

PLLA/ABS Blends Compatibilized by Reactive Comb Polymers: Double T_g Depression and Significantly Improved Toughness

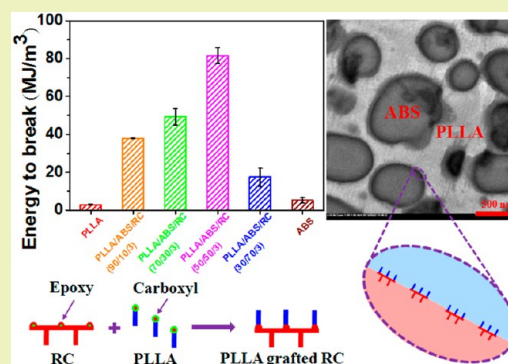
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Supporting Information

ABSTRACT: A reactive comb (RC) polymer, which was composed of one poly(methyl methacrylate) (PMMA) backbone, two PMMA side chains and a few epoxy groups that distributed randomly along the backbone, was applied as a compatibilizer in an immiscible poly(L-lactic acid)/acrylonitrile-butadiene-styrene system (PLLA/ABS). The morphological structures, the rheological, mechanical and thermal properties of the obtained PLLA/ABS blends were investigated systematically. For the first time in the reactive compatibilized system, we found that the glass transition temperature (T_g) of both PLLA and ABS phase depressed to lower temperature and the toughness of the compatibilized PLLA/ABS blend was significantly improved. The effect of blending composition showed that both the depression of T_g and the improvement of toughness were most significant at the weight ratio of 50/50, at which the area of PLLA/ABS interface was the largest. It is considered that the in-situ formed PLLA grafted RC polymers at the PLLA/ABS interface drastically improved the interfacial adhesion between the two phases. Thus the internal pressure, derived from the differentiation of the thermal contraction between the PLLA and ABS phase during cooling from the melt, significantly enhanced the mobility of the molecular chains of the both components on a microscopic scale, which was manifested by a double T_g depression phenomenon on a macroscopic scale. This investigation revealed that both the interfacial adhesion and asymmetric thermal shrinkage are important for the toughening of a rigid/rigid polymer blend.

KEYWORDS: Reactive compatibilization, Glass transition temperature, Poly(lactic acid), Interface, Reactive comb polymer



INTRODUCTION

In the past two decades, the rapid depletion of the nonrenewable petroleum resources and the improper disposal of the petroleum-based polymers have exerted enormous pressures on the sustainable development of the human race. Biodegradable and eco-friendly polymeric materials, especially those derived from renewable resources, have attracted much attention, as they were ideal candidates to replace the nonbiodegradable and petroleum-based polymers in many fields. As one of the most famous biobased polymers, poly(L-lactic acid) (PLLA) has high strength and modulus, which was comparable to conventional polymers; its inherent brittleness, low toughness, and poor heat resistance still needed to be overcome in order to compete with the petroleum-based polymers in many application fields.^{1–3}

Many efforts have been devoted to improve the toughness and thermal stability of PLLA by blending PLLA with biodegradable or nonbiodegradable polymers; most of the blending systems were immiscible or at most partially miscible, which often resulted in poor mechanical properties, and so a premade or in situ formed compatibilizer was often applied to improve the compatibility. The compatibilization of brittle PLLA and soft PCL (poly(ϵ -caprolactone)) has been successfully achieved by a premade diblock copolymers of

PCL-*b*-PEG (poly(ethylene glycol) or a diblock, triblock, or random copolymers of PLLA-PCL.^{4–7} With the aim of decreasing material cost and improving toughness, PLLA was also reported to be blended with a nonbiodegradable polymer LDPE (low density poly(ethylene)), compatibilized by a premade block copolymer of LDPE-*b*-PLLA.⁸

Reactive compatibilization was an efficient and economic pathway, and some supertough PLLA materials have been prepared by some authors according to this method. Oyama significantly improved the toughness of PLLA by reactive blending PLLA with EGMA (poly(ethylene-glycidyl methacrylate)) and indicated the importance of interface control in reactive compatibilization.⁹ Zhang et al. reported a super-toughened PLLA-based ternary blend, in which the EMAA-Zn (zinc ionomer of ethylene/methacrylic acid copolymer) domains were trapped in the EBA-GMA (ethylene/*n*-butyl acrylate/glycidyl methacrylate copolymer) particles and the particles were distributed homogeneously in the PLLA matrix; they further investigated in detail the impact of some factors, such as the metal ion type, the ionomer characteristics and the

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reactive blending temperature on toughening effect and interfacial compatibilization.^{10–14} Feng et al. first prepared POE-*g*-GMA (poly(ethylene octene) grafted with glycidyl methacrylate) by melt grafting, then used it to toughen PLLA and found that the impact strength of PLLA was significantly improved when the content of the POE-*g*-GMA was higher than 10 wt %; this was because the carboxyl end groups of PLLA reacted with the epoxide groups of POE-*g*-GMA and the in situ formed graft polymers at the interface decreased the interfacial tension and suppressed the coalescence of the dispersed phase.¹⁵ We also reported a novel kind of PLLA alloys by blending PLLA with E-AE-GMA (a copolymer of ethylene, acrylic ester, and glycidyl methacrylate) and the morphology could be tuned simply by blending time, which controlled the amount of PLLA grafted onto the backbone of E-AE-GMA. The thus obtained nanoalloys, when more PLLA chains were grafted at long blending time, displayed transparent and ductile properties; whereas the microalloys, when less PLLA chains were grafted at short blending time, had superior impact strength.¹⁶

The high price was another inhibition for PLLA to be widely used in consumer goods; blending PLLA with petroleum-based polymers was not only cost-effective but also it could prolong the service period of the PLLA product, because biodegradation would cause the mechanical properties of neat PLLA to deteriorate rapidly.^{17,18} In a previous paper, we reported the reactive compatibilization of PLLA and ABS (acrylonitrile–butadiene–styrene copolymer) by SAN-GMA (a copolymer of styrene, acrylonitrile, and glycidyl methacrylate), with PLLA as the matrix and ABS as the dispersed phase. Although the mechanical properties of the obtained blend was significantly improved compared to neat PLLA, in fact the maximum fracture strain was only one-fifth of the applied ABS and the blending process had to be catalyzed by ETPB (ethyltriphenyl phosphonium bromide).¹⁹ Recently, we reported the synthesis of reactive comb (RC) polymers and their applications as compatibilizers in PLLA/PVDF blends.²⁰ Herein, to improve the mechanical properties of the PLLA/ABS blend further, we applied RC polymers as compatibilizers in this blend and then investigated the morphological structures and the rheological, mechanical, and thermal properties of the PLLA/ABS blends compatibilized by RC polymers. We found that the significant synergistic effects of PLLA and ABS were achieved using the reactive RC as the compatibilizers. The obtained alloys exhibited superior ductility, which was much higher than that of both neat PLLA and neat ABS. We attributed this novel phenomenon to the negative pressure, which derived from the differentiation of the thermal contraction between two phases, had a positive influence on the toughness of the blends.

EXPERIMENTAL SECTION

Materials. PLLA (3001D) was purchased from Nature Works, US and ABS (TR558A) was obtained from LG Chemical, Korea. As shown in Figure S1, TEM images of ABS showed that it was a two-phase material, rubber particles (stained black) with a size of about 20 nm distributed homogeneously in styrene–acrylonitrile (SAN) matrix (stained gray). The RC (reactive comb) polymer was a random terpolymer of methyl methacrylate (MMA), glycidyl methyl acrylate (GMA), and MMA macromer; the weight ratio of GMA/MMA macromer/MMA in RC polymers was 2/2/6 and the MMA macromer had a number-average molecular weight (M_n) of 4800 g mol⁻¹ and a polydispersity (M_w/M_n) of 2.3, determined by GPC (gel permeation chromatography). The M_n and M_w/M_n of the obtained RC polymers were measured by GPC and the results were 38 000 g mol⁻¹ and 1.9,

respectively; every RC polymer was calculated to have two side chains, based on the M_n of the MMA macromer. Detailed synthesis and characterizations of RC polymers were given in the literature.²⁰

Sample Preparation. PLLA, ABS pellets, and RC polymers were dried overnight in a vacuum oven at 80 °C to remove the residual moisture before blending. The blends were prepared by melt mixing in a batch mixer (Haake PolyLab QC) at a rotation speed of 50 rpm at 190 °C for 10 min. For all blends, the weight ratio of PLLA/ABS was varied in a range from 90/10 to 30/70, whereas the content of RC was fixed at 3 wt % based on the total weight of PLLA and ABS. The uncompatibilized PLLA/ABS blends were also prepared by the same way for comparison. After blending, all samples were compression molded (Qien compression molder) to a sheet with a thickness of 0.5 mm at 200 °C under a pressure of 10 MPa between two poly(tetrafluoroethylene) films for 6 min and then the sheet was cooled to room temperature using circulated room temperature water.

CHARACTERIZATIONS AND MEASUREMENTS

Mechanical Test. Tensile testing was performed on an Instron universal material testing system (model 5966) at 23 °C at a crosshead speed of 10 mm/min. The specimens were punched out of the compression-molded films into dumbbell shape with gauge lengths of 18 mm, widths of 3 mm, and thicknesses of 0.5 mm. Each sample was tested for five replicated specimens to get an average test value. On the basis of the tensile results, the ductility of the PLLA/ABS/RC blends was determined by the following equation:^{21,22}

$$\text{ductility} = \frac{\text{failure strain}}{\text{yielding strain}} \quad (1)$$

Dynamic Mechanical Analysis (DMA). Dynamic mechanical properties of the blends were measured with the DMA Q800 (TA Instruments) in tension mode with an oscillating frequency of 5 Hz, an amplitude of 4 μm. The sample dimensions were 7.00 × 6.30 × 0.50 mm and the temperature was swept from -100 to +180 °C at a heating rate of 3 °C min⁻¹.

Differential Scanning Calorimetry (DSC). DSC was performed under a continuous nitrogen purge on a DSC Q2000 (TA Instruments). Both calibrations of heat flow and temperature were based on a run in which pure indium was heated through its melting point. Samples having a mass of about 10 mg were used and were heated from -50 to +200 °C at a heating rate of 10 °C min⁻¹ under nitrogen.

Transmission Electron Microscopy (TEM). The morphologies of the blends were recorded using a TEM (Hitachi HT-7700) at an accelerating voltage of 100 kV. Ultrathin sections (ca. 70 nm thick) were microtomed (Leica EM UC7) from the blends at room temperature with a diamond knife, collected on a 200 mesh copper grid, and exposed to the vapor of ruthenium tetroxide (RuO₄) for 4 h. RuO₄ preferentially stained the ABS phase to provide better contrast under TEM.

Rheological Characterization. Dynamic rheological properties of the blends and neat materials were tested using a rheometer (MCR301, Anton Paar Instrument) equipped with a parallel-plate fixture (25 mm diameter) in an oscillatory mode at a temperature of 200 °C in a nitrogen atmosphere. The gap between the plates was set to be 0.6 mm. The storage modulus (G'), loss modulus (G''), loss tangent $\tan \delta$, and complex viscosity (η^*) as a function of angular frequency (ω) ranging from 500 to 0.01 rad s⁻¹ at a fixed strain of 5% were measured by frequency sweep at 200 °C. To ensure the frequency sweep was in the linear viscoelastic range, strain sweep from 0.01% to

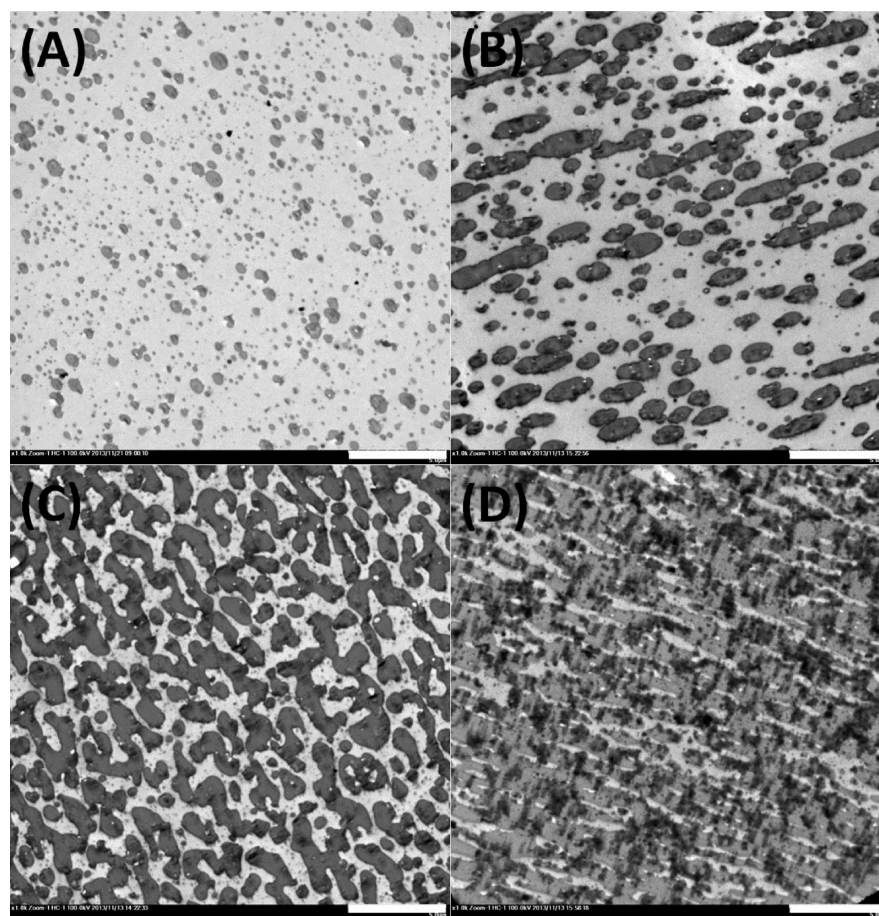


Figure 1. TEM images of compatibilized blends (A) PLLA/ABS/RC = 90/10/3, (B) PLLA/ABS/RC = 70/30/3, (C) PLLA/ABS/RC = 50/50/3, and (D) PLLA/ABS/RC = 30/70/3. The scale bar is 5 μm .

100% was performed first at a frequency of 10 rad s^{-1} and a temperature of 200 $^{\circ}\text{C}$.

Scanning Electron Microscopy (SEM). The fractured surfaces of the specimens after tensile test were sputter-coated with a thin layer of gold and then examined for morphological structures by SEM (ZEISS supra 55) at an accelerating voltage of 5 kV.

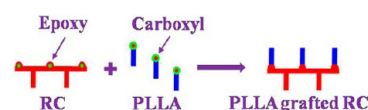
RESULTS

Morphological Studies. TEM images of the uncompatibilized blends showed that first, the rubber particles appeared dark, the SAN phase appeared gray, and the PLLA phase appeared white, due to their different staining rates (Figure S2); second, ABS and PLLA was a typical immiscible polymeric system.¹⁹ The morphologies of the PLLA/ABS blends at various compositions compatibilized by RC polymers are illustrated in Figure 1. In our previous report, the PLLA and ABS were blended at a weight ratio of 70/30 or 50/50 (PLLA/ABS), and although SAN-GMA could strengthen the interface and decrease the size of the dispersed phase, the ABS phase dispersed inhomogeneously in the PLLA matrix.¹⁹ In the present investigation, when the weight ratio of PLLA/ABS was more than 50/50, the ABS phase dispersed homogeneously in the PLLA matrix and at 50/50, the morphology transformed from matrix dispersed to cocontinuous morphology. With further decreasing the weight ratio, phase inversion occurred and the PLLA phase dispersed in the ABS matrix. The cocontinuous phase was particularly interesting, because the

both components could contribute to the properties of the blend.^{23,24}

As shown in Scheme 1, the RC polymer applied as compatibilizers was composed of a PMMA backbone, two

Scheme 1. Schematic of the Reaction between the Epoxy of RC Polymers and Carboxyl Ends of PLLA



PMMA side chains, and a few epoxy groups distributed randomly along the backbone. During reactive blending, the carboxyl ends of PLLA reacted with the epoxy groups of RC and PLLA grafted RC polymers (RC-g-PLLA) was in situ formed at the interface of PLLA and ABS.²⁰ The grafted PLLA chains protruded into and interacted with the PLLA phase and the PMMA side chains and backbones interacted with the SAN phase in ABS.^{25,26} Under external shear field, the RC-g-PLLA polymers anchored tightly at the PLLA/ABS interface and inhibited the dispersed phase from coalescence. So, we found that in the RC-compatibilized PLLA/ABS system, the dispersed phase was more homogeneous than our previously reported system compatibilized by SAN-GMA. At the same time, the interfacial tension was also reduced due to the emulsification effect of the RC-g-PLLA polymers at the interface.

Rheological Investigations. Brabender torque measurement was applied to investigate the chemical reactions in the melt state. The melt torque values of the uncompatibilized blends decreased gradually with increasing time because of the thermal degradation of PLLA at high temperature (Figure S3). In the compatibilized blends, as shown in Figure 2, the torque values started to increase from about 3 min, and this was because the graft reaction between PLLA and RC polymers significantly increased the viscosity of the blend.^{27–30}

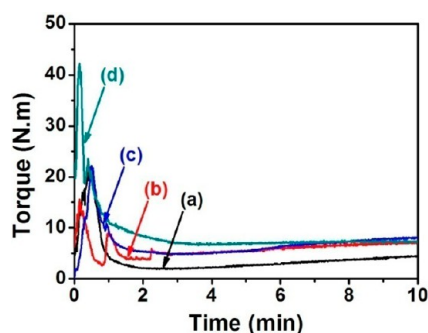


Figure 2. Torque-time curves of compatibilized blends (a) PLLA/ABS/RC = 90/10/3, (b) PLLA/ABS/RC = 70/30/3, (c) PLLA/ABS/RC = 50/50/3, and (d) PLLA/ABS/RC = 30/70/3.

The results of the linear viscoelastic shear oscillations at 190 °C are presented in Figure 3. The storage modulus (G') and

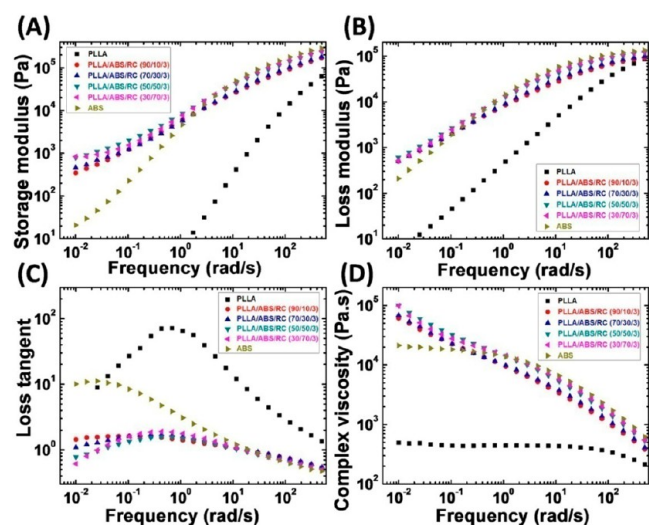


Figure 3. Linear rheological data of neat components and compatibilized blends (A) storage modulus (G'), (B) loss modulus (G''), (C) loss tangent ($\tan \delta$), and (D) complex viscosity (η^*) versus frequencies (ω) at 190 °C.

loss modulus (G'') versus frequency (ω) showed that at high frequencies, the G' and G'' curves of all the compatibilized blends were between those of the neat components, whereas at low frequencies they were higher than the neat components. The G' of the compatibilized blends displayed a frequency-independent plateau (a solid-like behavior) at low frequencies; this was because the in situ formed RC-g-PLLA polymers at the interface of PLLA and ABS significantly increased the interactions of these two phases.^{31–33} It was also interesting to note that the G' and G'' of the PLLA/ABS/RC (50/50/3) blend were higher than the others at low frequencies and this

might be related to the formation of the cocontinuous structure. The loss tangent ($\tan \delta$) as a function of temperature indicated that the curve of the PLLA/ABS/RC (90/10/3) blend flattened at low frequencies and with increasing the ABS content, the corresponding curves gradually displayed a semispherical shape; this meant that the viscosity decreased and the elasticity increased as the ABS content increasing.^{34,35} The complex viscosity (η^*) versus frequency results showed that PLLA exhibited a typical Newtonian fluid behavior with the invariant of the η^* in a wide range of frequencies, whereas ABS only displayed Newtonian fluid behavior at the lowest frequencies. The η^* of the compatibilized blends was significantly higher than the neat components at low frequencies and did not show a plateau anymore; some researchers attributed this phenomenon to a formation of network-like structures.³⁶

Mechanical Properties. The typical stress–strain curves of the neat blend components and the PLLA/ABS blends are illustrated in Figure 4A and the corresponding results are

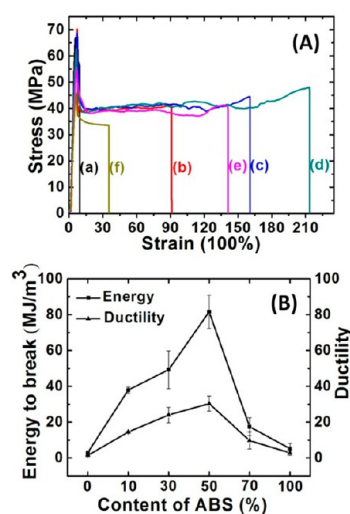
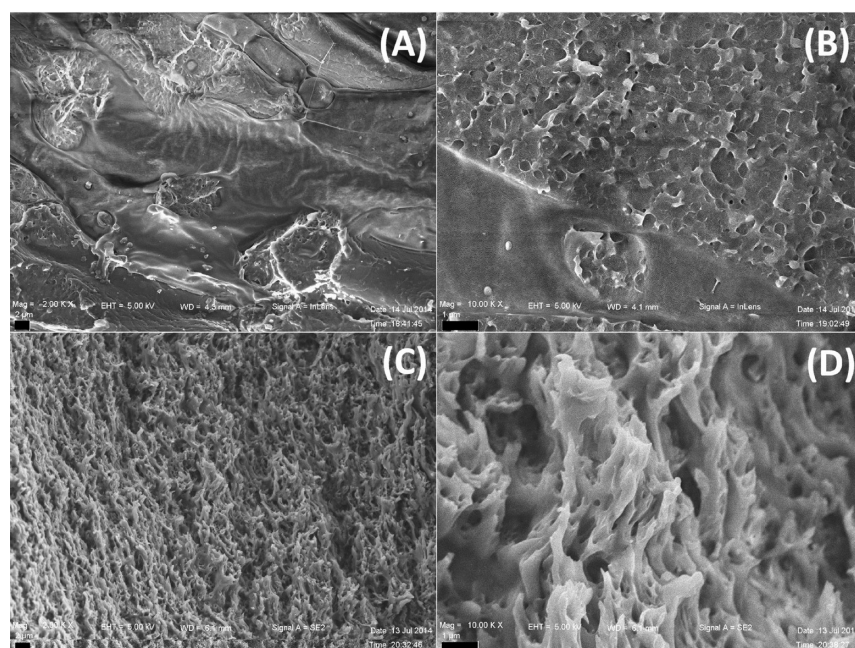


Figure 4. (A) Tensile stress–strain curves of neat components and compatibilized blends (a) PLLA, (b) PLLA/ABS/RC = 90/10/3, (c) PLLA/ABS/RC = 70/30/3, (d) PLLA/ABS/RC = 50/50/3, (e) PLLA/ABS/RC = 30/70/3, and (f) ABS. (B) Effect of the ABS content on the energy to break and the ductility in the compatibilized blends.

summarized in Table 1. PLLA was a brittle polymer and the specimen fractured suddenly when the deformation was just beyond the yield point. In our former reports, the PLLA/ABS blends compatibilized by SAN-GMA (styrene–acrylonitrile–glycidyl methacrylate) and catalyzed by ETPB (ethyltriphenyl phosphonium bromide) displayed a maximum fracture strain of about 23.8%, when the weight ratio of PLLA/ABS/SAN-GMA/ETPB was 70/30/5/0.02; this value was only one-fifth of the applied ABS (D-100, high impact grade, provided by Grand Pacific Petrochemical Corporation). At the same time, the yield stress decreased by 32% from 65.5 MPa (neat PLLA) to 44.6 MPa; the Young's modulus decreased by 33% from 2.024 GPa (neat PLLA) to 1.352 GPa.¹⁹ Interestingly, as shown in Table 1, when the RC polymer was applied as compatibilizers at a weight ratio of 50/50/3 (PLLA/ABS/RC), the maximum fracture strain was $196.2 \pm 26.3\%$, almost 7 times higher than that of the applied ABS (TR558A, LG Chemical). The energy to break and the ductility (measured from eq 1) as a function of

Table 1. Mechanical Properties of Neat Components and Compatibilized Blends

Sample	Young's modulus (GPa)	Yield stress (MPa)	fracture stress (MPa)	fracture strain (%)
PLLA	1.76 ± 0.12	64.4 ± 1.9	53.5 ± 2.2	8.2 ± 0.9
PLLA/ABS/RC (90/10/3)	1.87 ± 0.64	73.1 ± 0.2	43.3 ± 0.14	93.8 ± 6.2
PLLA/ABS/RC (70/30/3)	1.61 ± 0.98	63.4 ± 6.5	40.6 ± 7.3	151.8 ± 41.8
PLLA/ABS/RC (50/50/3)	1.72 ± 0.69	64.8 ± 1.8	47.1 ± 2.6	196.2 ± 26.3
PLLA/ABS/RC (30/70/3)	1.44 ± 0.94	56.4 ± 3.0	40.0 ± 2.3	63.6 ± 39.0
ABS	1.19 ± 0.12	45.5 ± 1.4	33.6 ± 0.7	17.4 ± 12.0

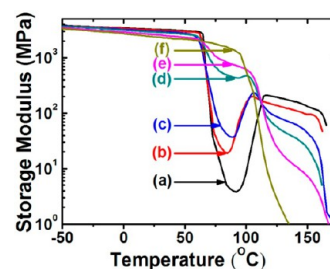
**Figure 5.** SEM images of the tensile fracture surfaces of (A, B) uncompatibilized PLLA/ABS = 50/50 and (C, D) compatibilized PLLA/ABS/RC = 50/50/3 blend. The scale bar is 2 μm in panels A and C and 1 μm in panels B and D.

ABS content are plotted in Figure 4B. It was clear that all the compatibilized blends showed significantly increased ductility and toughness than both neat PLLA and neat ABS, indicating the drastic synergistic effects of PLLA and ABS compatibilized by RC polymer. To our best knowledge, such behavior has not been reported for PLLA alloys so far. In addition, it was also found that the toughness and ductility of the alloys increased with the increasing of the ABS content and reached the maximum at 50 wt %, then decreased rapidly when the ABS was 70 wt %.

The morphologies of the tensile fracture surfaces were observed by SEM to investigate the toughening mechanism. As shown in Figure 5A,B, there was an obvious difference between the PLLA and ABS phase in the uncompatibilized PLLA/ABS (50/50) blends; the PLLA phase displayed a smooth surface, characteristic of brittle fracture, whereas the ABS phase displayed a rough surface with many voids, which was due to that the rubber phase was pulled out from the ABS matrix.^{37,38} This was because in the uncompatibilized blend, the interfacial adhesion was poor and the stress was hard to transfer across the interface. In the compatibilized PLLA/ABS/RC (50/50/3) blends, the in situ formed PLLA grafted RC polymers at the interface improved the interfacial strength and decreased the interfacial tension efficiently. So, the morphology discrimination between PLLA and ABS phase was not clear anymore and the whole fracture surface was constituted by homogeneously and densely distributed, oriented fibrillars, parallel to

the stress direction. The formation of the fibrillar structure was a typical plastic deformation and large energy was dissipated during this process, which resulted in a significantly improved ductility.^{39,40}

Thermal Behavior. The storage modulus curves of PLLA, ABS, and compatibilized PLLA/ABS blends at various compositions as a function of temperature are depicted in Figure 6. It was found that the thermal stability of neat PLLA was poor and the storage modulus depressed rapidly when the temperature was above the T_g (about 60 °C). With the addition of ABS, the thermal stability of the blend was improved compared to neat PLLA, especially when the content of ABS

**Figure 6.** Storage modulus of neat components and compatibilized blends as a function of temperature (a) PLLA, (b) PLLA/ABS/RC = 90/10/3, (c) PLLA/ABS/RC = 70/30/3, (d) PLLA/ABS/RC = 50/50/3, (e) PLLA/ABS/RC = 30/70/3, and (f) ABS.

was increased to 50 wt %, the depression of modulus became slow and sustained a high modulus value at high temperatures, which meant that the cocontinuous morphology also had some positive influences on the thermal stability.^{41–43}

DISCUSSION

We noted that Oyama once reported a supertough poly(lactic acid) material by blending PLLA with EGMA and found that the presence of the dispersed phase facilitated the crystallization of PLLA; she further deduced that the crystallization of the PLLA matrix played a key role in toughening.⁹ Bai et al. recently reported a PCL/PLLA blend, in which PCL played a role as an impact modifier and the crystallization of the PLLA matrix was tailored by a tiny amount of nucleating agent; they found that the toughness of the PLLA matrix increased linearly with the increasing of the PLLA crystalline content, whereas for the blends with amorphous PLLA matrix, the toughness was almost unchanged.⁴⁴

The first DSC heating curves of both the compatibilized and uncompatibilized PLLA/ABS blends with a series of compositions are shown in Figure S4 and the corresponding results are summarized in Table 2. It was found that in the

Table 2. Thermal Properties of Neat Components and Compatibilized Blends

material	T_m^a (°C)	χ^a (%)	T_g^b (°C)	T_g^b (°C)
PLLA	169.6	7.5	73.6	
PLLA/ABS (90/10)	167.7	2.9		
PLLA/ABS/RC (90/10/3)	162.2	2.4	73.4	111.1
PLLA/ABS (70/30)	167.3	14.8		
PLLA/ABS/RC (70/30/3)	165.0	4.6	73.5	111.9
PLLA/ABS (50/50)	167.0	10.7		
PLLA/ABS/RC (50/50/3)	164.5	6.2	69.8	111.8
PLLA/ABS (30/70)	167.7	8.2		
PLLA/ABS/RC (30/70/3)	162.0	6.0	70.2	115.3
ABS				115.6

^aDetermined by DSC. ^bDetermined by DMA.

uncompatibilized blends, the ABS phase had a positive influence on the crystallization of PLLA and the maximum crystallinity (χ) was 14.8%, when the weight ratio of PLLA/ABS was 70/30. In the compatibilized blends, the crystallinity of PLLA in the blends was always less than that of the neat PLLA. So, there must have existed some other factors that contributed to the improved ductility of the PLLA/ABS blends. We also found that the melting temperature (T_m) of PLLA decreased after reactive blending with ABS and this was because the grafted PLLA chains of RC-g-PLLA penetrated into the PLLA phase and interfere with the crystallization of the PLLA.^{4,45,46}

As reported by some researchers, when a hard matrix was toughened by a soft rubber, the differentiation of the thermal contraction between the two phases would generate a negative pressure in the rubber phase, which resulted in an increasing of the free volume and correspondingly a decreasing of the T_g of the rubber phase. The internal pressure also exerted a dilational stress field around the rubber phase and enhanced the local segmental motions in the matrix, which resulted in a depression of the β relaxation temperature (T_β) in the matrix and an improved ductility of the blend.^{47–51} In our previously reported PLLA/POM system, there existed strong interactions between

the $-C=O$ of PLLA and $-CH_2$ of POM. So, in the PLLA/POM blend, the interfacial adhesion was strong and the negative pressure would significantly influence the contraction of both the POM and the PLLA phase and we observed a double glass transition temperature (T_g) depression phenomenon.⁵² We have demonstrated in our previous report that RC polymer was a stable compatibilizer at the interface of the immiscible blend during reactive blending, because the PMMA side chains introduced by the macromer was miscible with the SAN phase of ABS and the epoxide groups could react with the carboxyl ends of PLLA and the grafted PLLA chains protruded into and entangled with the PLLA phase.^{20,25,26} The in situ formed RC-g-PLLA polymers anchored stably at the interface of ABS and PLLA and these two phases were held tightly by the RC-g-PLLA polymers. The strong interface was further confirmed by TEM and as shown in Figure 7, compared to the uncompatibilized blends, the compatibilized blends displayed a black and thick interface.⁵³

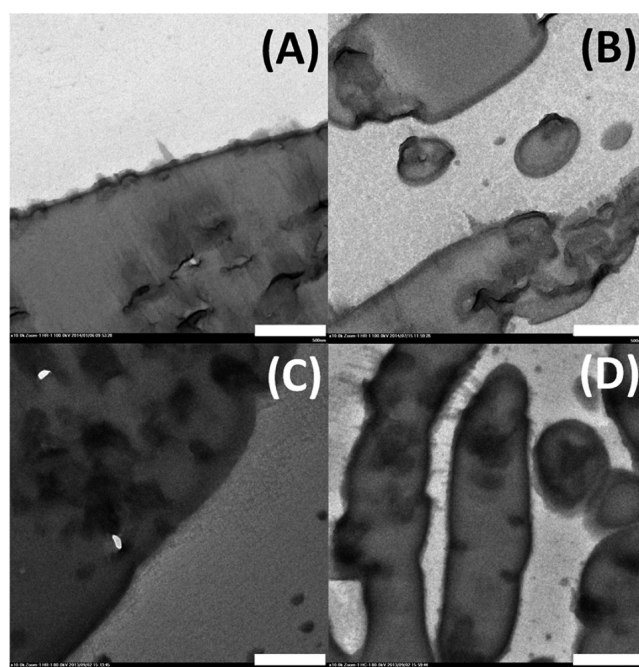


Figure 7. TEM images of the compatibilized and uncompatibilized blends (A) PLLA/ABS = 70/30, (B) PLLA/ABS/RC = 70/30/3, (C) PLLA/ABS = 50/50, and (D) PLLA/ABS/RC = 50/50/3. The scale bar is 500 nm.

As shown in Scheme 2, when the RC-compatibilized PLLA/ABS blend was cooled down from the molten state to the solid state, the internal pressure was so strong that it was not just the mobility of the local segmental chains in one of the two phases, but in both the matrix and the dispersed phase was significantly improved, so we also observed a double T_g depression phenomenon in the RC-compatibilized PLLA/ABS blend (Figure 8, and the corresponding results are summarized in Table 2). We deduced that the origin of the strong internal pressure in the RC-compatibilized PLLA/ABS blend was that first both PLLA and ABS had approximate and high Young's modulus, and second RC-g-PLLA polymers provided a strong interfacial adhesion. Some authors have indicated that the amount and the distribution of the free volumes were related to the mechanical and the rheological properties of polymers.^{54,55} As shown in Table 2, the T_g depressions of both the PLLA and

Scheme 2. Schematic of the Generation of the Internal Pressure and the Enlargement of the Free Volume in the Compatibilized Blend

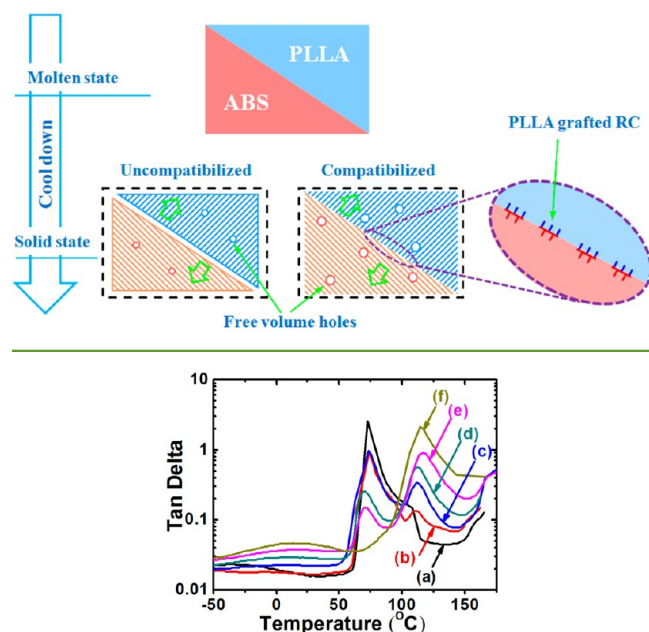


Figure 8. Tan δ –temperature curves of neat components and compatibilized blends (a) PLLA, (b) PLLA/ABS/RC = 90/10/3, (c) PLLA/ABS/RC = 70/30/3, (d) PLLA/ABS/RC = 50/50/3, (e) PLLA/ABS/RC = 30/70/3, and (f) ABS.

ABS phase were most significant when the weight ratio of PLLA/ABS/RC was 50/50/3; it was because the force exerted on both the PLLA and ABS phase was in proportional to the area of PLLA/ABS interface ($A_{\text{interface}}$) and it was obvious that the PLLA/ABS/RC (50/50/3) blend had the largest $A_{\text{interface}}$ so the highest toughness was obtained at this weight ratio. The reason that the maximum fracture strain of the RC-compatibilized PLLA/ABS blend was more than seven times higher than the applied ABS (TR558A) was clear by now. The increase of the free volume in both the PLLA and the ABS phase resulted in an increase of the mobility of the molecular chains, especially in the region adjacent to the interface and this was benefit for cold drawing.⁵⁶

CONCLUSION

A supertough PLLA/ABS blend has been successfully prepared by applying a small amount of reactive comb polymers as compatibilizers. The mechanical, thermal, and rheological properties of the compatibilized blends were significantly improved, compared to the neat components. We also observed a double T_g depression phenomenon in this system and this meant that the free volumes of both the PLLA and ABS phase have been enlarged after reactive compatibilization. This was ascribed to the excellent interfacial stability of PLLA-grafted RC at the interface of PLLA and ABS, and thus the stress could be transferred efficiently through the interface. So, when the blend was cooling down from the molten state to the solid state, the negative pressure, derived from the differentiation of the thermal contraction between these two phases, increased the chain mobility of both the PLLA and ABS phase and this resulted in the phenomenon that the maximum fracture strain of the compatibilized blend was 7 times higher than the applied

ABS. The results above revealed the importance of interfacial adhesion in toughening of a rigid/rigid polymer blend.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00740.

TEM images of ABS and uncompatibilized PLLA/ABS blends, torque-time curves of uncompatibilized blends and DSC curves of both compatibilized and uncompatibilized PLLA/ABS blends (PDF).

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Notes

The authors declare no competing financial interest.

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