

Enhanced toughness and strength of poly (D-lactide) by stereocomplexation with 5-arm poly (L-lactide)

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ABSTRACT: The enhancement of mechanical properties were achieved by solution blending of poly(D-lactide) (PDLA) and 5-arm poly(L-lactide) (5-arm PLLA). Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) results indicated almost complete stereocomplex could be obtained when 5-arm PLLA exceeded 30 wt %. Tensile test results showed that the addition of 5-arm PLLA in linear PDLA gave dramatically improvement both on tensile strength and elongation at break, which generally could not be increased simultaneously. Furthermore, this work transformed PDLA from brittle polymer into tough and flexible materials. The mechanism was proposed based on the TEM results: the stereocomplex crystallites formed during solvent evaporation on the blends were small enough (100–200 nm), which played the role of physical crosslinking points and increased the interaction strength between PDLA and 5-arm PLLA molecules, giving the blends high tensile strength and elongation at break. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42857.

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INTRODUCTION

Poly(lactic acid) (PLA) is recognized as one of the most promising compostable polymers to substitute conventional petroleum based polymers, because of its plant origins and degradability, as well as good mechanical properties.^{1–7} From the application's points of view, the toughness and heat distortion temperature (HDT) of PLA are the two aspects to be improved. As a semi-crystalline polymer, with crystallinity 5~10% through general processing methods, PLA has a quite low HDT, which is not higher than its glass transition temperature (T_g), i.e. 60°C.^{8,9} By adding nucleation agents into PLA resin and annealing under certain temperature, the crystallinity can be improved to some extent in short time, and the HDT can be improved effectively,^{10–14} but at the same time, the toughness of PLA becomes even much weaker. On the other hand, the toughness modification methods including adding low T_g rubbery polymer into PLA always decrease the HDT, as well as increase the toughness.

In spite of plenty literatures about the stereocomplexation between PLLA and PDLA,^{15–17} there are few reports focused on the mechanical properties of this stereocomplex. Cross-linking

agents are always used to increase the mechanical strength. Tamada¹⁸ prepared different PLA stereocomplex by melt processing and cross-linked with triallyl isocyanurate (TAIC) by electron beam irradiation. The mechanical properties including tensile strength, Young's modulus and elongation at break of PLA can be significantly improved by radiation-induced cross-linking at suitable radiation doses. S. Asai¹⁹ studied the effect of cross-linker (TAIC) on mechanical properties by supercritical carbon dioxide treatment, and the results showed that the cross-linking network inhibited crystallization and enhanced the rigidity, meanwhile, lowered the brittleness of stereocomplexed samples. The crosslinking structure introduced in PLA films improved the degradability, as well as the heat stability and mechanical properties.²⁰ Some other results exhibited that the diblock copolymers of L-lactide and LD-lactide as well as L-lactide and D-lactide show significant improvements on elongation at break and tensile strength compared to their counterpart homo polymer blends, and the PLLA/poly(LD-lactide) blends showed lower mechanical properties than those of their pure components due to phase separation when quenching to room temperature.²¹

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N. López-Rodríguez Improved the toughness of polylactides by stereocomplex crystal formation of pure PDLA and PLLA of high molecular weight, the elongation at break from 10.8% to 33.1%.²² H. Tsuji prepared 1:1 casting films from PLLA and PDLA solution within the M_w range 1×10^5 – 1×10^6 and investigated the mechanical properties and morphology.²³ The 1 : 1 blend films showed superior mechanical and heat resistance properties than those of the pure PLLA or PDLA films, because the micro-phase structure of stereocomplex crystallites generated during solvent evaporation of mixture solution acted as intermolecular cross-links that strengthen the interaction between crystallites through the so-called “tie chain”. Y Sakamoto prepared linear 1-arm, 2-arm and 4-arm PLLA/PDLA blends indicated that the chain direction and branching could increase the segmental mobility insignificantly, and the crystalline was affected by the length of per arm instead of molecular architecture.²⁴ So, the key point to increase both toughness and HDT is the distribution of PLA spherulites. If a part of the PLA molecules that constitute the crystalline dissolve into a continuous amorphous phase, the brittleness can be reduced to some extent.²⁵

In this work, a biocompatible and biodegradable material with high molecular weight 5-arm PLLA was chosen to modify linear PDLA. So the mechanical properties of the blends are good enough to satisfy the industrial uses, such as bags, films, electrostatic spinning and other functional materials. While compared with other toughen and strengthen agents, the cost of 5-arm PLLA is relative low. The blend films of PDLA/5-arm PLLA were prepared by solvent evaporation method, and the mechanical properties, thermal properties of the blends with different weight ratios were characterized. Based on the morphology results, a toughen and strengthen mechanism was proposed.

EXPERIMENTAL

Materials

Poly (D-lactic acid) was supplied by Zhejiang Hisun Biomaterials Co. Ltd, with M_n 5.5×10^4 and M_w/M_n 1.55. The 5-arm PLLA with M_n 7.5×10^4 and M_w/M_n 1.37 were synthesized by ring-opening polymerization of L-lactide in bulk using stannous octoate as catalyst and triglycerol as initiator (Supporting Information Figure S1). The samples were precipitated in ethanol after dissolved in dichloromethane to remove monomer residues. And then the 5-arm PLLA was further dried in a vacuum oven at 60°C for 48 h to evaporate residue solvent.

Preparation of Blend Films

PDLA, 5-arm PLLA were dissolved in dichloromethane separately, and the concentration of the solution was 20 g/dL. PDLA and 5-arm PLLA solution were admixed under vigorous stirring for 3 h, and then casted onto a dish coated with Teflon, followed by solvent evaporation at room temperature for 12 h. There was a piece of filter paper covered on the dish to slow the evaporation. The films were peeled off from the dish and dried in a vacuum oven at 50°C for 72 h to evaporate residue solvent.

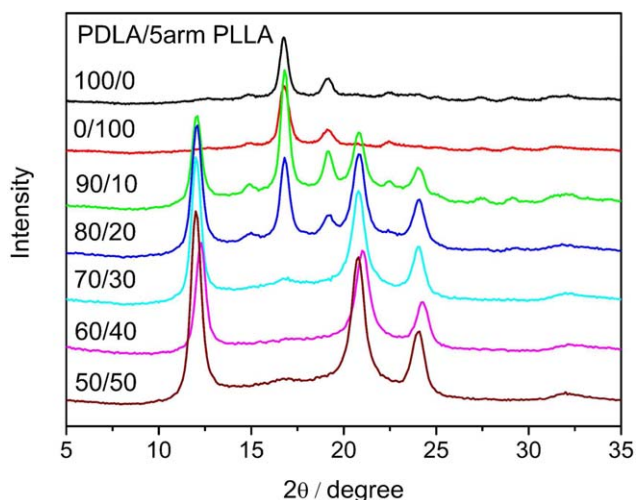


Figure 1. WAXD profiles of pure PDLA, 5-arm PLLA and their blends with different weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

Thermal properties of PDLA/5-arm PLLA blends were determined with a TA Q100 differential scanning calorimeter (DSC Q100, TA instruments). Specimens (ca. 5–8 mg) were heated from room temperature to 250°C at the rate of 10°C/min under nitrogen atmosphere.

The wide-angle X-ray diffraction (WAXD) measurement was carried out at room temperature on a Bruker D8 Advance X-ray diffractometer, using a Cu K α source; the scattering angle 2θ ranged from 5° to 35° at a scan speed of 3°/min.

Specimens for tensile tests were cut from blend films with dimension around 70 mm \times 5 mm \times 0.2 mm. Tensile tests were performed with Instron 1211 at a crosshead speed of 5 mm/min. For each sample, three specimens were tested and the data reported were the average calculation means. The dynamic mechanical properties were carried out by a dynamic mechanical analyzer DMA/SDTA861e. Samples, cut into the shape of 50 mm \times 5 mm \times 0.2 mm, were measured in tensile mode at a constant frequency of 1.0 Hz at a heating rate of 3°C/min from 20°C to 220°C under nitrogen flow.

The transmission electron microscopy (TEM) (JEOL 100 CX) was used to analyze the morphology of PDLA/5-arm PLLA blends at an accelerating voltage of 100 kV. The diluted blend solution with the concentration of 2 g/dL was casted onto the surface of copper mesh and allowed to dry in air at room temperature for 12 h, and then transferred to vacuum oven at 50°C for 72 h prior to the experiment.

RESULTS AND DISCUSSION

Stereocomplex Formation between PDLA And 5-Arm PLLA

By slowly evaporating the solvent from PDLA/5-arm PLLA mixture solution, the PLA films are prepared. The strong diffraction peaks of WAXD spectra around 16°, 18°, and 22.5° are observed in neat PDLA and 5-arm PLLA films, as shown in Figure 1, which means that a typical α -form crystalline structure is formed during the solvent evaporation.²⁶ The diffraction peaks

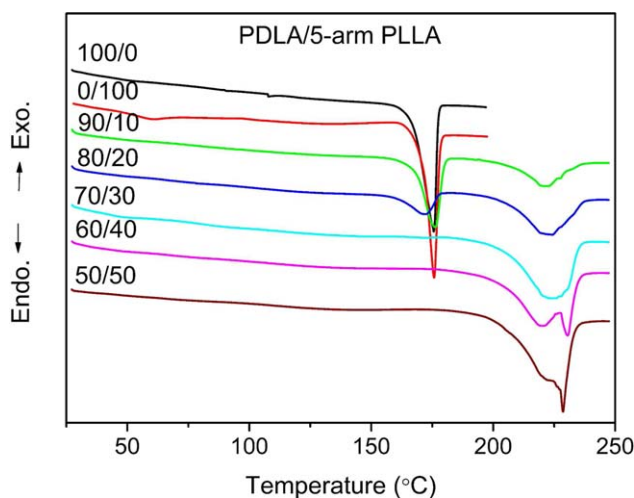


Figure 2. DSC traces of pure PDLA, 5-arm PLLA and their blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 12°, 21° and 24° that belong to stereocomplex crystalline (sc) increase with the addition of 5-arm PLLA, accompanied by reduction of diffraction intensity of homo crystalline (hc). The diffraction peaks around 17° belong to hc become too weak to be found, when the 5-arm PLLA weight ratio exceeds 30 wt %. Thus the hc hardly form in these situations.

Thermal characterization of the blends is carried out to examine the stereocomplex formation situation, and the first heating curves are shown in Figure 2. Both hc and sc appear when the weight ratios of 5-arm PLLA are 10 wt % and 20 wt %, and the melting enthalpy of stereocomplex increases with the 5-arm PLLA content. On the other hand, the melting enthalpy of hc decreases with the addition of 5-arm PLLA, and disappears when 5-arm PLLA's weight ratio exceeds 30 wt %. These results are conflict with conventional opinions that a total stereocomplex formed at weight ratio of PLLA/PDLA from 40/60 to 60/40.²⁷ These discrepancies can be explained from two aspects: on one hand, the solvent evaporation speed in this study is kept to a very slow state, so the stereocomplexation has more chance to complete, since the stereocomplexation process is favorable in thermodynamics.^{28,29} On the other hand, one molecular of 5-arm PLLA has five tails which could act as mobile ends. So the existence of 5-arm PLLA molecular chains gives much contact chance between PDLA and PLLA, which favors the formation of stereocomplex.

The detailed information about the thermal properties of PDLA/5-arm PLLA blends are shown in Table I. The WAXD and DSC data show that the sc formed during the solvent evaporation process, and hc hardly formed when 5-arm PLLA content exceeds 30 wt % in the blends. While the melting enthalpy of sc ($\Delta H_{m,sc}$) increased with the addition of 5-arm PLLA. The amount of sc does not increase proportionally with the decreases of hc, which attributed to the dynamic restriction. For the sc are composed of PDLA and 5-arm PLLA, if some PDLA chains couldn't diffuse to the domain of 5-arm PLLA, the sc couldn't form, and the polymers exist in the form of amor-

phousness. Therefore, the formation of stereocomplex are influenced by the ratio of PDLA and 5-arm PLLA, and the maximum of $\Delta H_{m,sc}$ appears nearby the ratio of 1 : 1.

Mechanical Properties of PDLA/5-Arm PLLA Blends

The tensile properties and elongation at break, stress-strain curves of pure PDLA, 5-arm PLLA, and their blend films are shown in Figures 3 and 4. Pure PDLA and 5-arm PLLA are brittle material with low elongation at break, and 5-arm PLLA shows tensile strength about 10 MPa higher than pure PDLA because of its higher molecular weight. By adding 5-arm PLLA, the blend films show an obviously increase both on tensile strength and elongation at break. As the amount of 5-arm PLLA increases, the tensile strength and the elongation at break increase from 35 MPa, 5% to 47 MPa, 99%, respectively. The elongation at break of 20–30 wt % 5-arm PLLA addition are equivalent with that of neat 5-arm PLLA, and further addition makes elongation at break increase enormously. The ¹HNMR spectrum (Supporting Information Figure S2) reveals that the molecular weight of 5-arm PLLA is 41424, and the average degree of polymerization for each arm is 57. Because of high degrees of polymerization, each arm of 5-arm PLLA could either form homocrystallites by itself and other arms or form stereocomplex with linear PDLA. As a result of crystalline, physical crosslinking structure formed, which could enhance the tensile strength and the elongation at break, and this will be discussed later.

Dynamic Mechanical Properties of PDLA/5-Arm PLLA Blends

Dynamic mechanical properties for PDLA/5-arm PLLA blends are investigated by dynamic mechanical analyzer. As shown in Figure 5, the large variations of storage modulus are found between neat PDLA, 5-arm PLLA and the blends with various PDLA contents. The results indicate that the storage modulus of neat PDLA drop sharply even to zero when the temperature is higher than T_g , which reflects that the neat PDLA has certain storage modulus only in quite low temperature. The storage modulus of neat 5-arm PLLA is higher than neat PDLA, and decreases quickly when the temperature reaches melting temperature (T_m) of homo crystalline crystallite ($T_{m,hc}$). The samples with 10–20 wt % 5-arm PLLA show better heat resistant performance than neat PDLA and 5-arm PLLA. The storage modulus of the blend decreases slowly with the increase of temperature before the $T_{m,hc}$ (about 170°C), and due to the melting of homo crystalline, it drops drastically at $T_{m,hc}$. When

Table I. Thermal Properties of PDLA/5-Arm PLLA Blend Films

PDLA/5-arm PLLA	$T_{m,hc}$ °C	$\Delta H_{m,hc}$ (J/g)	$T_{m,sc}$ °C	$\Delta H_{m,sc}$ (J/g)
100/0	175.6	28.2	-	-
0/100	175.8	25.4	-	-
90/10	170	19.1	223.7	16.5
80/20	168.5	7.0	226.4	29.6
70/30	170	1.1	228.9	29.6
60/40	-	-	225.6	48.2
50/50	-	-	222.6	47.4

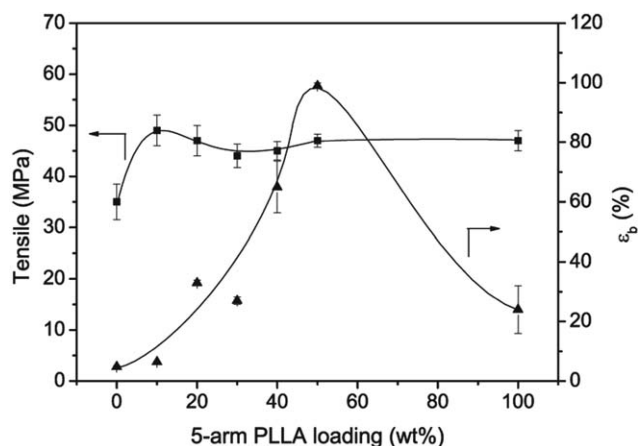


Figure 3. Tensile properties and elongation at break obtained for PDLA/5-arm PLLA blend films.

temperature is higher than $T_{m,hc}$ the storage modulus keeps a relative high level until it reaches the T_m of stereocomplex crystalline ($T_{m,sc}$). While the storage modulus curves of 30–50 wt % 5-arm PLLA reflect brilliant dynamic mechanical performances. The storage modulus keeps stable until reaching $T_{m,sc}$ (about 220°C), and the melting peak of the hc disappeared, which is highly consistent with the results of DSC. Within our scope, the thermal resistance performance increases with the addition of 5-arm PLLA, until the content of 5-arm PLLA reaches 50 wt %.

Possible Toughing Mechanism

Tsuji *et al.* had studied the mechanical properties of PLLA/PDLA and revealed that the blend films rich in stereocomplex crystallites had better tensile properties than non-blended films rich in homo-crystallites.²³ In this study, the same results are observed. A curious tensile behavior is that the stress curves after yielding increase to some extent, which is different compared with typical stress–strain curve of tough polymer. These unique stress–strain curves are caused by the tiny stereocomplexes that formed by the PDLA and 5-arm PLLA. Because of

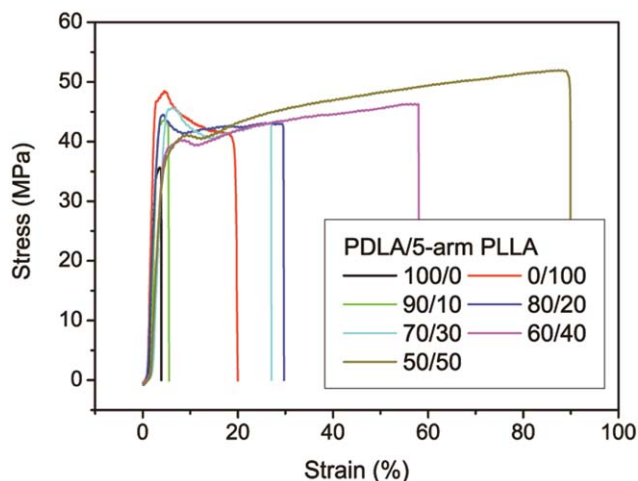


Figure 4. Stress–strain curves for PDLA/5-arm PLLA blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

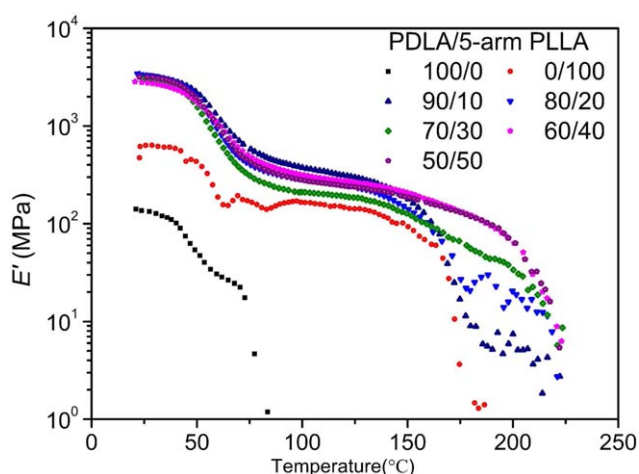


Figure 5. Storage modulus with temperature curves of dynamic mechanical analysis of PDLA/5-arm PLLA blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the brilliant compatibility, they could enhance the strong interaction during the mixing process. The strong interaction and compatibility transfer the stress to the branching point, the core of 5-arm PLLA, which could result in higher tensile strength than the pure linear PDLA. As shown in Figure 6, there are three types of molecule state in the blends, free PDLA, 5-arm PLLA and crystallites (sc or hc or their mixture). During the tensile tests, the free amorphous PDLA molecules first start to deform until the appearance of yielding point, and then the force is transformed to the crystallites and/or PLLA branching points, resulting in increase of tensile strength. The samples rich in hc, i.e. blends with 10 wt % 5-arm PLLA show inferior

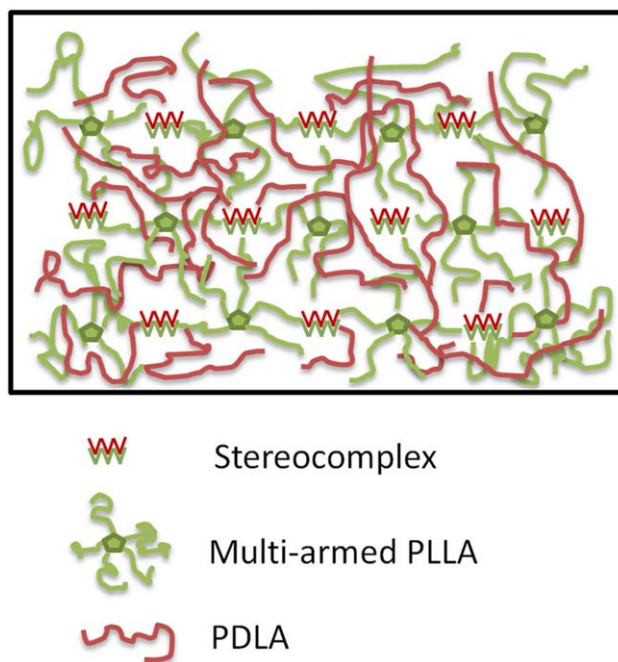


Figure 6. The physical 3D crosslink structure of PDLA/5-arm PLLA blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

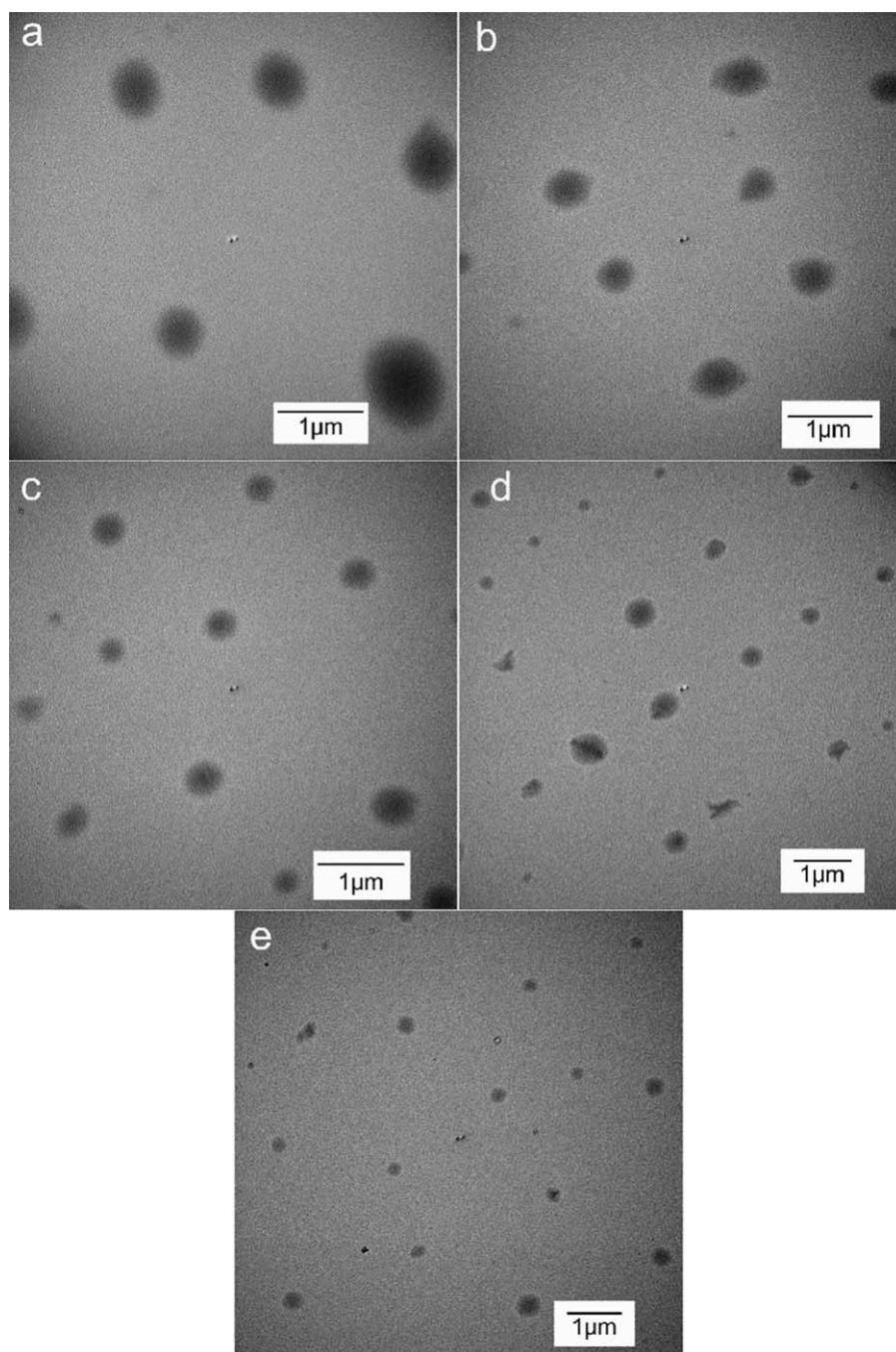


Figure 7. TEM graphs of the coated PDLA/5-arm PLLA blend films with different weight ratios. a) 90/10, b) 80/20, c) 70/30, d) 60/40, e) 50/50.

tensile strength and elongation at break than those of the blends with other higher weight ratios rich in sc. The reason is that the amount of cross-linking points in these samples of less 5-arm PLLA content cannot construct strong physical 3D crosslink network.

Based on previous studies, the size and density of crystallites play an important role in toughening PLA,^{10,30} thus TEM is used to investigate the size and distribution of crystallites in the blends. As seen in Figure 7, where PDLA/5-arm PLLA blends with different weight ratios are shown. Just as expected, the crystallite (dark particles) size of PDLA/5-arm PLLA decreases-

with 5-arm PLLA content, and the distribution of the crystallites become uniform at the same time. For example, the crystallite diameter of PDLA/5-arm PLLA 90/10 sample is about 0.5-1 μm [Figure 7(a)], and this crystallite diameter decreases to 0.3-0.5 μm when the 5-arm PLLA content exceeds 20 wt % [Figure 7(b,c,d)]. The diameter of crystallites decreases continuously even to 100-200 nm when the ratio of PDLA/5-arm PLLA is 50/50 [Figure 7(e)]. The high content of 5-arm PLLA could offer large amount of mobile PLLA segments, and these segments could form equivalent stereocomplex with PDLA as nucleating agent. Thus the blends are inclined to form even smaller crystallites.

The relationship among the crystallite size, distribution and the mechanical properties need to be confirmed,^{30,31} but the existence of this stereocomplex strengthens the interaction between PDLA and PLLA objectively. And these tiny stereocomplex crystallites, together with the branching points of 5-arm PLLA constitute physical cross-linking like structure. The correlation among crystallite size, distribution and mechanical properties suggest that the small uniform distributed stereocomplex crystallites enhance toughness and stiffness of the blends effectively by transforming force from amorphous polymer to stiff crystallites, while the interaction among the branching points of 5-arm PLLA and stereocomplex contribute to the toughness. In semi-crystalline polymers, such as PLA, rigid equiaxed particles could play the role of toughening agent when the polymer could undergo large strain plastic extension of interparticle ligaments in slow stress.³² The effect of nanoparticles depends on their distribution, size and particle interaction.³³ Thus the main interaction points between PDLA and 5-arm PLLA are the tiny stereocomplex crystallites, which are easy to slide from each other when the stress was large enough.

CONCLUSIONS

In this study, the stereocomplexation behavior and mechanical properties of PDLA blended with different 5-arm PLLA ratios were examined by film casting method. The elongation at break of the blends reaches 99%, which is higher than other PDLA and PLLA systems.²² From WAXD and DSC results, nearly complete stereocomplex could be obtained when 5-arm PLLA content exceeded 30 wt %. Furthermore, the DMA curves suggested that the PDLA/5-arm PLLA blends showed better thermal resistance performances than neat PDLA and 5-arm PLLA, especially when the content of 5-arm PLLA exceeded 30 wt %. The small and uniformly distributed stereocomplex crystallites that combined with branching point formed physical 3D cross-linking network through 5-arm PLLA, which increased both tensile strength and elongation at break simultaneously. In addition, the diameter of crystallites decreased from 0.5–1 μm to 100–200 nm with the increasing of 5-arm PLLA content.

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