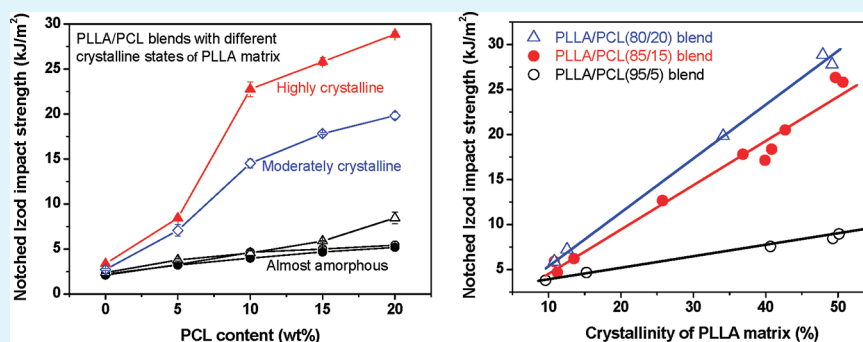


Tailoring Impact Toughness of Poly(L-lactide)/Poly(ϵ -caprolactone) (PLLA/PCL) Blends by Controlling Crystallization of PLLA Matrix

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ABSTRACT: Melt blending poly(L-lactide) (PLLA) with various biodegradable polymers has been thought to be the most economic and effective route to toughen PLLA without compromising its biodegradability. Unfortunately, only very limited improvement in notched impact toughness can be achieved, although most of these blends show significant enhancement in tensile toughness. In this work, biodegradable poly(ϵ -caprolactone) (PCL) was used as an impact modifier to toughen PLLA and a nucleating agent was utilized to tailor the crystallization of PLLA matrix. Depending on the nucleating agent concentrations in the matrix and mold temperatures in injection molding, PLLA/PCL blends with a wide range of matrix crystallinity (10–50%) were prepared by practical injection molding. The results show that there is a linear relationship between PLLA matrix crystallinity and impact toughness. With the increase in PLLA crystalline content, toughening becomes much easier to achieve. PLLA crystals are believed to provide a path for the propagation of shear yielding needed for effective impact energy absorption, and then, excellent toughening effect can be obtained when these crystals percolate through the whole matrix. This investigation provides not only a new route to prepare sustainable PLLA products with good impact toughness but also a fresh insight into the importance of matrix crystallization in the toughening of semicrystalline polymers with a flexible polymer.

KEYWORDS: biodegradable polymer, renewable resource, poly(L-lactide), toughness, crystallization, sustainable materials

1. INTRODUCTION

With increasing concerns about environmental and sustainability issues associated with traditional petroleum-based polymers, poly(L-lactide) (PLLA) has gained much attention in recent years as a biodegradable polymer produced from renewable resources.^{1–6} Due to its excellent biocompatibility, easy processability, and good mechanical strength, PLLA exhibits great potential applications in many fields, such as biomedical devices, packaging, and automotive industries. However, in many cases, the practical applications of PLLA have been significantly limited by its inherent brittleness, as evidenced by poor tensile toughness and low impact strength. Extensive approaches have been developed to improve its toughness.^{7–20} Melt blending PLLA with various flexible polymers, such as poly(ϵ -caprolactone) (PCL),^{8,9} poly(butylene succinate) (PBS),^{10,11} and polyamide elastomer,¹² is one of the most effective and economic routes to toughen PLLA. Unfortunately, although most of these blends show significant enhancement in tensile toughness, only very slight improvement in notched impact toughness can be obtained

even in the case of reactive blending of PLLA with poly(ethylene-glycidyl methacrylate) (EGMA).^{7–9,14,15} Very interestingly, annealing at 90 °C for 2.5 h gives rise to a dramatic increase in the notched impact strength of the PLLA/EGMA blends, and the crystallization of PLLA matrix is considered to play a decisive role in the toughening.¹⁵ However, the toughening mechanisms involved were not clarified in this work.

Toughening mechanisms of polymers with elastomer particles have been widely studied in the past decades. It is generally accepted that, despite cavitation of elastomer particles itself does make a small contribution to the fracture energy, cavitated particles can relax the locally triaxial stress state that favors brittle fracture and then promote energy dissipation through initiating crazing or/and shear yielding of the matrix around them.^{21–23} Shear yielding is a much more effective

Received: November 9, 2011

Accepted: January 3, 2012

Published: January 3, 2012

energy dissipation mechanism compared with crazing; therefore, the key to achieve a desired toughening effect is believed to make the matrix shear yielding.^{22,24,25} Crazing and shear yielding are two competitive deformation mechanisms, which one dominates mainly depends on the properties of the matrix.^{22,25–27} Generally, the fracture process is dominated by crazing in the case of glassy amorphous matrixes (e.g., polystyrene (PS) and poly(methyl methacrylate) (PMMA)), whereas it is governed by shear yielding in the case of semicrystalline matrixes (e.g., polypropylene (PP) and polyamide (PA)). These experimental phenomena suggest that toughening may become easier to achieve with the increase of matrix crystallinity. Unfortunately, to the best of our knowledge, the relationship between impact toughness and matrix crystallinity for a given blend is not yet clear at present, probably because it is difficult to adjust the crystallinity of such semicrystalline matrixes in a wide range. For PLLA, it is very difficult to obtain a highly crystalline article through practical processing methods (e.g., injection molding) due to its slow crystallization rate.^{28,29} Very recently, we reported that the crystallization of PLLA can be largely enhanced by adding a highly active nucleating agent *N,N',N''*-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-328).³⁰ At isothermal crystallization temperatures ranging from 115 to 135 °C, the overall crystallization time of PLLA can be shortened to less than 3 min in the presence of 0.2–0.5 wt % TMC-328, which makes it possible to prepare PLLA/elastomer blends with relatively high crystallinity of PLLA matrix using practical injection molding. Compared with the long-term annealing induced crystallization of amorphous PLLA matrix, the dramatically accelerated crystallization by adding active nucleating agent is more favorable in industry. More importantly, the absence of annealing effect (i.e., the precise adjustment of fine crystalline structures at the later stage of annealing, such as chain rearrangements in the mobile amorphous and rigid amorphous phases, as proposed in our previous works on the annealing of PP and its blends with ethylene-octene copolymer (POE)^{31–33}) for the injection molded samples allows for a complete understanding of how matrix crystallization affects ultimate impact toughness in the blends.

In this work, therefore, TMC-328 was used to tailor the crystallization of PLLA matrix in biodegradable PLLA/PCL blends prepared by injection molding. Depending on the TMC-328 concentrations and mold temperatures, PLLA matrix with a wide range of crystallinity (10–50%) in the blends was obtained. Then, the effect of PLLA matrix crystallinity on the notched impact toughness of the blends and the toughening mechanisms involved were systematically investigated. The results show that significantly improved toughness of PLLA/PCL blends can be easily achieved in highly crystalline PLLA matrix, where it is easier to trigger large-scale matrix shear yielding compared with glassy amorphous PLLA matrix. From the viewpoint of practical application, the blend with highly crystalline matrix is far more favorable than that with amorphous matrix not only because of its excellent impact toughness but also because it is expected to have a much better heat resistance and can be more easily prepared by practical processing methods (e.g., injection molding) as a result of the remarkably accelerated crystallization of PLLA matrix in the presence of highly active nucleating agent.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. All the materials used in this study are commercially available. PLLA (4032D, NatureWorks LLC) with high stereoregularity (1.2–1.6% D-isomer lactide) was used as the matrix polymer. It exhibits a density of 1.25 g/cm³. The weight-averaged molecular weight (M_w) and polydispersity are 207 kDa and 1.74, respectively. PCL (CAPA 6800, Perstorp UK Ltd.) with an M_w of 120 kDa and a melt flow rate (MFR) of 3 g/10 min (160 °C/2.16 kg) was selected as the impact modifier. A highly active nucleating agent *N,N',N''*-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-328) with a melt temperature of about 375 °C was obtained from Shanxi Provincial Institute of Chemical Industry, China. The chemical structure of TMC-328 has been given in our previous work.³⁰

Blends of PLLA with various contents of PCL and TMC-328 (PLLA/PCL/TMC) were prepared using a corotating twin-screw extruder (TSSJ-25, China) at barrel temperatures ranging from 170 to 190 °C. To achieve desired loading and good dispersion of small amounts of nucleating agent (below 0.5 wt %) in PLLA matrix, a master batch of 5 wt % TMC-328 in PLLA (PLLA/STMC) was first prepared and then melt blended with different contents of PLLA and PCL to obtain the corresponding blends. After making droplets, the pellets were injection molded using a HAAKE MiniJet (Thermo Scientific, USA) at a barrel temperature of 200 °C. Several mold temperatures (from 50 to 130 °C) were chosen to evaluate the effect of crystallization of PLLA matrix. Solidification time of the blend melts in a preheated mold was fixed to be 3 min. For comparison, PLLA/PCL blends without TMC-328 was also processed with the same method. The concentrations of TMC-328 on the basis of actual weight of PLLA matrix in the blends were 0.1, 0.2, 0.3, and 0.5 wt %. For convenience, the specimens processed at different mold temperatures were denoted as a code of PLLA/PCL/TMC-*x*, where *x* indicates the corresponding solidification temperature. Before extrusion and injection molding, all the materials were dried in a vacuum oven at 50 °C for at least 12 h. To further investigate the importance of PLLA matrix crystallization on the impact toughness of the blends, an injection molded specimen (i.e., PLLA/15PCL/0.3TMC-50) with an amorphous PLLA matrix was annealed in a conventional oven at a temperature of 130 °C for different periods to obtain samples with different crystalline contents.

2.2. Differential Scanning Calorimetry (DSC). Thermal analysis was carried out on a Perkin–Elmer pyris-1 DSC (USA) in a dry nitrogen atmosphere. The instrument was calibrated prior to the measurements by the melting of indium. For each measurement, around 5 mg of sample taken from a cross section in the center of the molded bar was heated from 30 to 200 °C at a heating rate of 10 °C/min. The degree of crystallinity of both PLLA matrix ($X_{c,PLLA}$) and PCL dispersed phase ($X_{c,PCL}$) in the injection specimen were evaluated according to the most commonly used equation:^{15–17}

$$X_c = \frac{\Delta H_m - \Delta H_c}{w_f \Delta H_m^0} \quad (1)$$

where ΔH_m and ΔH_c are the measured enthalpies of melting and cold crystallization, respectively, w_f is the weight percent of the corresponding component in the specimen, and ΔH_m^0 is the melting enthalpy of 100% crystalline polymer (93.7 J/g³⁴ for PLLA and 136 J/g³⁵ for PCL). In particular, for PCL, the value of ΔH_c is equal to 0.

2.3. Polarized Optical Microscopy (POM). To observe the crystal morphology of PLLA matrix in the injection molded bars, thin sections (about 15 μm) were cut from the middle part of the molded bars along the flow direction using a Leica microtome (Germany) and inserted between microscope coverslips. The optical micrographs were recorded with a polarized optical microscopy (POM, Leica DMLP, Germany) equipped with a Cannon digital camera.

2.4. Mechanical Testing. The notched Izod impact strength was measured according to ISO180/179 using an impact tester (VJ-40, China) on the standard sized rectangular bars. The measurement was carried out at room temperature (23 °C), and the average value reported was derived from at least five specimens.

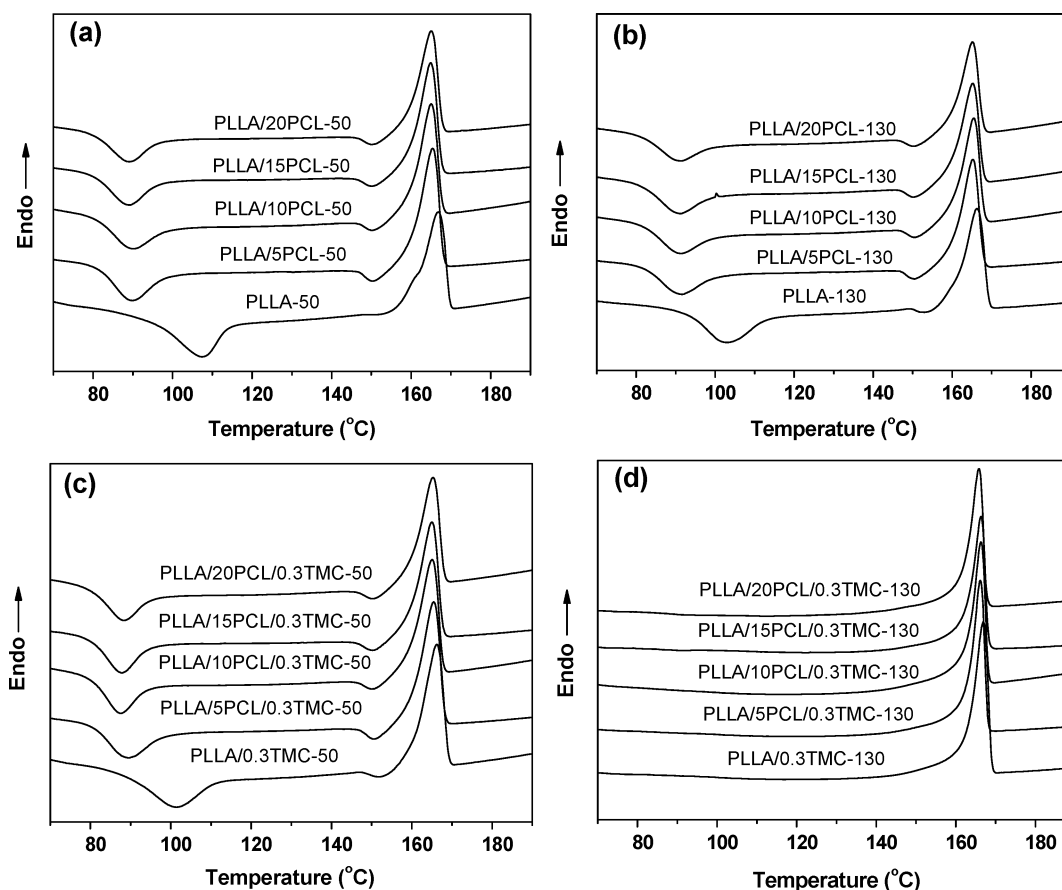


Figure 1. DSC melting curves of PLLA matrix in PLLA/PCL and PLLA/PCL/TMC blends processed at different conditions. The samples were prepared by injection molding into a preheated mold (50 or 130 °C), followed by isothermal solidification for 3 min.

2.5. Scanning Electron Microscopy (SEM). The phase morphology of PLLA/PCL blends with and without TMC-328 was characterized with an FEI Inspect F field emission scanning electron microscope (FE-SEM, USA) at an accelerating voltage of 10 kV. Samples for the SEM observation were prepared by cryofracture of the injection molded bars under liquid nitrogen along the direction perpendicular to flow direction. The particle size of PCL phase dispersed in PLLA matrix was analyzed using an Image-Pro Plus software. For each specimen, at least 300 particles from several independent SEM micrographs were measured. The number-average particle size (d_n) and particle size distribution parameter (σ) were calculated from the following equations:

$$d_n = \frac{\sum_{i=1}^N n_i d_i}{\sum_{i=1}^N n_i} \quad (2)$$

$$\ln \sigma = \sqrt{\frac{\sum_{i=1}^N n_i (\ln d_i - \ln d)^2}{\sum_{i=1}^N n_i}} \quad (3)$$

where n_i is the number of PCL particles with the diameter of d_i . In the case of monodispersity, σ is equal to 1, and when there is polydispersity, σ is greater than 1. Then, the matrix ligament thickness between PCL particles (τ) can be obtained from the equation modified by Liu et al.³⁶

$$\tau = d_n [(\pi/6\phi)^{1/3} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma)] \quad (4)$$

where ϕ is the volume fraction of the dispersed PCL phase. Especially, weight-average particle size (d_w) is usually believed to give a better correlation with impact toughness than d_n ; therefore, d_w was also determined by means of

$$d_w = \frac{\sum_{i=1}^N n_i d_i^2}{\sum_{i=1}^N n_i d_i} \quad (5)$$

The impact-fracture behaviors of the specimens were also investigated by FE-SEM. The impact-fractured surface was obtained from the notched Izod impact testing. To observe the deformed zone underneath the impact-fractured surface, the broken bar was immersed in liquid nitrogen for at least 30 min and then cryogenically fractured along a plane perpendicular to the thickness direction, as described in literatures reported by Chan et al.^{37,38} The observations were focused on the regions of crack initiation. Before SEM characterizations, all the surfaces were sputter-coated with a gold layer.

3. RESULTS AND DISCUSSION

3.1. Crystallization of PLLA Matrix. Figure 1 shows the DSC heating thermograms of PLLA matrix in PLLA/PCL and PLLA/PCL/TMC blends prepared by injection molding at different mold temperatures (i.e., 50 and 130 °C). As presented in Figure 1a,c, both PLLA/PCL-50 and PLLA/PCL/TMC-50 blends exhibit multiple transitions upon heating: a cold crystallization peak and a melting peak at higher temperatures. The cold crystallization peak of PLLA in the blends is about 10 °C lower than that in neat PLLA, indicating an enhancement effect of PLLA crystallization induced by locally activated chain mobility at phase interface resulting from limited miscibility of PLLA and PCL.³⁹ Additionally, a small exothermic peak appears prior to the main melting peak of PLLA because of the phase transition from disordered α' -form crystal to ordered α -form one during heating scan.⁴⁰ For PLLA/PCL-130 blends,

the very similar thermograms can be clearly observed in Figure 1b. However, the melting behaviors of PLLA in PLLA/PCL/0.3TMC-130 blends are considerably different from those in these blends. All the thermograms show only main melting peaks while cold crystallization peaks are almost absent (Figure 1d), indicating that the crystallization of PLLA matrix can be largely enhanced with the addition of 0.3 wt % TMC-328 for the blends processed at a mold temperature of 130 °C.

For quantitative analysis, the crystallinity of PLLA matrix ($X_{c,PLLA}$) obtained from the DSC heating thermograms is plotted as a function of PCL content in Figure 2. As expected,

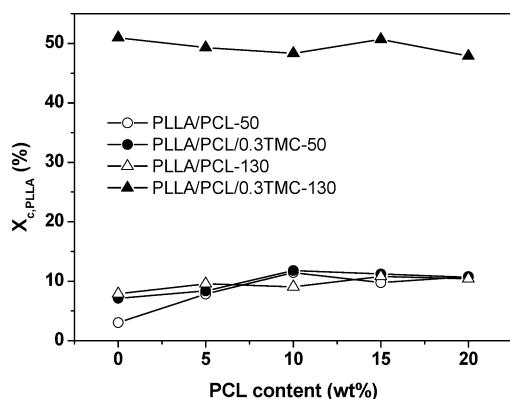


Figure 2. Crystallinity of PLLA matrix ($X_{c,PLLA}$) in PLLA/PCL and PLLA/PCL/TMC blends processed at different mold temperatures (i.e., 50 and 130 °C). The data were obtained from DSC measurements.

$X_{c,PLLA}$ in the blends of PLLA/PCL-50, PLLA/PCL-130, and PLLA/PCL/0.3TMC-50 is at the same low level (<10%), indicating almost amorphous PLLA matrix in the blends. However, for PLLA/PCL/0.3TMC-130 blends, $X_{c,PLLA}$ is as high as 50%, suggesting that the presence of 0.3 wt % TMC-328 induces the formation of highly crystalline PLLA matrix during injection molding at a mold temperature of 130 °C.

Note that the melting of PCL is very close to the glass transition (or usually observed physical aging peak^{41,42}) of PLLA, and then, it is really difficult to correctly analyze the melting behavior of PCL in the blends when its content is lower than 15 wt %; therefore, the temperature range corresponding to the melting of PCL is not displayed in Figure 1. Herein, the DSC heating thermograms of PLLA/15PCL/TMC-130 blends in a wider temperature range of 40 to 180 °C are used. As shown in Figure 3, both the position of PCL melting peak and the crystallinity of PCL phase ($X_{c,PCL}$) in the blends are found to be hardly influenced by the introduction of TMC-328, although the endothermic physical aging peak of PLLA gradually decreases with increasing TMC-328 concentration up to 0.5 wt % due to the dramatically enhanced $X_{c,PLLA}$. This indicates that crystallization of PCL is independent of the crystalline state of PLLA matrix in the injection molded blends with the same PCL content. Therefore, for a given composition of PLLA/PCL blend, PCL is expected to exhibit almost the same crystallization behavior regardless of matrix crystallinity.

3.2. Dependence of Impact Strength of PLLA/PCL Blends on Crystalline State of PLLA Matrix. As mentioned above, the relationship between crystallinity of polymer matrix and impact toughness of elastomer toughened blends are still not clear. Herein, the role of crystalline state of PLLA matrix

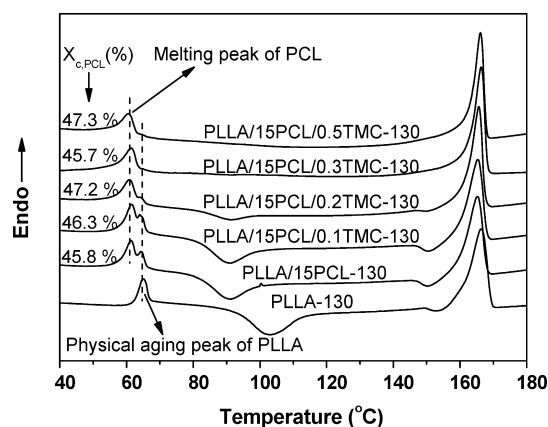


Figure 3. DSC melting curves of PLLA/15PCL/TMC blends prepared by isothermal crystallization in a preheated mold at 130 °C for 3 min. The melting enthalpy of PCL phase was determined by a peak-fitting procedure using Gaussian function, and then, the values of PCL crystallinity ($X_{c,PCL}$) are given in the profile.

(i.e., amorphous and crystalline) in the toughening of PLLA/PCL blends was first discussed before analyzing such relationship in detail. As shown in Figure 4, for the blends

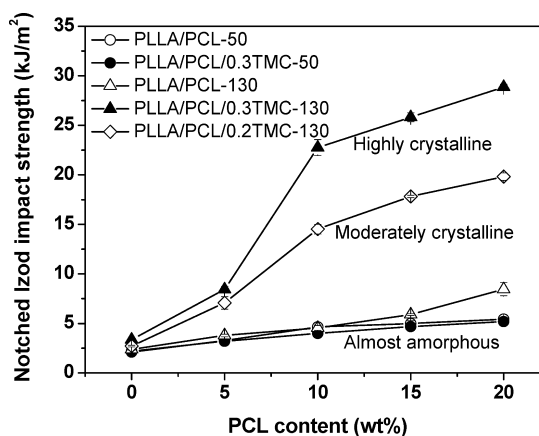


Figure 4. Notched Izod impact strength of PLLA/PCL and PLLA/PCL/TMC blends processed at different mold temperatures (i.e., 50 and 130 °C). The crystalline state of PLLA matrix in the corresponding blends is given in the profile.

with amorphous PLLA matrix, only very limited improvement in impact toughness can be obtained with respect to that of neat PLLA. For instance, the notched Izod impact strength of PLLA/20PCL/0.3TMC-50 blend is only 5.2 kJ/m², about 2.5 times of that for neat PLLA (2.2 kJ/m²). Similar results have been widely reported in the literature.^{7–9,14,15} However, it is very interesting to find that PLLA/PCL/0.3TMC-130 blends with highly crystalline PLLA matrix exhibit a definite brittle-ductile (B-D) transition in impact toughness, which is typical of semicrystalline polymers toughened by elastomer.^{21,22,43–47} The notched Izod impact strength enhances significantly from 8.4 to 22.8 kJ/m² when PCL content increases from 5 to 10 wt %, but the toughening efficiency becomes less noticeable with further increasing PCL content up to 20 wt %. Especially, the PLLA/20PCL/0.3TMC-130 blend shows impact strength of 28.9 kJ/m², more than 13-fold over that of neat PLLA. Obviously, toughening is much easier to achieve for the toughened blend with highly crystalline PLLA matrix, as

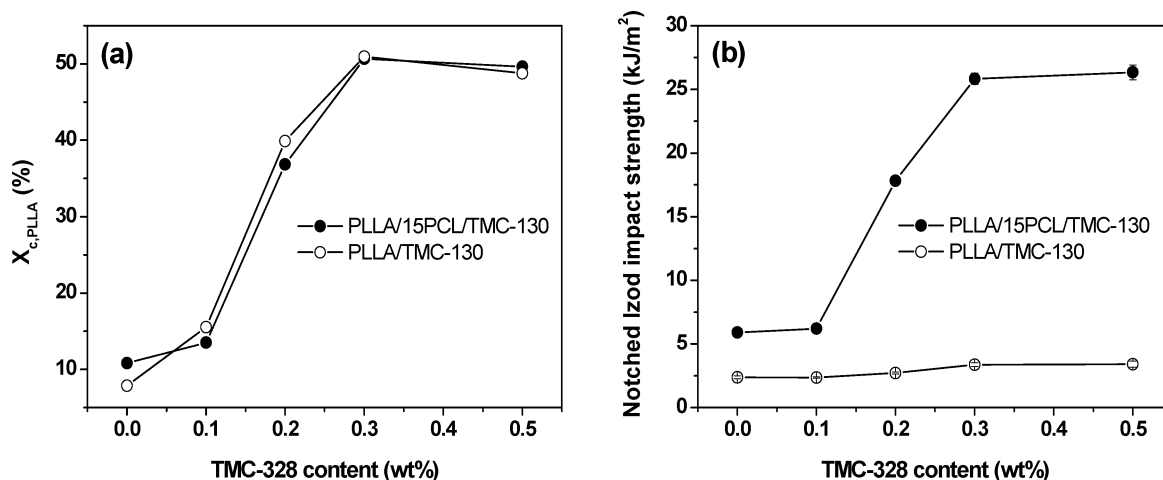


Figure 5. Effect of TMC-328 content on (a) crystallinity of PLLA matrix ($X_{c,PLLA}$) and (b) notched Izod impact strength of PLLA/TMC and PLLA/PCL/TMC blends prepared by isothermal crystallization in a preheated mold at 130 °C for 3 min.

compared to amorphous one. Furthermore, to demonstrate the reliability of this conclusion, the impact strength of PLLA/PCL/0.2TMC-130 blends with moderately crystalline PLLA matrix ($X_{c,PLLA}$ is about 35%) is also presented in Figure 3. As expected, the blends display not only an apparent B-D transition but also an intermediate toughness level between that of highly crystalline PLLA blends and amorphous ones.

3.3. Relationship between PLLA Matrix Crystallinity and Impact Toughness. In order to investigate the detailed relationship between PLLA matrix crystallinity and notched impact strength of PLLA/PCL blends, PLLA/15PCL/TMC blends were selected as model blends and PLLA matrix with a wide range of crystallinity (10–50%) was prepared by varying TMC-328 concentrations (i.e., 0, 0.1, 0.2, 0.3, 0.5 wt %) in the blends and mold temperatures (90–140 °C) in the injection molding. Please note that, for brevity, only the data obtained from the blends with different TMC-328 concentrations are presented in Figure 5. It can be clearly seen that both the PLLA matrix crystallinity ($X_{c,PLLA}$) and impact strength follow the same trend with the increase of TMC-328 content, suggesting the possibility of a linear correlation between them. This assumption is well supported by the curve of impact strength vs $X_{c,PLLA}$, as shown in Figure 6, where the notched Izod impact strength of injection molded PLLA/PCL/TMC blends increases almost linearly with increasing $X_{c,PLLA}$. Very interestingly, such linear relationship can also be observed even in thermally annealed PLLA/15PCL/TMC blends. Clearly, all the investigated blends show a linear relationship between matrix crystallinity and impact toughness regardless of the method for the crystallization of PLLA matrix: injection molding or annealing. On the other hand, it is noteworthy that the greatly increased $X_{c,PLLA}$ only gives rise to a very limited improvement in the impact toughness of PLLA/TMC systems and the effective toughening of PLLA can be achieved only if sufficient amount of PCL is introduced into a highly crystalline PLLA matrix. Furthermore, as shown in Figure 5a, the presence of TMC-328 can largely enhance the crystallization of PLLA in both the cases of PLLA/TMC and PLLA/PCL/TMC blends, but the nucleation effect becomes saturated when its concentration exceeds a critical level (0.3 wt %). This finding coincides with the widely reported investigations on the crystallization of PP nucleated with active nucleating agents.^{48,49} More importantly, the $X_{c,PLLA}$ in PLLA/15PCL/

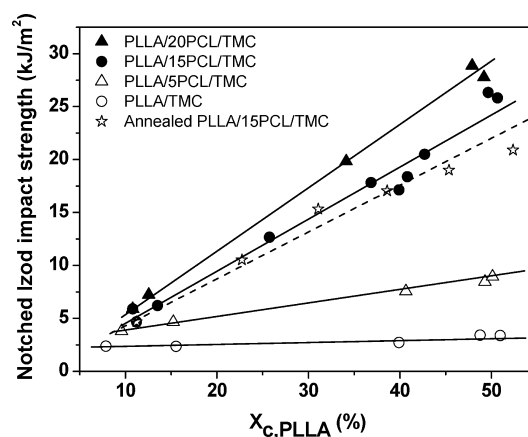


Figure 6. Notched Izod impact strength as a function of crystallinity of PLLA matrix ($X_{c,PLLA}$) for injection molded PLLA/TMC and PLLA/PCL/TMC blends. For the purpose of comparison, the experimental data obtained from the thermally annealed PLLA/15PCL/TMC blends are also presented in this figure.

TMC blends is found to be almost the same as that in PLLA/TMC systems, suggesting that TMC-328 is mainly dispersed in PLLA matrix rather than in PCL phase. By this way, the crystallization of PLLA matrix in the blends is exclusively determined by the selectively dispersed TMC-328.

It is well-known that semicrystalline polymers exhibit remarkably complex solid-state structure such as crystalline form and crystal morphology. In this way, even at the same crystallinity, different effects on the performance may be obtained due to the different lamellar organizations.^{50,51} Because the presence of TMC-328 has no influence on the crystalline form,³⁰ crystal morphologies of PLLA matrix in the injection molded blends were observed by POM to gain more insight into the linear dependence of impact toughness on PLLA matrix crystallinity. As shown in Figure 7a, only very few spherulites are formed in PLLA/15PCL-130 blend with a matrix crystallinity of 10%. However, with the addition of 0.2 wt % TMC-328 into the blend, the spherulite number increases dramatically and many isolated spherulites with an average diameter of $21.0 \pm 3.8 \mu\text{m}$ (determined using an Image-Pro Plus software) are clearly observed (Figure 7b), indicating an increased crystalline content in the presence of TMC-328 as

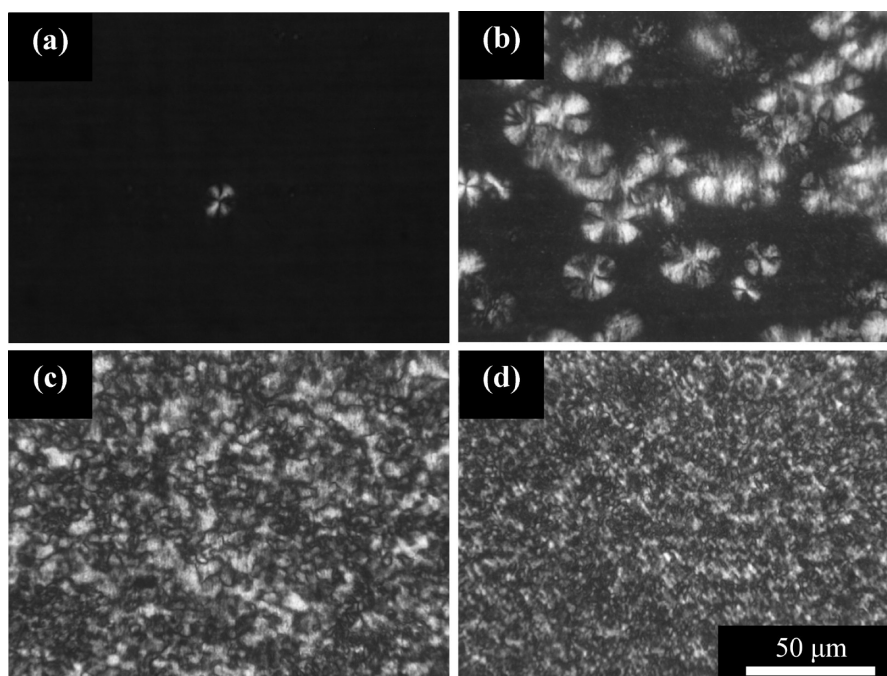


Figure 7. POM micrographs of the crystal morphology for the blends: (a) PLLA/15PCL-130, (b) PLLA/15PCL/0.2TMC-130, (c) PLLA/15PCL/0.3TMC-130, and (d) PLLA/15PCL/0.5TMC-130. The samples were cut from the middle part of the molded bars along the flow direction.

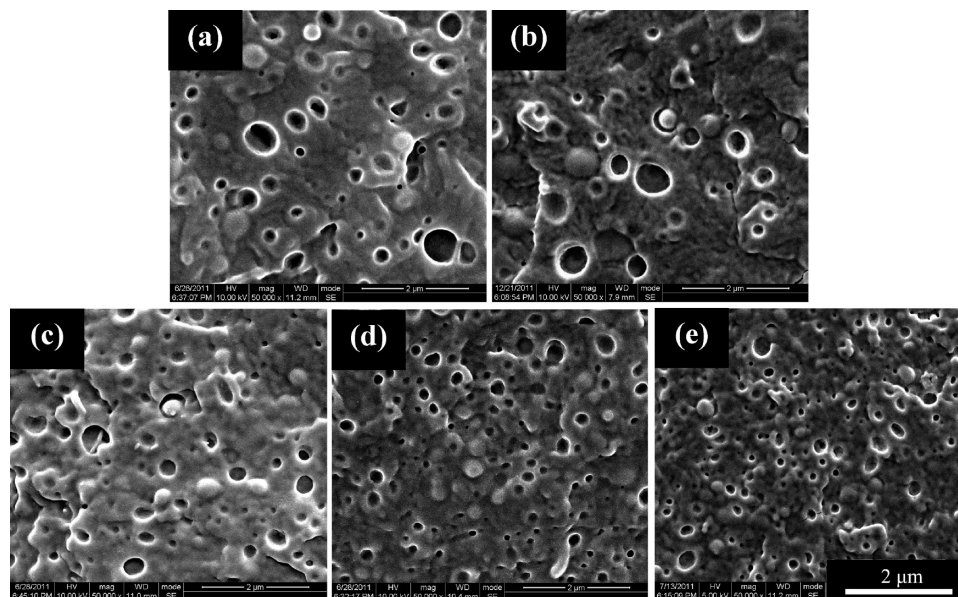


Figure 8. SEM micrographs of cryogenic fractured surfaces of the blends: (a) PLLA/15PCL-130, (b) PLLA/15PCL/0.2TMC-130, (c) PLLA/15PCL/0.3TMC-130, (d) PLLA/15PCL/0.5TMC-130, and (e) PLLA/15PCL-50.

expected. This is in good agreement with the result obtained from DSC measurement (Figure 5a), where the crystallinity of PLLA matrix increases significantly from 10% to 36% with the introduction of 0.2 wt % TMC-328. With further increasing TMC-328 concentration to 0.3–0.5 wt %, the nucleation effect of TMC-328 on PLLA matrix crystallization is largely enhanced and then a great number of tiny crystals that have impinged on each other are formed. Considering the fact that, although the presence of 0.5 wt % TMC-328 gives rise to a much higher nucleation density in the PLLA matrix as compared to 0.3 wt % TMC-328 (Figure 7c,d), almost the same impact strength is obtained in both cases (Figure 5b) due to the similar matrix

crystallinity (about 50%; Figure 5a). Therefore, the significantly improved impact toughness of the nucleated blends is believed to be mainly associated with the increase in matrix crystallinity, rather than the change of crystal morphology (e.g., the decreased size of PLLA crystals) as usually reported in PP/POE blends modified with nucleating agent.^{52–54}

3.4. Phase Morphology. Besides the crystallization of polymer matrix, phase morphology also plays a decisive role in determining the physical properties of elastomer toughened polymers.^{43,44} Therefore, an investigation of phase morphology in the obtained blends is considered to be in favor of revealing the toughening mechanism involved. For clarity, SEM micro-

graphs of PLLA/15PCL-130 blends with varying TMC-328 concentration are particularly taken into account. As shown in Figure 8, all blends exhibit a phase-separated morphology with PCL particles dispersed in PLLA matrix. To make a clear comparison, the statistical results of the PCL particle size and its distribution are summarized in Table 1. As can be clearly

Table 1. Weight-Average Particle Size of PCL Dispersed Phase (d_w), Number-Average Particles Size (d_n), and Particles Size Distribution Parameter (σ) for PLLA/15PCL/TMC Blends

sample	d_w (μm)	d_n (μm)	σ
PLLA/15PCL-130	0.39	0.34	1.52
PLLA/15PCL/0.2TMC-130	0.38	0.33	1.50
PLLA/15PCL/0.3TMC-130	0.33	0.29	1.44
PLLA/15PCL/0.5TMC-130	0.28	0.25	1.41
PLLA/15PCL-50	0.27	0.24	1.40

seen, a substantial decrease in the particle size and its distribution can be observed with increasing TMC-328 concentration up to 0.5 wt %, possibly due to the strong suppressing effect of dramatically accelerated crystallization of PLLA matrix on the PCL particle coalescence in the presence of TMC-328 at a critical concentration (0.3 wt %) or a supercritical concentration (0.5 wt %). More interestingly, compared with PLLA/15PCL-50 blend, where the blend melt is sharply cooled to below the glass transition temperature of PLLA matrix during injection molding and then its phase morphology is immediately frozen, no obvious change in the phase morphology can be observed in the PLLA/15PCL/0.5TMC-130 blend because of the strong suppressing effect, as presented in Figure 8d,e. The number-average particles size (d_n) and its distribution parameter (σ) in both the blends are about 0.25 μm and 1.41, respectively. In this case, one may argue that the finer phase morphology (smaller PCL particles size and narrower size distribution) seems to be an important contributing factor in giving rise to the significantly improved impact toughness of PLLA/PCL blends nucleated with TMC-328. However, this assumption as a main contributor can be easily ruled out. On the one hand, with the introduction of 0.2 wt % TMC-328, the slight decrease in the PCL particle size because of the relatively slow crystallization rate of PLLA matrix does lead to a significant increase in the impact toughness of PLLA/PCL-130 blends rather than a very limited improvement; on the other hand, the impact strength of PLLA/15PCL/0.5TMC-130 blend with a highly crystalline matrix is dramatically higher than that of PLLA/15PCL-50 blend with an amorphous one, although both the blends have essentially the same phase morphology. Therefore, the substantial difference in the toughness level between highly crystalline PLLA blends and amorphous ones should depend on the matrix crystallinity rather than phase morphology. Furthermore, interfacial adhesion between the dispersed phase and matrix has been demonstrated to play an important role in the toughening of polymers;¹⁷ however, no compatibilizing reaction (such as transesterification reaction) between PLLA and PCL during melt blending can be detected using Fourier transform infrared spectroscopy (FTIR). (The detailed results are not shown here.)

From above considerations, the greatly improved impact toughness of nucleated PLLA/PCL blends is mainly attributed to the enhanced crystallinity of PLLA matrix, although some

changes in the crystal morphology and phase morphology are observed. Therefore, the possible toughening mechanism involved will be discussed mainly on the basis of the linear relationship between PLLA crystalline content and impact toughness.

3.5. Toughening Mechanism. To understand how toughening efficiency depends on the crystallinity of PLLA matrix, the impact fractured surfaces of the nucleated PLLA/15PCL-130 blends with different crystalline contents were characterized using SEM with a special attention on the extent of matrix shear yielding, and the results are shown in Figure 9.

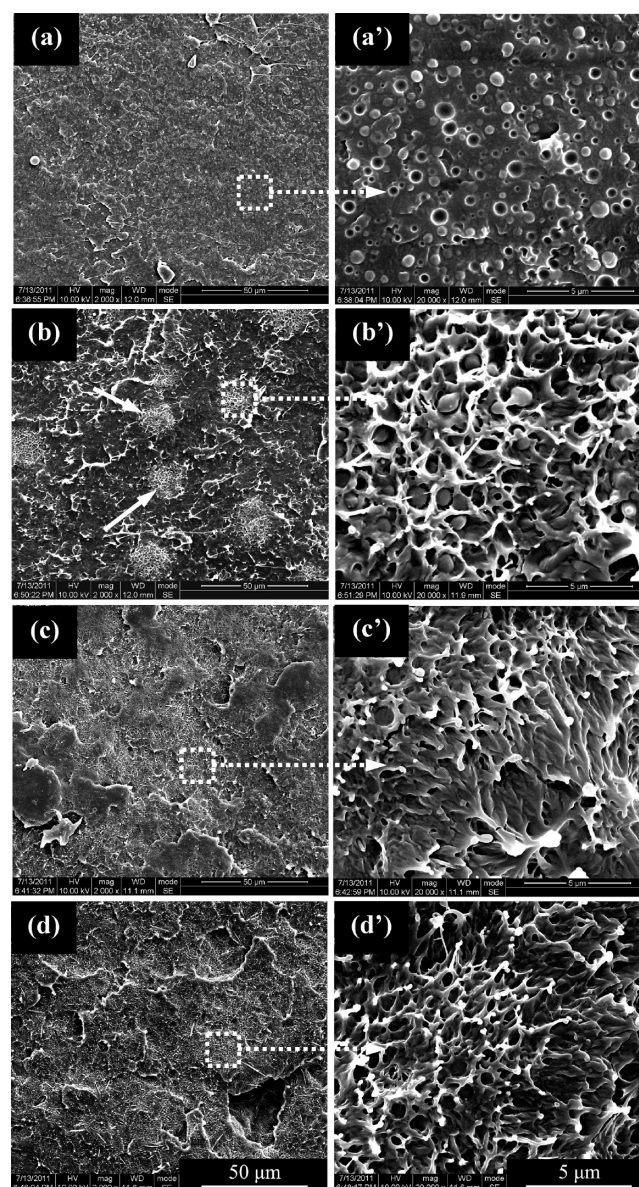


Figure 9. SEM micrographs of impact fractured surfaces of the blends: (a) PLLA/15PCL-130, (b) PLLA/15PCL/0.2TMC-130, (c) PLLA/15PCL/0.3TMC-130, and (d) PLLA/15PCL/0.5TMC-130.

As described in the Introduction section, crazing and shear yielding are two competitive energy dissipation mechanisms. For PLLA/15PCL-130 blend with an amorphous matrix, a great number of cavities resulting from interfacial debonding between PCL and PLLA phases are clearly observed, but no perceptible deformation of PLLA matrix occurs (Figure 9a). It

suggests that the amorphous PLLA matrix undergoes brittle failure through unstable crazing. However, as indicated by the arrows in Figure 9b, not only cavities but also localized shear yielding deformation of PLLA matrix around the PCL particles appear in the PLLA/15PCL/0.2TMC-130 blend with a moderate matrix crystallinity (36%), indicating that the nucleated crystallization can promote localized plastic deformation of PLLA matrix and then cause effective energy dissipation during impact fracture. However, for the PLLA matrix away from these deformation zones, its fracture feature (the SEM micrograph is not shown here) is essentially identical to that in the PLLA/15PCL-130 blend with an amorphous matrix (Figure 9a'). More interestingly, the size of these localized deformation zones (average diameter of about $22.1 \pm 4.2 \mu\text{m}$) is found to be comparable to that of PLLA crystals in the matrix ($21.0 \pm 3.8 \mu\text{m}$, Figure 7b). It seems that the localized shear yielding deformation is associated with the crystalline zones of the PLLA matrix, where it is easier to trigger shear yielding deformation by PCL particles as compared with amorphous ones. Then, when the blend is subjected to an external impact force, the fracture energy is dissipated through shear yielding in the crystalline zones and crazing in the amorphous zones. In this case, the crystalline zones can be considered as a path for the propagation of shear yielding deformation. The higher the crystalline content in PLLA matrix, the larger is the area of matrix shear yielding zones. This conclusion can be further supported by the observation of impact fractured surfaces of PLLA/15PCL-130 blend with a highly crystalline PLLA matrix (crystallinity of about 50%), where PLLA crystals impinge on one another (Figure 7c,d) and the plastic deformation of the PLLA matrix prevails throughout the whole fractured surfaces as expected (Figure 9c,d). In order to get more in-depth evidence for the proposed toughening mechanism, the cross sections underneath the impact fractured surfaces of PLLA/15PCL-130 blends with varying PLLA crystalline contents were observed with SEM. As shown in Figure 10a, although no signs

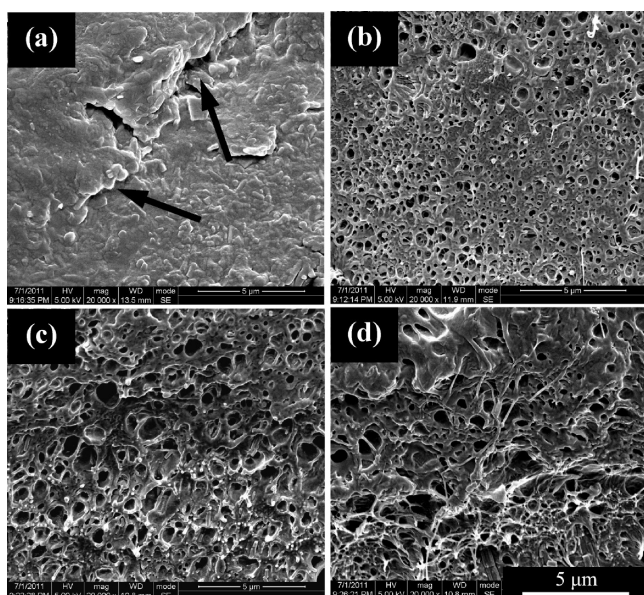


Figure 10. SEM micrographs of the cross sections underneath the impact fractured surfaces of the blends: (a) PLLA/15PCL-130, (b) PLLA/15PCL/0.2TMC-130, (c) PLLA/15PCL/0.3TMC-130, and (d) PLLA/15PCL/0.5TMC-130.

of plastic deformation of PLLA matrix can be observed, the PLLA/15PCL-130 blend shows a typical craze structure and craze-crack transition (as indicated by the arrows), suggesting that the deformation mechanism of the amorphous PLLA matrix is dominated by crazing as expected. In contrast, extensive cavities caused by the shear yielding of the PLLA matrix are formed in the blends with moderate matrix crystallinity (Figure 10b), and the extent of plastic deformation is enhanced greatly with further increasing PLLA matrix crystallinity (Figure 10c,d). It further confirms that the nucleated crystallization of PLLA matrix facilitates the initiation of shear yielding during impact fracture.

On the basis of above discussion, it is very clear that the crystallization of PLLA matrix plays an important role in the toughening of PLLA with PCL. In the process of impact fracture, shearing yield dominates the deformation mechanism of crystalline matrix, whereas crazing governs that of amorphous matrix. The volume of PLLA matrix involved in the plastic deformation enlarges with the increase of PLLA crystalline content, thus giving rise to a largely improved impact toughness of nucleated PLLA/PCL blends. Unfortunately, the reason why toughening of glassy amorphous PLLA is much more difficult to achieve as compared to that of the highly crystalline one is not definitively known at present, although the deformation mechanism of PLLA has been reported to be changed from crazing to shear yielding as crystallization occurs.⁵⁵ Recently, Corté and Leibler⁵⁶ proposed that the relatively large shear yield stresses and nanoscale heterogeneities may be the two main determining factors, on the basis of the result that toughening of semicrystalline polymers is efficient if elastomer particles can initiate surrounding matrix yielding and bring average matrix ligament thickness (τ) below the characteristic length scale of matrix heterogeneity. These two factors make the shear yielding of amorphous PLLA matrix really difficult to be triggered until large amounts of elastomer particles are introduced. The in-depth investigation on this issue will be carried out in our future work. For the investigated blends with highly crystalline PLLA matrix, a minimum PCL content (10 wt %) is found to be required to achieve largely improved toughness as expected (Figure 4), where the critical matrix ligament thickness (τ_c) may be reached because the τ of PLLA/10PCL/0.3MC blend ($0.31 \mu\text{m}$) is much smaller than the reported τ_c of PLLA ($1 \mu\text{m}$ ^{57,58}), and then, the PLLA matrix yielding percolates through the whole impact fractured surfaces. Therefore, the effective toughening of PLLA can only be achieved if it is a highly crystalline one and the critical confinement is reached. In this case, both the percolation of PCL particles and that of crystalline zones in PLLA matrix take place simultaneously, namely, the connected shear yielding networks are formed throughout the matrix, thus causing effective high impact energy dissipation.

4. CONCLUSION

In summary, we have demonstrated that the crystallization of PLLA matrix plays a key role in determining the notched impact strength of biodegradable PLLA/PCL blends. For the blends with amorphous PLLA matrix, only a slightly enhanced toughness is observed with the addition of PCL phase; however, a significantly improved toughness can be easily achieved in the case of highly crystallized PLLA matrix. Further investigation shows that there is a linear relationship between PLLA matrix crystallinity and impact toughness. The impact fracture process is dominated by shear yielding in the case of

crystalline matrix and crazing in the case of amorphous matrix; therefore, the volume of the PLLA matrix that is involved in the shear yielding deformation enlarges linearly with increasing PLLA crystalline content, thus giving rise to the significantly improved impact toughness.

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ACKNOWLEDGMENTS

We would like to express our sincere thanks to the National Natural Science Foundation of China for Financial Support (50903048, 51121001).

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