Dynamic Mechanical and Thermal Properties of Plasticized Poly(lactic acid)

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ABSTRACT: The blends of low molecular weight triacetin (TAC) and oligomeric poly(1,3-butylene glycol adipate) (PBGA) were used as multiple plasticizers to lubricate poly(lactic acid) (PLA) in this study. The thermal and mechanical properties of plasticized polymers were investigated by means of dynamic mechanical analysis and differential scanning calorimetry. Atomic force microscopy (AFM) was used to analyze the morphologies of the blends. Multiple plasticizers were effective in lowering the glass transition temperature (T_g) and the melting temperature (T_m) of PLA. Moreover, crystallinity of PLA increased with increasing the content of multiple plasticizers. Tensile strength of the blends decreased following the increasing of the plasticizers, but increased in elongation at break. AFM topographic images showed that the multiple plasticizers dispersed between interfibrillar regions. Moreover, the fibrillar crystallite formed the quasicrosslinkings, which is another cause for the increase in elongation at break. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1583–1590, 2006

Key words: poly(lactic acid); thermal properties; mechanical properties

INTRODUCTION

Poly(lactic acid) (PLA) is a thermoplastic polymer that can be produced from lactic acid obtained through fermentation of renewable resources.[1] The polymer has a number of interesting properties, including biodegradability, biocompatibility,[2,3] good mechanical properties. For these reasons it is used in a great number of fields, such as sutures, orthopedic implants, and drug delivery systems of the medical applications. In addition, PLA is suitable for use in household and engineering applications. Thanks to PLA's mechanical properties comparable to those of polystyrene, now PLA is expected to substitute conventional polymers in the packing field. But PLA is a material that has an inherent brittleness and thermal instability,[4] and the low elongation at break limits its applications.

Nevertheless, the flexibility of PLA can be improved by modifying its physical properties. This can, for instance, be carried out through copolymerization,[5–8] and the mechanical properties can also be affected by blending PLA with a plasticizer or a second polymer. A large number of investigations have been performed on the blending of PLA with various polymers, for example, poly(ethylene glycol),[9] poly(ε-caprolactone),[10] poly(hydroxy butyrate),[11] poly(hexamethylene succinate).[12] Low molecular weight compounds have also been used as plasticizers for PLA, e.g., glycerol,[9] triactine,[13] and low molecular weight citrates.[14]

The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. For packaging and hygiene application, only nontoxic substances approved for food contact and personal care can be considered as plasticizing agents. There are numerous other demands put on the plasticizers, but the following ones are especially important. The plasticizer should be miscible with PLA, thus creating a homogeneous blend. The plasticizer should not be too volatile because this would cause evaporation to occur at the elevated temperature used at processing. Furthermore, the plasticizer should not be prone to migration because this would cause contamination of the materials in contact with the plasticized PLA. It would also cause the blended materials to regain the brittleness of pure PLA.

It has previously been reported[15] that low molecular weight plasticizers, such as tributyl citrate and triactine drastically lowered the glass transition temperature of PLA, thus creating homogeneous and flexible materials. The reason for the good solubility of PLA in

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the plasticizers would be the polar interactions occurring between the plasticizers and PLA. However, it was observed that upon aging of the plasticized materials, the plasticizers had a tendency to migrate to the surface. A possible way to prevent the migration would be to increase the molecular weight of the plasticizers. In this way solubility could be maintained through the polar interactions, whereas the higher molecular weight would decrease the tendency to migrate. However, increasing the molecular weight too much would eventually decrease the solubility causing phase separation and formation of a two-phase system.[16,17] We chose the blends of low molecular weight triacetine (TAC) and the oligomeric poly(1,3-butylene glycol adipate) (PBGA) to improve brittleness of PLA in the present study. In this way, we overcame the difficulties mentioned earlier. The study is mainly focused on the miscibility of PLA and the multiple plasticizers, and the thermal and dynamic mechanical properties of the blends.

EXPERIMENTAL

Materials

The poly(lactic acid) (PLA) that was used was supplied by Mitsui Chemicals (Tokyo, Japan). The chemical structure of the repeat unit is $[OCH(CH_3)CO]_n$. The weight–average molecular weight (M_w) of PLA is 2.074×10^5 with a polydispersity index of 1.71, as determined by gel permeation chromatography. Triacetin (TAC) was purchased from Jiangsu Yixing Fenshui Chemical–auxiliary Factory (Jiangsu, China), and the chemical structure is $(CH_3CO_2CH_2)_2CH(O_2CCH_3)$. Poly(1,3-butylene glycol adipate) (PBGA) was purchased from Tianjin Epoch Chemical (Tianjin, China), the chemical structure of the repeat unit is $[OC(CH_2)_4CO_2(CH_2)_2CH(CH_3)O]_n$. Chloroform (AR) was purchased from Beijing Beihua Fine Chemicals (Beijing, China). All substances were used as received.

Blending procedure

Cosolvent blending

PLA/TAC/PBGA mixtures with different contents were solubilized in choloroform. After blending a homogeneous solution was formed, and the solvent was allowed to evaporate at 40°C for 24 h. The blends were then cut into small granules. In the blending series, different contents of plasticizers (5–29%) were added into PLA. All blends were pressed into 1-mm flake under 160°C and 5 MPa for 10 min.

Solution casting

PLA/TAC/PBGA mixtures with different contents were solubilized in choloroform. The solutions (100 mg ml^{-1}) were cast on glass or silicon wafers, and the solvent was allowed to evaporate at 100°C for 10 h to eliminate residual solvent. Then films were peeled off for differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) wide angle X-ray diffraction (WAXD) and atomic force microscopy (AFM) measurements. The solution (5 mg ml^{-1}) was cast on glass or silicon wafers, and put in an oven at 180°C for 10 min, then switched to 130°C for 30 min rapidly. The treated samples were used for polarizing optical microscopy.

Characterization methods

Mechanical properties were assessed with a testing machine (Instron 1211)at room temperature. The cross section of tensile test bar was 1×4 mm^2. The cross-head speed was 10 mm min^{-1}. Tensile strength and elongation at break were measured. Each value reported is an average of four specimens.

Dynamic mechanical analysis (DMA) was carried out on a DMA-983 (Dupont). Test bars were cut from the tensile bar specimens (dimensions W $\times$ H $\times$ L = 1 $\times$ 4 $\times$ 5 mm^3). The experimental temperature ranged from -40 to 140°C, at a heating rate of 3°C min^{-1}. The amplitude was set at 5 μm, with a frequency of 1 Hz. Storage modulus, loss modulus, and $T_g\delta_d$ were recorded as a function of temperature.

DSC was performed using a Perkin–Elmer DSC 7. The samples (about 8–10 mg) were initially heated to 200°C to erase previous thermal history, then quenched to -40°C, and finally heated at 10°C min^{-1} -40 to 200°C. The glass transition temperature was taken both at the midpoint of the specific heat increment and at the onset of step, determined as the intercept between the baseline preceding the transition and the steepest tangent to the step. The melting temperature and crystallization temperature were taken as the top values of the melting and crystallization endotherms, respectively. The enthalpies of fusion were calculated from the integral of endothermic melting peaks in DSC curves.

FTIR spectra were obtained with a Bio-Rad FTS-7 spectrophotometer. A total of 32 scans were taken with a resolution of 4 cm^{-1} in all cases.

AFM studies were performed in an SPA300HV with a SPI3800 probe station (Seiko Instruments, Japan) in the tapping mode. Silicon tips on cantilevers (resonance frequency 70 kHz) with a spring constant of 2 N m^{-1} were used. Scan rates were chosen in the range of 0.5–1.5 Hz.

RESULTS AND DISCUSSION

Blending

The choice of the plasticizers was made to meet the criteria mentioned earlier. The miscibility of plasticiz-

TABLE I
Densities and Solubility Parameters for PLA and Plasticizers as Calculated with Group Molar Attraction Constants from the Hoy Series

Substance	ρ (g cm^{-3})	δ (J cm^{-3})$^{1/2}$
PLA	1.25	20.7
TAC	1.16	20.2
PBGA	1.08	18.7
[a]1 : 1(w/w) TAC and PBGA		[b]19.4

[a] w/w is the weight ratio.
[b] The solubility parameter of the blends was calculated by δ(J cm^{-3})$^{1/2}$.

ers and polymers can be estimated by comparing the solubility parameters of the materials. In this study, the solubility parameters for PLA and multiple plasticizers were calculated according to the eqs. (1) and (2). In eq. (1), δ represents the solubility parameter, ρ is the density, M_0 is the molecular mass, and

$$\delta = \frac{\sum F \rho}{M_0} \tag{1}$$

$$\delta_m = \phi_1 \delta_1 + \phi_2 \delta_2 \tag{2}$$

F is the group molar attraction constants according to Hoy series.[18] Equation 2 is used to calculate the solubility parameters of mixtures, $\hat{O}$ represents the volume fraction of one component in the mixture.[19] As shown in Table I, we had calculated the solubility parameter of 1 : 1 (w/w) TAC and PBGA multiple plasticizers, and it was close to that of PLA, which indicated that they should be miscible.

Thermal and crystallization behavior

DSC experiment was carried out to investigate the thermal properties of the blended materials. Figure 1 shows DSC traces comparing pure PLA with the different contents of multiple plasticizers' blends. The curves display glass transition, cold crystallization, and melting peaks, and their shapes are similar. The thermal characteristics are summarized in Table II. In Table II, there is a decrease in glass transition temperature with increasing content of multiple plasticizers. T_g decreased from 59.71°C of pure PLA to 37.35°C of 29% multiple plasticizers' blends. This decrease in T_g is a good indication of the extent of the plasticizing effect provided by multiple plasticizers. This result is in good agreement with those reported in a previous investigation on the effects of plasticizing PLA with citrates, conducted by Labreque et al.[14]

From Table II, we found the T_m gradually fell with increasing content of multiple plasticizers. It is known that T_m of the crystalline component in a blend de-

pends on both morphological and thermodynamic factors.[20] Considering that all blends were prepared under the same conditions in the present report, the T_m changes of components depending on composition could be seen as a result of interaction between components, with reference to the literature reports.[21,22] Adding multiple plasticizers would enhance chain mobility and decrease the chemical potential of amorphous PLA chains, and so the T_m was gradually depressing.[23] It is also known that the melting point of a crystalline polymer is depressed by low molecular weight diluents because of the increase of chain end.[24]

Interestingly, most melting endotherms showed two distinct peaks, as shown Figure 1. There may be two causes. Few authors had reported[25] this behavior as a result of lamellar rearrangement during crystallization of PLA: low-temperature peak was formed on the melting endotherm of the original crystallites, and the high-temperature peak was formed on the melting endotherm of the recrystal crystallites. In another case, the two melting peaks may be a result of the polymorphic crystalline transition of PLA. The existence of three kinds of crystal modification, α, β, γ, has been reported for PLA. The structure of the α crystal modification is pseudo-orthorhombic with the chains in a $-10/3$ helical conformation as determined by De Santis and Kovacs.[26] Eling et al.[27] reported, for the first time, the existence of another modification, which they called the β structure. But it appeared only for fibers hot-drawn to relatively high draw ratios. Puiggali et al.[28] got the crystal structure formed upon stretching or stroking of PLA, that is γ modification. Considering the form condition of β and γ modification, the crystal state we got may be α crystal. The results of WAXD and FTIR confirmed that the assumption was correct. As shown in Figure 2, PLA and the various blends had IR absorption bands at 922
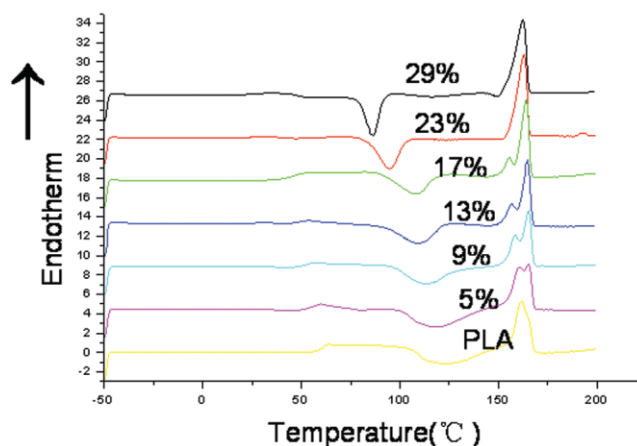
Figure 1 DSC traces of pure and plasticized PLA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Data Obtained by DSC Measurements for Neat and Plasticized PLA

[a]Content of plasticizer (%)	T_g^{2nd} (°C)	T_{cc}^{2nd} (°C)	T_m^{2nd} (°C)	ΔH_m^{1st}	C_r (%)
0	59.71	122.8	164.6	36.88	39.40
5	55.09	118.5	165.3	37.84	42.30
9	51.59	114.4	165.3	35.41	41.60
13	47.49	110.4	164.8	34.70	42.56
17	44.87	108.5	164.0	33.80	43.50
23	39.06	94.66	162.8	33.16	46.00
29	37.35	86.17	162.3	32.72	49.20

[a] Indicates weight ratio.
1st is first-heating run in DSC measurement.
2nd is second-heating run in DSC measurement.

cm^{-1} assigned to the CH$_3$ rocking modes of α crystal.[29] Of course, in the course of the experiment, we found that the multiple plasticizers had no IR absorption bands at 922 cm^{-1}. In addition, Figure 3 shows WAXD curves, of the pure PLA and PLA of various blends had the same peak positions, which were independent on the amount of multiple plasticizers, only different intensities. Twenty of about 16.4 assigned to crystallographic plane (110) and (200) of α crystal and 18.6 assigned to crystallographic plane (210).[30,31] This result also confirmed that PLA had no polymorphic crystalline transition. It is consistent with the results of FTIR. So the pure PLA and various blends had the same crystalline structure. Therefore, we can conclude that the second endotherm of the two melting endotherm corresponded to a melt process of more stable crystals (crystal perfection or lamellar thickening). From Figure 1, we also found that the endotherm of the low-temperature peak of melting gradually diminished. Even with multiple plasticizers up to 23%, the peak disappeared. This behavior indi-

cated that multiple plasticizers made crystallization of PLA more easy and complete. So when the content of multiple plasticizers was very high (about 23%), the PLA did not have the melting peak of recrystal crystallites, and its crystallinity was perfect. This result was in agreement with the change of cold crystallization temperature (T_{cc}). Theoretically, the increase or decrease of T_{cc} changes of a component may indicate that the crystallization of this component becomes more difficult or easier, respectively, upon blending with another component.[32] In the present blends, as shown in Table II, compared with that of pure PLA, the T_{cc}s of the blends shifted to the lower temperature, indicating the facility of crystallization of PLA in the blends. This result confirmed the effect of multiple plasticizers on the crystallization of PLA.

Mechanical properties

Dynamic mechanical analysis

The DMA results for the blends with various multiple plasticizers contents are present in Figure 4 (A). The
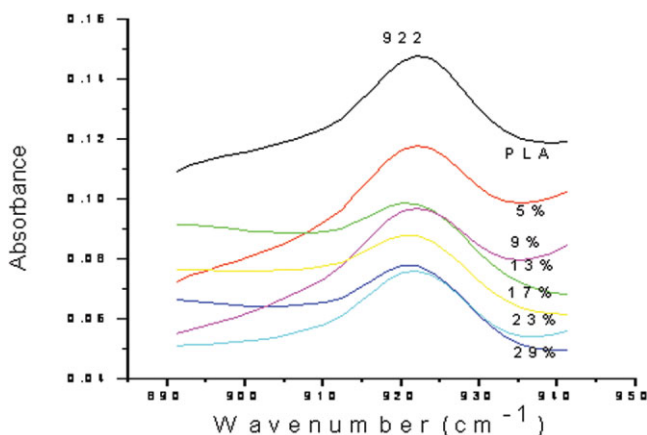

Figure 2 FTIR spectra in the —CH$_3$ rocking mode region for pure PLA and different contents of mutiple plasticizers' various blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
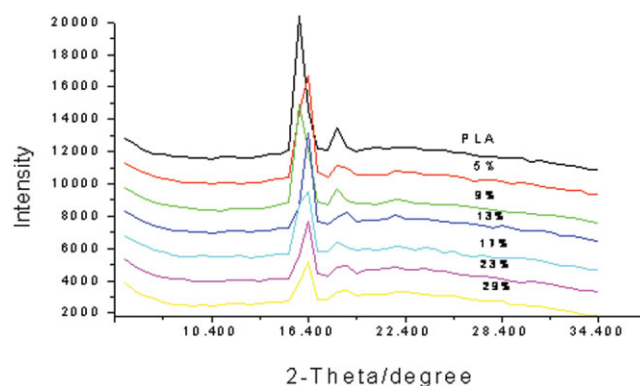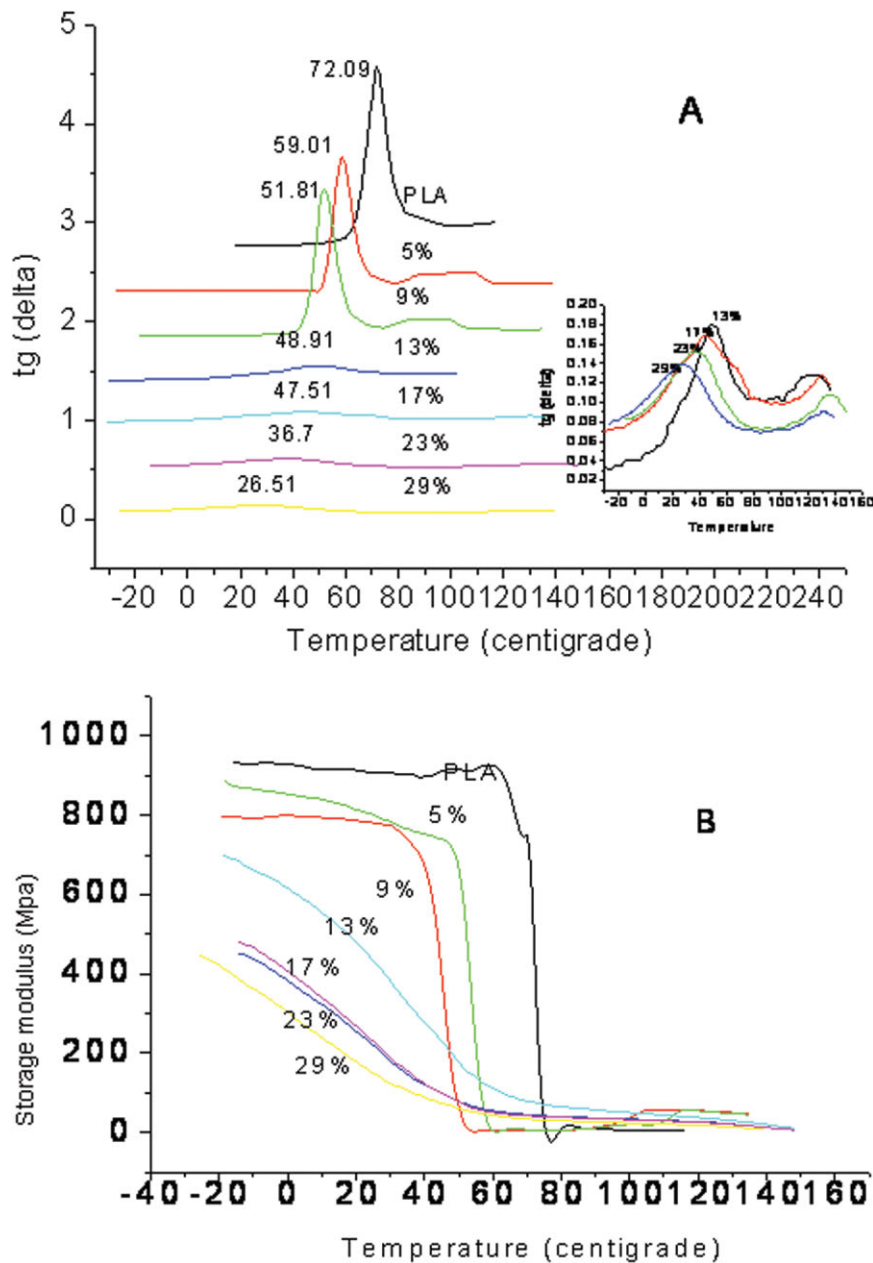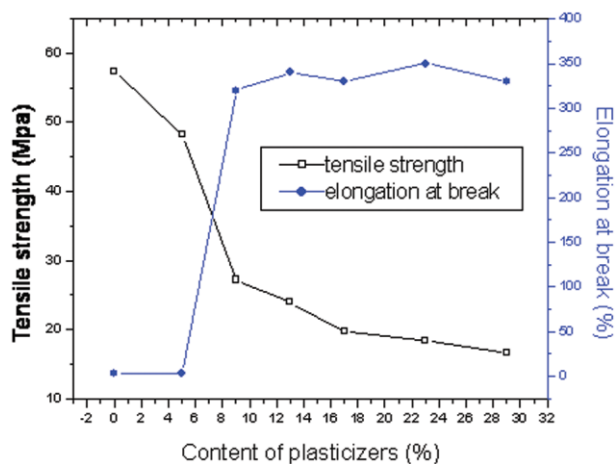

Figure 3 WAXD patterns of PLA and blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 DMA of pure PLA and blends with various multiple plasticizers content: (A) $T_g\delta_d$ and (B) storage modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

α-relaxation processes associated with the glass transition of the amorphous phase of PLA could be determined, The α-relaxation temperature (T_α), taken at the maximum of respective tan δ peaks, was seen to decrease with increasing multiple plasticizers. As expected, the T_α values associated with the glass transition of PLA differed significantly from the T_g results found by DSC. But they have the same trend. In addition when the multiple plasticizers were few, tan δ peaks were high and sharp. On the contrary, tan δ peaks were short and broad. It indicated blended sys-

tem of the fewer multiple plasticizers was comparatively homogeneous. Except the α-relaxation, we also could observe another tan δ peaks after them. This might be a result of cold crystallization. The storage modulus of the blends had similar patterns as the temperature increased: a decrease first, then a slight increase [Fig. 4 (B)]. But we find the pure PLA had a hump before a rapid decrease, this could be caused by the rearrangement of the molecules, relieving the stress generated in processing. Multiple plasticizers could increase the mobility and make PLA have the

Figure 5 Tensile properties of pure PLA and various blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lowest potential energy, and thus PLA was no more the rearrangement of molecules. This just was the reason for the others not having this phenomenon. The modulus decreased as the multiple plasticizers content increased because the multiple plasticizers increased the mobility of amorphous phase. Above T_g, storage modulus has a slight increase, and this is a result of cold crystallization.

Tensile properties

The major function of a plasticizer is to improve the elongation at break and increase the toughness of a polymeric material. The tradeoffs include reduced tensile strength. The tensile strength and elongation at break are shown in Figure 5. The tensile strength of blends decreased as the content of plasticizers increased. Elongation at break also significantly improved with increase of the content of plasticizers. It leveled off at the plasticizers contents ranging from 0 to 5%, but increased dramatically at about 5–9%. It indicated that the blends were brittle at less than 5% plasticizers contents and were ductile at greater than 9% plasticizers contents.

Morphology

A polymer has a high elongation at break, and the high mobility of the amorphous chains is required; only multiple plasticizers met this need. PLA is semicrystalline polymer. Mechanical properties of materials are dependent on the interior defects and flaws. Interface between the amorphous part and crystalline part affect the mechanical properties greatly. AFM topographic images in Figure 6 show the morpholo-

gies of pure PLA and various blends. We could consider the higher part in the images as the stiffer part, which is the crystallization part of semicrystalline PLA. If so, we also could see that the crystallization of PLA displayed the threadlike states. This may be the result of plasticizers dispersing in spherulites and the entanglement between lamellas of spherulites. The main cause of the formed morphologies was that the crystalline rate was lower than the diffusing rate of plasticizers.[33] Analyzing topographic images, we also could find that the threadlike crystallines were slender and tighter, when the content of multiple plasticizers increased. The results indicated that the degree of PLA crystalline perfection became higher, and at the same time the crystallite sizes of PLA became smaller. So we can conclude that the crystallization part of PLA formed the quasicrosslinkings not by chemical crosslinking reactions but physical molecular entanglement.[23] Theoretically, high crystallinity could reduce the elongation at break. But the kind of physical crosslinkings formed through physical hypobonds made the blends elastic and have a high elongation at break. From Figure 6, we also can see that this quasicrosslinking became tighter as multiple plasticizers increased. This just was one cause of the increase of elongation at break when multiple plasticizers increased. So the increase of crystallinity and the increase of elongation at break were not contradictive in present study.

Generally, multiple plasticizers and PLA had good miscibility through the polar interactions between the ester groups of PLA and multiple plasticizers. T_g of the blends was obviously decreased, because of the multiple plasticizers increasing the chain mobility of PLA, Just so, increasing the content of multiple plasticizers, the blends had the increasing crystallinity. In the amorphous part of semicrystalline blends, the multiple plasticizers improved the elongation at break of PLA, but the physical crosslinkings formed through physical hypobonds of crystallite also made the blends elastic.

CONCLUSIONS

To improve the mechanical properties of PLA, we added a multiple plasticizer to it. The effects of the addition of the plasticizers on the mechanical, thermal properties and morphologies of PLA have been investigated. We deduced the following conclusions: the presence of multiple plasticizers made the PLA have a higher crystallinity. The melting point and the glass transition temperature decreased remarkably with increasing multiple plasticizers content; tensile strength was clearly decreased following the increasing of multiple plasticizers; but the elongation at break of PLA was increased when the content of multiple plasticiz-
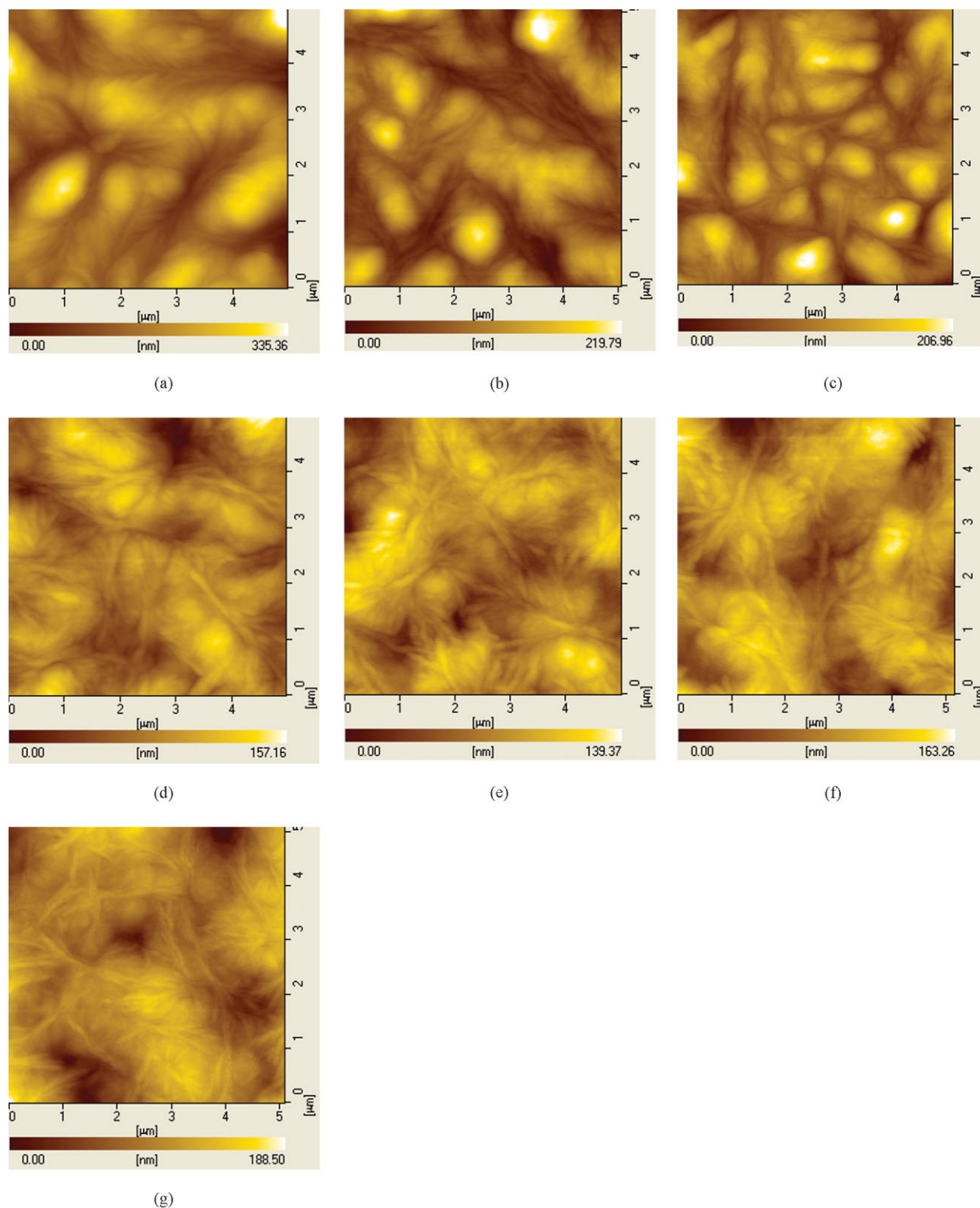
Figure 6 AFM images of different blends. (A) PLA, (B) 5%, (C) 9%, (D) 13%, (E) 17%, (F) 23%, and (G) 29%.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ers increased. AFM topographic images showed that the crystallization part of PLA formed the quasi-crosslinkings by physical molecular entanglement.

The kind of physical crosslinkings formed through physical hypobonds made the blends elastic and have a high elongation at break.

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