4.6
PLA/S25	0.045 ± 0.012	37.0 ± 6.2	—	—
PLA/SM5	0.075 ± 0.006	34.7 ± 2.4	0.028 ± 0.001	37.2 ± 1.2
PLA/SM15	0.048 ± 0.004	35.0 ± 2.1	0.025 ± 0.004	34.3 ± 4.3
PLA/PEG	3.00 ± 0.87	17.4 ± 1.5	0.272 ± 0.031	22.1 ± 2.5
PLA/PEG/SM15	1.31 ± 0.49	13.2 ± 1	0.155 ± 0.022	18.4 ± 1.3

PLA/starch blends, the melting enthalpy was about 39 J/g of PLA. The melting enthalpy of PLA/PEG and polymer matrix in PLA/PEG/15SM was about 30–31 J/g, that is 34 J/g for the PLA component. In the case of crystalline, plasticized materials, the glass transition was very broad and diffuse and nearly indiscernible by a DSC method.

The PLA-based blends with high starch contents behaved similarly to neat PLA, whereas PLA/PEG/SM15 behaved in the same way as PLA/PEG. The influence of PEG on the thermal properties of PLA, amorphous and crystalline, was described in detail by Kulinski and Piorkowska elsewhere.[14]

No nucleation effect of starch on PLA crystallization was found during direct observations of the isothermal crystallization of PLA/starch blends and also PLA/PEG/SM15 by polarized light microscopy, as shown in Figure 3.

Exemplary thermogravimetric analysis (TGA) thermograms of the studied materials are collected in Figures 4 and 5. PLA decomposed in a nitrogen atmosphere above 300°C at a peak rate at 375°C, whereas starch decomposed above 260°C, with peak rates at 316 and 310°C for modified and unmodified starch, respectively. A small low-temperature peak of the decomposition rate, below 100°C, most likely originated from the evaporation of residual water. The decomposition rate of the PLA/starch blends always exhibited two peaks corresponding to the decomposition of starch and PLA. PLA/PEG decomposed earlier than neat PLA, with a peak rate at 367°C and shoulders on both slopes of the main peak, as shown in ref. 24. The temperature of the shoulder on the descending slope corresponded to the temperature of the decomposition of PEG, 410°C. PLA/PEG/SM15 decomposed in a very similar way. The decomposition in an air atmosphere of PLA and PLA/starch blends was very similar to that in nitrogen; only minor shifts of the decomposition rate peak temperature (1–4°C) were observed. PEG decomposed earlier in air than in nitrogen, with a peak rate at 286°C, therefore, PLA/PEG also decomposed earlier, with a peak rate at about 360°C, as shown in ref. 24. The position of the main peak of the PLA/PEG/SM15 decomposition was not affected by starch; the decomposition of starch showed up as a separate peak, more clearly than in nitrogen.

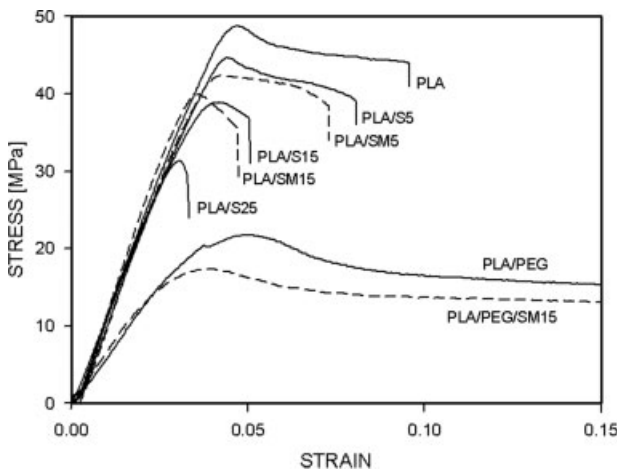

Figure 6 Stress–strain plots for amorphous neat PLA and PLA/S, PLA/SM, PLA/PEG, and PLA/PEG/SM15 blends.

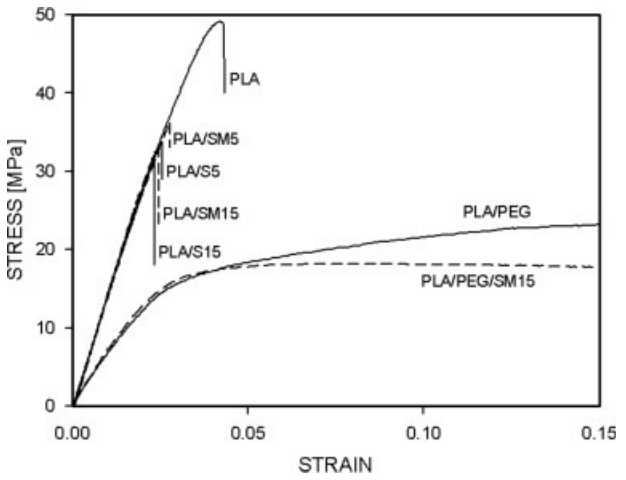

Figure 7 Stress–strain plots for crystallized neat PLA and PLA/S, PLA/SM, PLA/PEG, and PLA/PEG/SM15 blends.

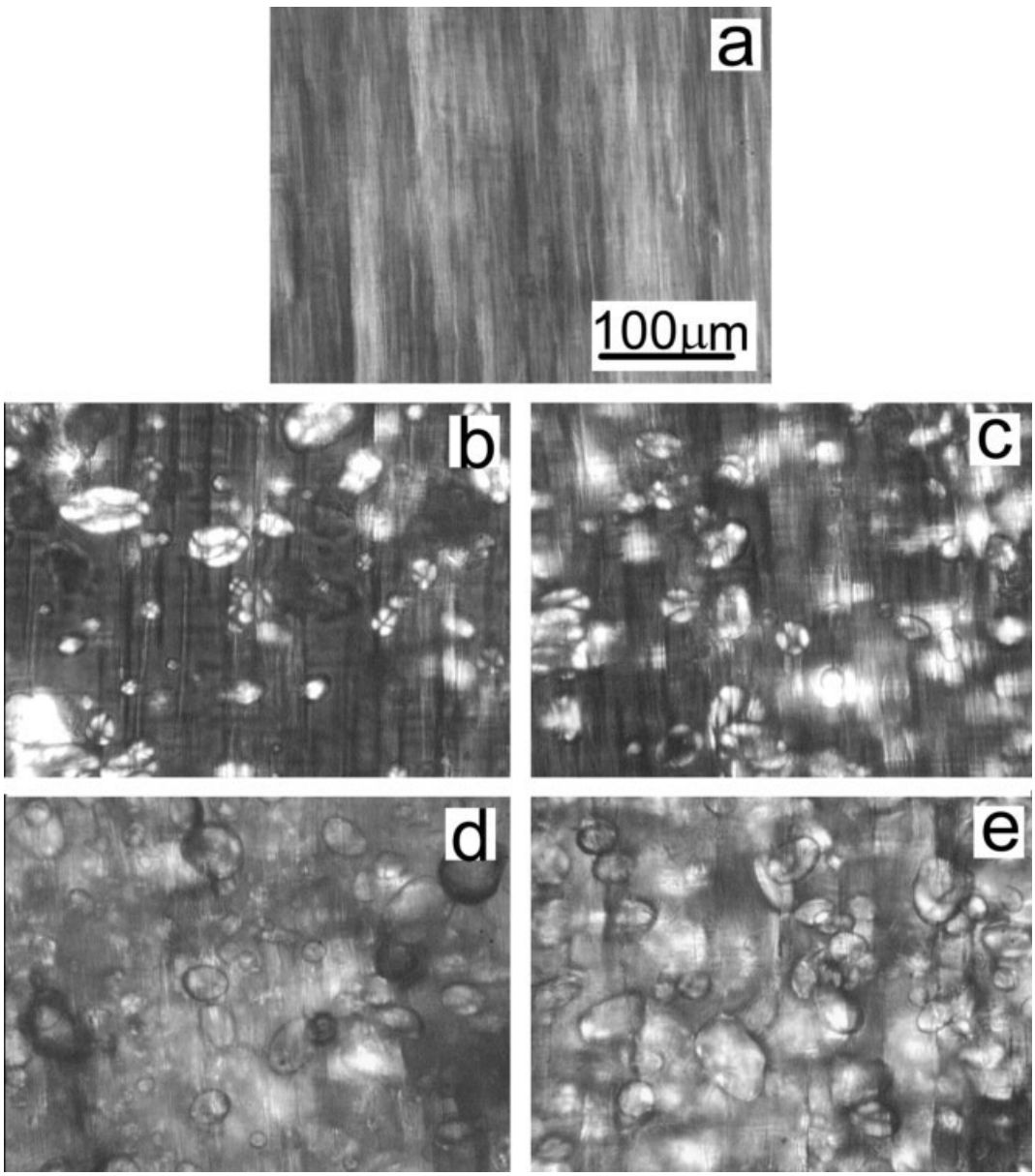

Figure 8 Polarized light micrographs of the gauge regions of amorphous materials: (a) neat PLA, (b) PLA/S5, (c) PLA/SM5, (d) PLA/S15, and (e) PLA/SM15 (horizontal drawing direction).

The tensile properties of the blends of PLA with starch are collected in Table I, whereas exemplary stress–strain plots are shown in Figures 6 and 7. The yield stress of the amorphous specimens decreased from the value of 50 MPa, measured for neat PLA, to 42–38 MPa for the blends. The stress and elongation at break also decreased with an increase in the starch content. PLA/S5 and PLA/SM5 exhibited slightly better drawability than the blends with higher starch contents. The stress–strain dependence of PLA/SM5 deviated from linearity before the yield, which was less pronounced than that of PLA/S5. In other aspects, PLA/S blends and PLA/SM blends behaved similarly. The results showed that the hydrophobization of the starch surface little affected the tensile properties of the blends, except that the tensile data were less scattered in the case of blends with modified starch than in the case of those with unmodified starch. The crystallized materials fractured early, before yielding. The starch, independently of whether it was modified or not, facilitated the early fracture.

PLA plasticized with PEG exhibited good drawability; this was similar to the findings in ref. 14. The PLA/PEG/SM15 blend behaved in a similar way, although the elongation at break, about 1.3, was smaller than the value of 3 measured for the PLA/PEG blend under the same conditions. Crystallization reduced the drawability of the PLA/PEG blend similarly to the way reported in ref. 14. Although the elongation at break of PLA/PEG, 0.27, was larger than that of

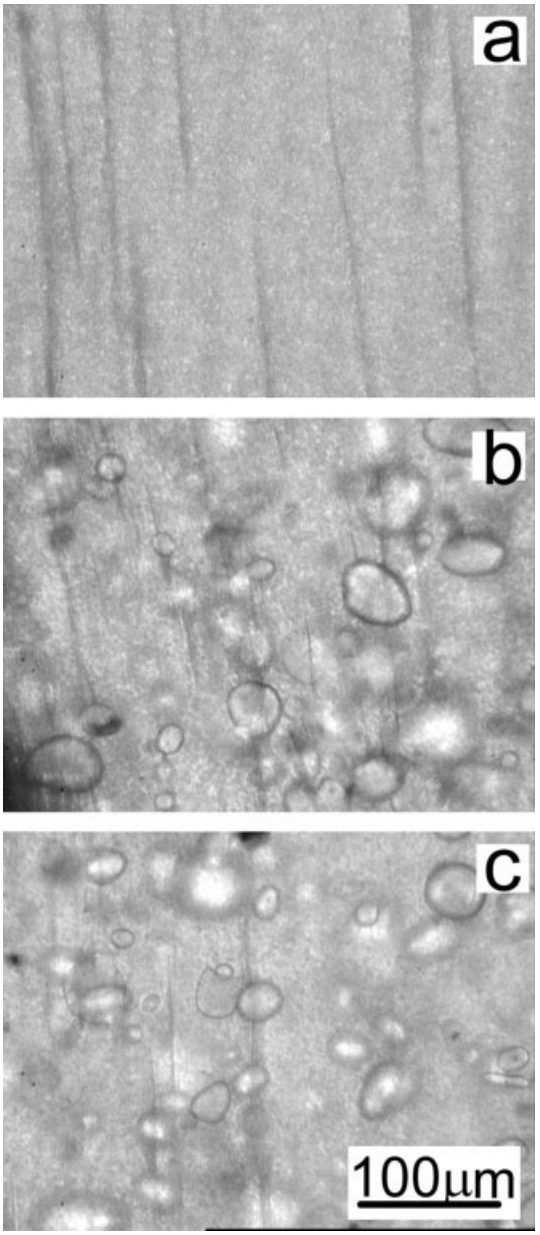

Figure 9 Polarized light micrographs of the gauge regions (near the fracture surface) of crystallized materials: (a) neat PLA, (b) PLA/S5, and (c) PLA/SM5 (horizontal drawing direction).

PLA/PE/MS15, 0.16, the yield stress and stress at break of PLA/PEG/MS15 were lower than those of PLA/PEG.

Thus, the plasticization of the PLA matrix increased the drawability of the PLA-based blends with starch.

Neither the amorphous nor semicrystalline PLA/PEG blend, studied here as a control, exhibited any significant increase in the yield stress or decrease in the elongation at break when tested 1 week and 1 month after the film preparation. We are aware, however, that others[25] have observed the migration of PEG with a molecular weight of 1000 g/mol to a film surface in PLA/PEG blend films stored for months. The migration depleted PLA of the plasticizer and undoubtedly affected the mechanical properties.

Figures 8–10 show typical light micrographs of the gauge regions of the specimens deformed to fracture. In the micrographs of amorphous PLA and PLA/starch blends, a relatively uniform distribution of the whitened craze zones is visible, as shown in Figure 8. In crystallized PLA, PLA/S5, and PLA/SM5, dark fissures are observable near the fracture surface (Fig. 9), and these are most likely crazes. In micrographs of blends, they are associated with starch grains. In the gauge region of the amorphous PLA/PEG/SM15

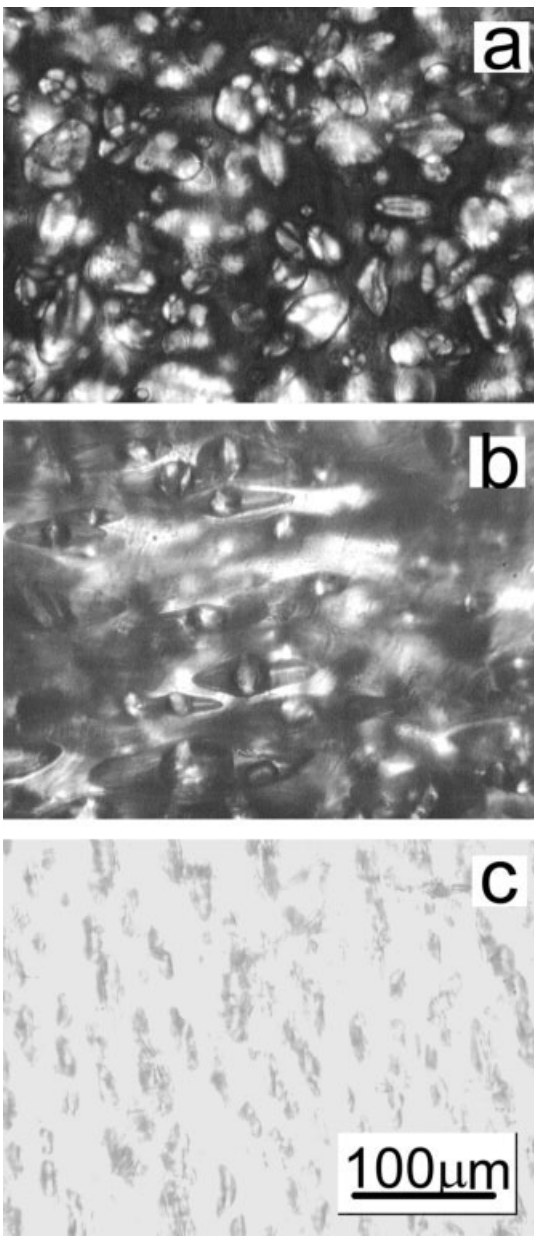

Figure 10 Polarized light micrographs of amorphous blends: (a) PLA/PEG/SM15 before deformation and gauge regions of (b) PLA/PEG/SM15 and (c) PLA/PEG (horizontal drawing direction).

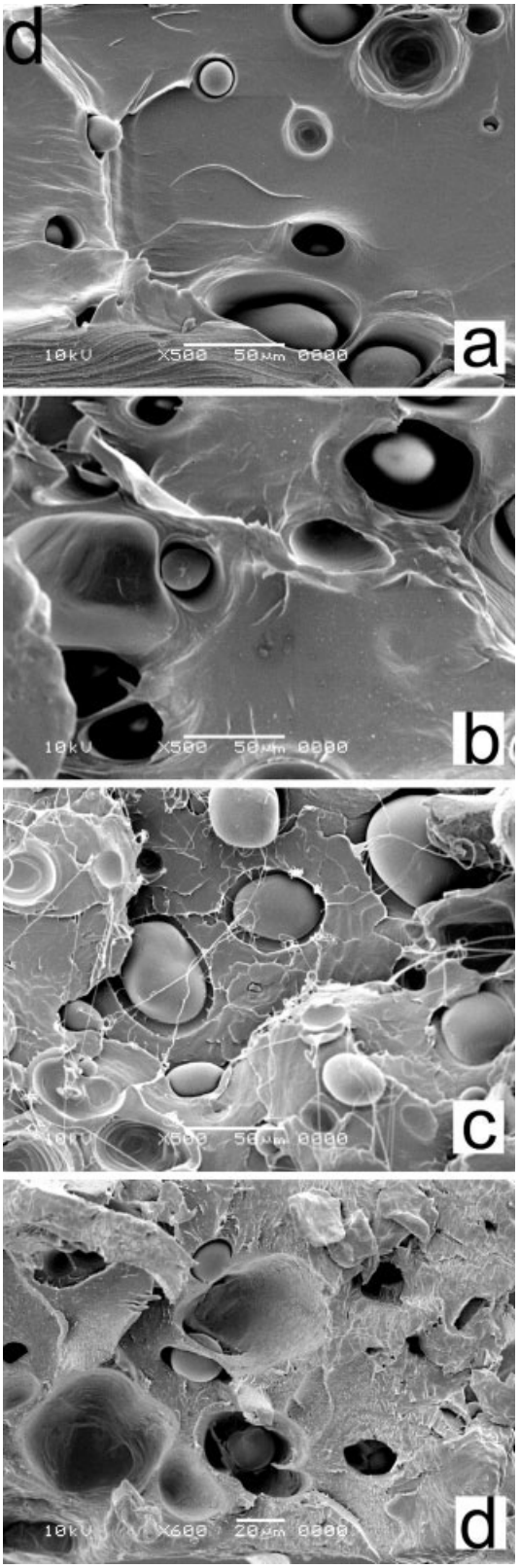

Figure 11 SEM micrographs of fracture surfaces of amorphous blends: (a) PLA/S5, (b) PLA/SM5, (c) PLA/SM15, and (d) PLA/PEG/SM15.

blend, the separation of starch inclusions from matrix is visible (Fig. 10). Bright zones of the deformed matrix show up between elongated cavities formed around the starch grains. PLA/PEG exhibited intense brightening in polarized light because of orientation and strain-induced crystallization and black bands normal to the drawing direction, presumably voids, that conforms to observations in ref. 14. Both the PLA/PEG and PLA/PEG/SM15 blends exhibited intense stress whitening, reflecting the presence of light-scattering voids. The brightening observed in the

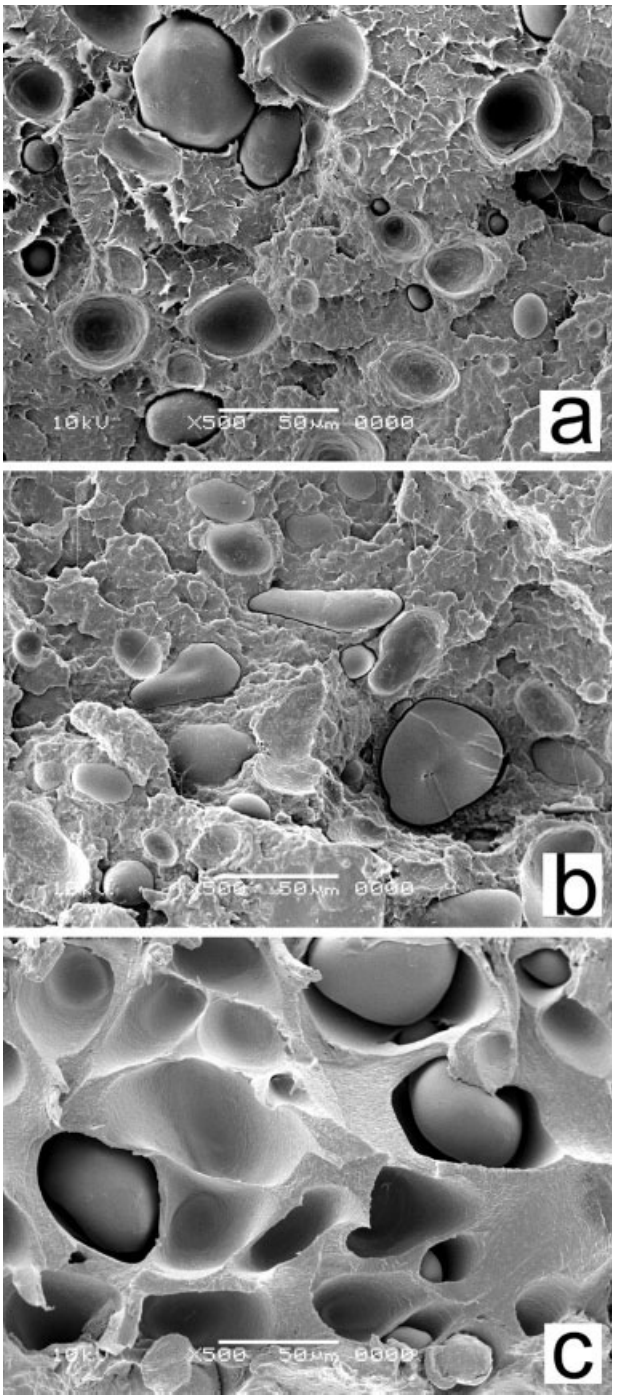

Figure 12 SEM micrographs of fracture surfaces of crystallized blends: (a) PLA/S15, (b) PLA/SM15, and (c) PLA/PEG/SM15.

PLA/PEG/SM15 blend was most likely related not only to orientation but also to strain-induced crystallization of PLA. In other blends, features related to the deformation and fracture process were indiscernible by light microscopy.

The fracture surfaces of neat PLA and PLA/PEG, amorphous and semicrystalline, revealed the same features described in detail in ref. 14. PLA fractured in a brittle way, whereas on the fracture surfaces of PLA/PEG, a plastically deformed polymer could be seen. The dominant feature visible in SEM micrographs of the fracture surfaces of the amorphous PLA/starch blends (Fig. 11) is the separation of starch grains from the polymer matrix. This is more visible in the blends with 5 wt % starch, which fractured at a larger elongation, and also in the plasticized blend. A similar picture was found by an SEM technique for crystalline blends, in which the separation of starch grains from the matrix was clearly evidenced (Fig. 12). Cellular structures, such as those visible in Figure 12(a,b), have been attributed by others to the fracture of crazes in semicrystalline polymers.[26]

CONCLUSIONS

The PLA/starch blends had similar properties, which were independent of whether the starch was hydrophobized or not. The starch did not markedly influence the thermal properties of the blends, which were studied by a DSC technique. The starch did not nucleate the crystallization of PLA, independently of whether PLA was plasticized or not. The decomposition of PLA/starch and PLA/PEG/starch blends during TGA experiments was composed of two processes: the decomposition of starch with a peak rate at a lower temperature and the decomposition of the PLA or PLA/PEG matrix with a peak rate at a higher temperature.

Generally, the presence of starch worsened the mechanical properties of the studied materials, reducing the stress and elongation at break of the blends with an amorphous or crystalline matrix. The deformation and fracture of the amorphous and crystalline PLA/starch blends were related to crazing, as evidenced by light microscopy and SEM studies of tensile specimens. It has been established in the past that a low crystallinity level and a fine spherulitic structure, like those in the PLA studied, are advantageous for the development of crazes in semicrystalline polymers.[26] The early fracture of the blends is facilitated by a separation of the starch from the polymer matrix, which is clearly observable by an SEM technique.

The plasticization of the PLA matrix enhanced the drawability of the PLA/starch blends. Although again the separation of the starch from the matrix led to premature fracture, the PLA/PEG/SM15 blend reached a considerable elongation at break of 1.3.

The authors gratefully acknowledge Cargill–Dow Polymers, LLC, for supplying the poly(L-lactide) and CMMS PAS for supporting the research.

References

1. Jacobsen, S.; Degee, P.; Fritz, H. G.; Dubois, P.; Jerome, R. Polym Eng Sci 1999, 39, 1311.
2. Pluta, M.; Galeski, A. J Appl Polym Sci 2002, 86, 1386.
3. Brochu, S.; Prud'homme, R. E.; Barakat, I.; Jerome, P. Macromolecules 1995, 28, 5230.
4. Cohen, D.; Younes, H. J Biomed Mater Res 1988, 22, 993.
5. Gajria, A. M.; Dave, V.; Gross, R. A.; MaCarthy, S. P. Polymer 1996, 37, 437.
6. Eguiburu, J. L.; Iruin, J. J.; Fernandez-Berridi, M. J.; Roman, J. S. Polymer 1998, 39, 6891.
7. Focarete, M. L.; Ceccorulli, G.; Scandola, M.; Kowalczuk, M. Macromolecules 1998, 31, 8485.
8. Nijenhuis, A. J.; Colstee, E.; Grijpma, D. W.; Pennings, A. J. Polymer 1996, 37, 5849.
9. Labrecque, L. V.; Kumar, R. A.; Dave, V.; Gross, R. A.; McCarthy, S. P. J Appl Polym Sci 1997, 66, 1507.
10. Ljungberg, N.; Wesselen, B. J Appl Polym Sci 2002, 86, 1227.
11. Jacobsen, S.; Fritz, H. G. Polym Eng Sci 1999, 39, 1303.
12. Sheth, M.; Kumar, R. A.; Dave, V.; Gross, A. R.; McCarthy, S. P. J Appl Polym Sci 1997, 66, 1495.
13. Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. J Appl Polym Sci 2003, 90, 1731.
14. Kulinski, Z.; Piorkowska, E. Polymer 2005, 46, 10290.
15. Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. Biomacromolecules 2006, 7, 2128.
16. Park, J. W.; Im, S. S.; Kim, S. H.; Kim, Y. H. Polym Eng Sci 2000, 40, 2539.
17. Martin, O.; Averous, L. Polymer 2001, 42, 6209.
18. Koenig, M. F.; Huang, S. J. Polymer 1995, 36, 1877.
19. Lenk, R. S. Polymer 1980, 21, 371.
20. Owens, D. K.; Wendt, R. C. J Appl Polym Sci 1969, 13, 1741.
21. Adamson, A. W. Physical Chemistry of Surfaces; Interscience: New York, 1960.
22. Bamford, C. H.; Al-Lamee, K. G. Polymer 1996, 37, 4885.
23. Szymanowski, H.; Kaczmarek, M.; Gazicki-Lipman, M.; Klimek, L.; Wozniak, B. Surf Coat Technol 2005, 200, 539.
24. Masirek, R.; Kulinski, Z.; Chionna, D.; Piorkowska, E.; Pracella, M. J Appl Polym Sci 2007, to appear.
25. Pluta, M.; Paul, M. A.; Alexandre, M.; Dubois, P. J Polym Sci Part B: Polym Phys 2006, 44, 312.
26. Friedrich, K. Adv Polym Sci 1983, 52, 225.