

## Reactive compatibilization of poly(L-lactic acid)/poly(propylene carbonate) blends: Thermal, thermomechanical, and morphological properties

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**ABSTRACT:** Poly(L-lactic acid) (PLLA) was blended with poly(propylene carbonate) (PPC) with various compositions by a melt-blending process to evaluate their general properties for a potential flexible packaging field. The mechanical properties, including the tensile strength and modulus, revealed a tendency to decrease with the addition of ductile PPC; this was induced by the poor interfacial adhesion between PLLA and PPC with the cavities and clear edges and was observed through morphological observation. Reactive compatibilization was applied to improve the interfacial adhesion between PLLA and PPC, and the elongation at break was profoundly enhanced because of the improved interfacial adhesion between the two phases. The compatibilized PLLA/PPC blends showed considerable improvements in the storage modulus in the transition region with stable thermal stability; this could be a benefit for thermal processing. The addition of PPC had a great effect on the solidlike behavior and increased the elasticity of the PLLA/PPC blends. Up to 2.0 phr maleic anhydride showed a great efficiency in enhancing the dynamic storage modulus and complex viscosity of the PLLA/PPC blends. We also confirmed that it was feasible to fabricate PLLA/PPC blends with controllable barrier properties with combination of PLLA and PPC under reactive compatibilization while retaining the biodegradability. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43388.

**KEYWORDS:** blends; compatibilization; mechanical properties

Received 13 May 2015; accepted 26 December 2015

DOI: 10.1002/app.43388

### INTRODUCTION

Poly(lactic acid) (PLA) is a widely researched biodegradable and compostable aliphatic polyester obtained from renewable sources. It is well known that PLA has good mechanical properties, which are comparable to polystyrene and poly(ethylene terephthalate), and this has increased interest in PLA for the food and flexible packaging research fields. However, its brittleness still limits it in a variety of industrial applications.<sup>1,2</sup> The melt-blending technique is one widely used technique for polymer modification or blending of two or more polymers because of its low cost and easy processability. The blending of PLA with other nonbiodegradable or biodegradable polymers has also been investigated extensively to overcome its brittleness. Wang and Hillmyer<sup>3</sup> investigated PLA/low-density polyethylene blends and found that the PLA crystallinity had a considerable effect on the toughness of the blends. Reddy *et al.*<sup>5</sup> also reported that a PLA/polypropylene blend showed an improvement in the resistance of PLA to hydrolysis and the dyeability of PLA.<sup>4</sup> PLA/poly[(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate)]

blends prepared by solvent casting showed partial molecular interaction, although phase separation was found; this indicated that the blends were not compatible. It was reported that the addition of poly(ethylene oxide) and poly(propylene oxide) had a great effect on the improvement of the toughness of poly(L-lactic acid) (PLLA)/poly(DL-lactic acid) blends, and it also increased the elongation at break of PLLA/polycaprolactone blends.<sup>6</sup> We also previously reported that PLLA/corn starch blends showed enhanced interfacial adhesion between PLLA and starch because of the reactive compatibilization effect of maleic anhydride (MA) grafted onto PLLA and starch.<sup>7</sup>

Poly(propylene carbonate) (PPC) synthesized from carbon dioxide (CO<sub>2</sub>) and PPC have recently gained a great attention because of their biodegradability and good properties such as ductility, compatibility, high barrier to oxygen (O<sub>2</sub>), and impact strength.<sup>8,9</sup> However, the improvement of the thermal stability and low glass-transition temperature ( $T_g$ ) is still a challenge, and various approaches have been studied to enhance these properties.<sup>10,11</sup> Zeng *et al.*<sup>12</sup> investigated biodegradable PPC blends with starch

acetate with different degrees of substitution, and they found that starch acetate acted as a reinforcement filler for PPC, with strong interfacial adhesion between PPC and starch acetate; this resulted in improved mechanical properties and thermal stability. Wang *et al.*<sup>13</sup> reported that the addition of poly(ethylene-*co*-vinyl alcohol) in PPC had a great effect on the enhancement of the thermal stability of PPC. Yao *et al.*<sup>14</sup> investigated the effect of MA on PLA/PPC blends and found that the strain at break was considerably enhanced compared to that of the PLA/PPC blend.

In this study, the general properties of PLLA/PPC blends were investigated to evaluate the compatibility of the blends for their potential packaging applications. In addition, the reactive compatibilization of the PLLA/PPC blends was performed, and the thermal, mechanical, rheological, and barrier properties of simple PLLA/PPC blends and compatibilized PLLA/PPC blends were assessed.

## EXPERIMENTAL

### Materials

PLLA (4032D grade, 98% L-lactic acid) was obtained from NatureWorks LLC (Minnetonka, MN), and PPC resin (QPAC 40 grade) was purchased from EMPOWER Materials, Inc. (New Castle, DE). All of the resins were vacuum-dried at 60 °C for 24 h to remove residual moisture before use. 2,5-Bis(*tert*-butyl peroxy)-2,5-dimethylhexane [Luperox 101 (L101)] and MA (briquettes, 99%) were provided from Sigma-Aldrich (St. Louis, MO) and were used as received for reactive compatibilization.

### Preparation of the PLLA/PPC Blends and Compatibilized PLLA/PPC Blends

Simple PLLA/PPC blends with various compositions were prepared by their mixture in an internal mixer (Plasti-Corder rheometer, Brabender, Duisburg, Germany) at 190 °C at a 50-rpm rotor speed. The blend composition used in this study is given in Table I, and the total mixing time was fixed at 5 min to prevent the possible thermal degradation of the PLLA and PPC. The blend sample melts were cooled to room temperature and then compression-molded into a film with a thickness of 200–250 μm by an automatic hydraulic laboratory press (model QM900A, QMESYS, Gyangmyung, South Korea) at 200 °C. All of the samples were dried in a vacuum oven before they were used in the test. Compatibilized poly(L-lactic acid)/poly(propylene carbonate) (cPPC) blends with 80:20 weight ratios were fabricated through the reactive compatibilization process; this was accomplished by the addition of the radical initiator, L101, and the compatibilizer, MA. The premixed PLLA and PPC were first melted for 2 min in the mixer, and then, L101 was added and mixed for an additional 2 min. Then, MA was added. The total mixing time was fixed at 8 min under the same conditions.

### Characterization

**Spectrophotometric Analysis.** The Fourier transform infrared (FTIR) spectroscopic analysis of the PLLA/PPC blends and cPPC blend was performed with a Varian FTIR spectrometer (660-IR, Palo Alto, CA). A total of 40 scans and the percentage transmission mode were carried out in a 4000–650 cm<sup>-1</sup> wavenumber scan range.

**Thermal Properties.** A Diamond differential scanning calorimeter (PerkinElmer, Waltham, MA) was used to assess the thermal

**Table I.** Blend Compositions of the Simple PLLA/PPC Binary Blends and cPPC Blends

Sample	PLLA (wt %)	PPC (wt %)	L101 (phr)	MA (phr)
Neat PLLA (PPC0)	100	0	—	—
PPC05	95	5		
PPC10	90	10		
PPC20	80	20		
PPC30	70	30		
cPPC10	80	20	0.1	0
cPPC11				1
cPPC12				2
cPPC13				3
cPPC14				4
cPPC15				5
cPPC20	80	20	0.2	0
cPPC21				1
cPPC22				2
cPPC23				3
cPPC24				4
cPPC25				5
Neat PPC (PPC100)	0	100	—	—

properties, including  $T_g$ , melting temperature ( $T_m$ ), and percentage crystallinity ( $X_c$ ), of the blend samples. The thermal analysis was performed under a nitrogen atmosphere at a temperatures from 20 to 220 °C at a 10 °C/min of heating rate, and the results were analyzed by Diamond Analysis software. The heat of fusion (93.1 J/g) for 100% PLA<sup>15</sup> was applied to determine  $X_c$  from the following equation:

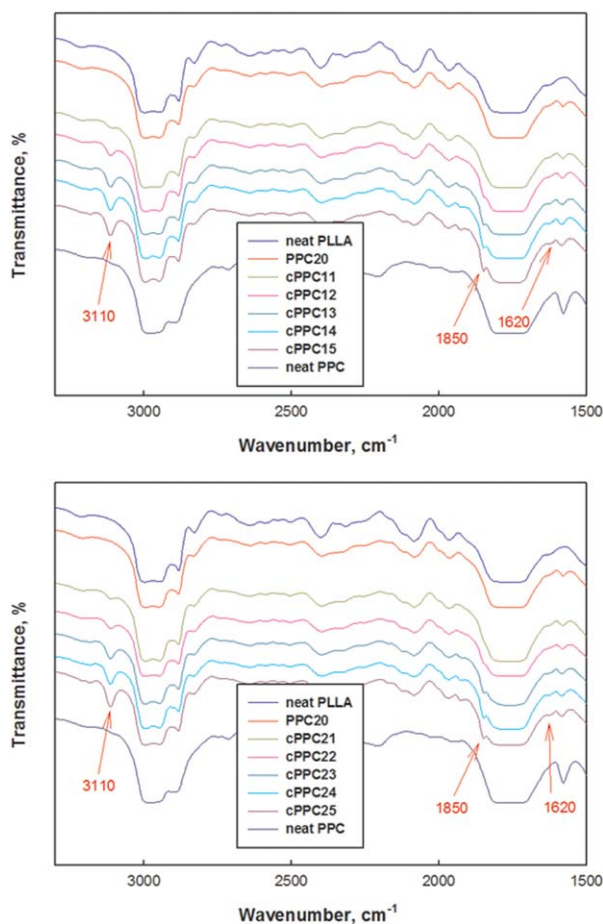
$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c(1-x)} \quad (1)$$

where  $\Delta H_m$  is the enthalpy of fusion,  $\Delta H_c$  is the enthalpy of cold crystallization,  $\Delta H_m^c$  is the enthalpy of fusion of the pure crystalline PLA, and  $x$  is the weight fraction of PPC.

Thermogravimetric analysis (TGA; Q600, TA Instruments, New Castle, DE) was used to assess the thermal stability of the PLLA/PPC blend samples. The tests were performed under a nitrogen atmosphere at temperatures of up to 800 °C at a 10 °C/min heating rate.

**Mechanical Properties.** The tensile strength, Young's modulus, and elongation at break were determined with a universal testing machine (Instron 4465, Instron, Canton, MA) according to ASTM D 882-02. The samples were cut into rectangular strips with dimensions of 1 × 6 cm<sup>2</sup> and conditioned at 23 °C and 50% relative humidity for at least 24 h. The test specimens were also prepared with a DSM microinjection molder (DSM Xplore, The Netherlands) at 200 °C. At least five samples of each blend composition were tested at a crosshead speed of 10 mm/min.

**Morphological Observations.** The morphology of the blend film samples and injection-molded samples was observed with a



**Figure 1.** FTIR spectra of the PLLA/PPC blends with different concentrations of MA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

field emission scanning electron microscope (SU8020, Hitachi, Tokyo, Japan). Both film and molded samples were fractured after they were frozen in liquid nitrogen to prevent deformation during fracture. The PPC phase and residual MA in the fractured samples were also extracted with an acetone/ethanol (1:1 v/v) mixed solution at 35 °C in a shaking water bath (Lab companion BS-21, JEIO Tech, Daejeon, South Korea) and then vacuum-dried at 30 °C for 24 h before observation.

**Thermomechanical Properties.** The dynamic mechanical analysis of the samples was carried out with a RSA-G2 solid analyzer (TA Instruments, New Castle, DE). Samples  $6.0 \pm 0.5$  mm in width and  $10 \pm 0.5$  mm in length were tested in tension mode. The sample dimensions were entered on the basis of the mean value of five points, and the storage modulus ( $E'$ ), loss modulus, and  $\tan \delta$  were determined at a 5 °C/min heating rate with a temperature range of 0–180 °C at a 1-Hz frequency.

**Rheological Properties.** A rotational rheometer (MCR302, Anton Paar GmbH, Graz, Austria) with a 25-mm parallel plate was used to determine the rheological properties of the samples. All of the samples were vacuum-dried at 50 °C for 8 h before the test was conducted, and measurements were carried out at 190 °C under a nitrogen atmosphere to prevent degradation. A dynamic frequency

sweep test with a frequency range of 0.1–100 Hz was applied for the testing.

**Oxygen Permeability.** The O<sub>2</sub>-barrier properties of the samples were determined with a Mocon OX-TRAN 702 instrument (MOCON, Inc., MN) according to ASTM 3985. Aluminum masks (5 cm<sup>2</sup>) were used to prepare the samples, and the permeation test was performed at 23 °C and 0% relative humidity with 100% oxygen at a flow rate of 10 sccm.

## RESULTS AND DISCUSSION

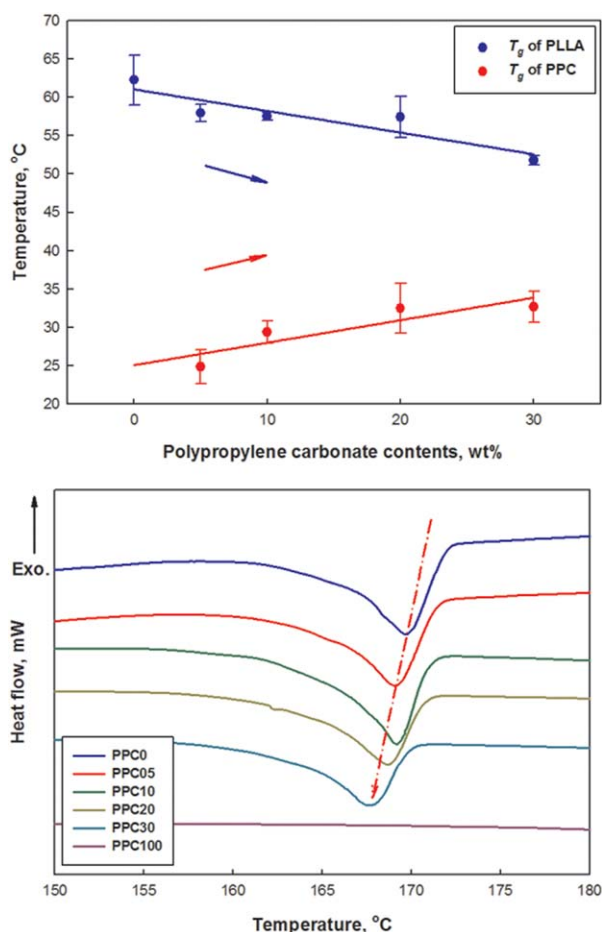
### Spectrophotometric Analysis

The FTIR spectra results of the cPPC blends with different concentrations of MA in the presence of 0.1- and 0.2-phr L101 is shown in Figure 1. The adsorption peak bands at 1850 and 1620 cm<sup>-1</sup> corresponded to the asymmetric stretching of the carbonyl group (C=O) of the cyclic anhydride and the cyclic C=C stretching of anhydride, respectively. The adsorption peaks at 1620 cm<sup>-1</sup> were absent for the cPPC11, cPPC21, and cPPC22 blend samples, and this might suggest that there were some chemical interactions, such as a grafting reaction of MA with the PLLA and PPC in the blends, and the absence of the peak band at 695 cm<sup>-1</sup> corresponding to aromatic C–H bending was also observed.

### Thermal Properties

Figure 2 presents the shift in  $T_g$  of both PLLA and PPC in the blends, and the results of  $T_m$  analysis for the simple PLLA/PPC blend samples are presented in Figure 2. We found that the  $T_g$ 's of PLLA and PPC shifted toward direction; this indicated the partial miscibility and chemical interaction between PLLA and PPC. The PPC20 blend sample showed about a 4% decrease in  $T_g$  for PLLA and a 32% increase in  $T_g$  for PPC. Ma *et al.*<sup>16</sup> reported a great  $T_g$  shift of PPC from 22 to 43 °C for the 70:30 blend composition of PLA/PPC supporting a partially miscible blend of PLA and PPC through several specific interactions between C–H and O–C– or C–H and O=C–.<sup>16</sup> We observed that the intermolecular chain mobility between PLLA and PPC resulted in these shifts, and a greater effect was found in the PPC phase influenced by PLLA molecular chain movements in the blends.  $T_m$  of PLLA/PPC blend samples also showed a tendency to decrease that was due to increased chain flexibility.  $X_c$  of the PLLA/PPC blends was found to increase; this resulted from the high chain mobility and led to molecular rearrangements in the blend.

The results of thermal analysis for PPC20 and cPPC in the presence of L101 and MA are given in Table II. We found that L101 did not have much effect on the  $T_g$  change of PLLA, whereas it had a great effect on decreasing the  $T_g$  of PPC, and we assumed that the free-radical reaction predominantly occurred at PPC as compared to PLLA affecting the reduction of  $T_g$  of PPC. The addition of MA to the blend resulted in the further decrease in  $T_g$  of both PLLA and PPC because of the plasticizing effect of MA with increased chain mobility. We also found that the magnitude of reduction in  $T_g$  of PPC was much higher than the  $T_g$  of PLLA, and we observed that the grafting reaction of MA onto PPC occurred dominantly compared to that of MA onto PLLA. Therefore, we concluded that the plasticized PPC acted



**Figure 2.**  $T_g$  shift and  $T_m$  of the PLLA/PPC blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

as a macroplasticizer for PLLA.  $X_c$  increased considerably because of the molecular rearrangement from the higher chain mobility.

The TGA thermograms of PLLA, PPC, simple PLLA/PPC blends, and cPPC are shown in Figures 3 and 4. The addition of PPC in PLLA had a profound effect on the decrease in the onset decomposition temperature of the PLLA/PPC blends; this indicated that the thermal stability of the PLLA/PPC dramatically decreased because of the relatively lower thermal stability of PPC compared to that of PLLA. We reported that the PPC was easily decomposed to cyclic carbonate at elevated temperature.<sup>17</sup> The addition of L101 only in the PLLA/PPC blends significantly influenced the reduction of the thermal stability because of chain scission induced by the radical reaction. The slight increase in the thermal stability of cPPC with 0.1-phr L101 could have been due to the higher chain entanglement from the grafting reaction, whereas excess radical in the presence of 0.2-phr L101 could make more chain scission than grafting and could result in a further decrease in the thermal stability.

### Mechanical Properties

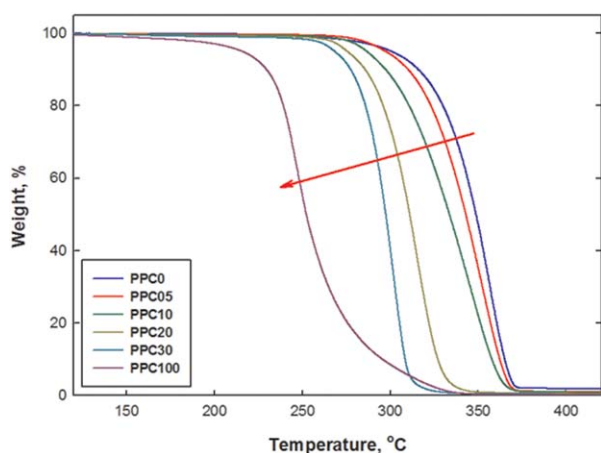
The reduction of the tensile strength and modulus with the addition of PPC in the PLLA was observed in the simple PLLA/PPC blends, and this was attributed to the fact that the ductile PPC had an effect on the flexibility of the PLLA/PPC blends, and the elongation at break increased in the simple PLLA/PPC blends. The results of the neat PLLA, PPC20, and cPPC samples are given Table III, and the specimen pictures after the test are provided in Figure 5.

The reactive compatibilization of MA on the blends was found to be effective up to 2.0-phr MA, and excess MA in the blends resulted in the reduction of tensile strength. This was attributed to the plasticizing effect of MA from chain branching, and it provided more chain mobility. The modulus was found to remain constant. With respect to the elongation at break, the addition of 20 wt % PPC enhanced it about 700% as compared to neat PLLA (7.8%); this indicated that PLLA/PPC was a partially miscible blend, as confirmed from the  $T_g$  shift. We also

**Table II.** Differential Scanning Calorimetry Results for the Simple PLLA/PPC and cPPC Blends

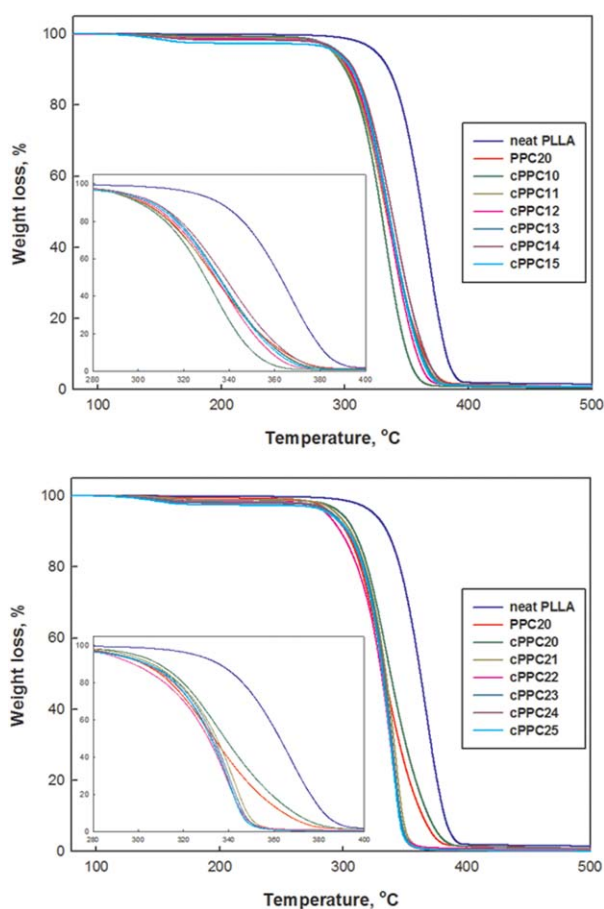
Sample	$T_m$ (°C)	PPC $T_g$ (°C)	PLLA $T_g$ (°C)	$X_c$ (%)
Neat PLLA	170.5 ± 0.3	—	62.3 ± 2.3	4.6 ± 1.8
PPC20	169.4 ± 0.2	32.5 ± 2.3	57.4 ± 1.9	9.9 ± 2.8
cPPC10	166.9 ± 0.5	29.0 ± 0.7	56.0 ± 2.9	27.2 ± 0.9
cPPC11	168.0 ± 0.7	25.9 ± 1.9	56.3 ± 1.8	34.7 ± 0.5
cPPC12	162.6 ± 2.4	18.2 ± 0.3	50.7 ± 1.6	38.5 ± 2.5
cPPC13	163.4 ± 0.7	16.6 ± 0.3	48.8 ± 1.6	35.5 ± 1.3
cPPC14	161.7 ± 2.0	14.0 ± 0.7	47.1 ± 0.4	39.8 ± 1.6
cPPC15	163.0 ± 0.2	12.5 ± 0.1	46.8 ± 0.4	36.3 ± 1.2
cPPC20	165.1 ± 0.9	18.2 ± 7.2	55.9 ± 2.6	32.0 ± 9.0
cPPC21	164.8 ± 0.5	20.4 ± 3.2	52.3 ± 0.9	37.8 ± 0.7
cPPC22	165.8 ± 0.4	16.9 ± 1.5	53.3 ± 0.6	39.2 ± 0.9
cPPC23	161.5 ± 1.8	15.5 ± 0.2	47.7 ± 2.5	40.2 ± 1.2
cPPC24	163.0 ± 0.5	18.0 ± 0.5	50.5 ± 2.3	39.9 ± 0.6
cPPC25	162.0 ± 0.4	11.2 ± 2.3	41.5 ± 3.9	36.8 ± 1.1
Neat PPC	n/a	24.1 ± 1.5	—	n/a





**Figure 3.** TGA thermograms of the PLLA/PPC blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

found that the addition of L101 only to the PLLA/PPC blend resulted in the reduction of the elongation at break because of chain scission from the radical reaction. The elongation at break showed an increasing tendency after the introduction of MA in the blend; this indicated that the interfacial adhesion between



**Figure 4.** TGA thermograms of the compatibilized PLLA/PPC blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Mechanical Properties of the PLLA, PPC, and PLLA/PPC Blends

Sample	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
Neat PLLA	69.7 ± 1.5	1.9 ± 0.0	7.8 ± 0.6
PPC20	59.6 ± 0.3	1.8 ± 0.1	63.8 ± 8.8
cPPC10	61.3 ± 0.8	2.0 ± 0.1	21.6 ± 8.4
cPPC11	62.9 ± 1.5	1.9 ± 0.2	77.0 ± 8.0
cPPC12	58.2 ± 3.4	1.8 ± 0.0	110.3 ± 29.7
cPPC13	54.1 ± 4.7	1.8 ± 0.4	157.2 ± 3.6
cPPC14	57.2 ± 2.0	1.8 ± 0.1	157.1 ± 9.3
cPPC15	51.8 ± 3.3	1.6 ± 0.1	166.3 ± 7.1
cPPC20	63.7 ± 0.9	1.9 ± 0.1	37.7 ± 22.2
cPPC21	64.6 ± 2.3	1.8 ± 0.2	42.1 ± 48.3
cPPC22	58.8 ± 0.9	1.7 ± 0.1	90.1 ± 2.3
cPPC23	58.3 ± 3.9	1.8 ± 0.2	96.3 ± 10.6
cPPC24	56.3 ± 5.4	1.7 ± 0.2	87.7 ± 21.1
cPPC25	53.0 ± 1.5	1.4 ± 0.1	124.0 ± 32.9
Neat PPC	9.9 ± 0.6	0.4 ± 0.3	404.0 ± 49.8

PLLA and PPC was significantly improved by the reactive compatibilization process.

#### Morphological Observations

The scanning electron microscopy (SEM) micrographs of the simple PLLA/PPC blend film samples after fracture was given in Figure 6. The PPC domain size got larger with increasing amount of PPC, and poor interfacial adhesion between PLLA and PPC was observed with cavities and voids at the interface between the PLLA matrix and PPC domains.

Figure 7 presents the SEM micrographs of the cPPC blend injection-molded samples after fracture and solvent extraction. We found that the PPC domain size significantly decreased with the addition of L101 and MA as compared to that of the simple PLLA/PPC blend. This confirmed that the reactive compatibilization was successfully accomplished; this resulted in increased compatibility of the blends and improved the elongation properties of the PLLA/PPC blend. Similar results were also observed in the study of Yao *et al.*,<sup>14</sup> and they found a reduction of the PPC domain size in the PLA matrix with the addition of MA in the PLA/PPC blend after the etching process.

#### Thermomechanical Properties

Figures 8 and 9 show the  $E'$  values of the neat PLLA, PPC, and cPPC blends. The addition of 20 wt % PPC in the blend showed a reinforcing effect, increasing  $E'$  before  $T_g$  of PPC, and  $E'$  gradually decreased after  $T_g$  was reached. This increase could have been due to the partial interaction between PLLA and PPC, as shown by the elongation at break, and the addition of 0.2-phr L101 dramatically reduced  $E'$  because of chain scission and the chain branching effect. In the presence of 0.1-phr L101, MA did not have a significant effect on  $E'$  except in the sample with 5.0-phr MA; this resulted in a profound reduction in  $E'$  because of the plasticizing effect. In the presence of 0.2-phr L101, the addition of MA resulted in a significant reduction in

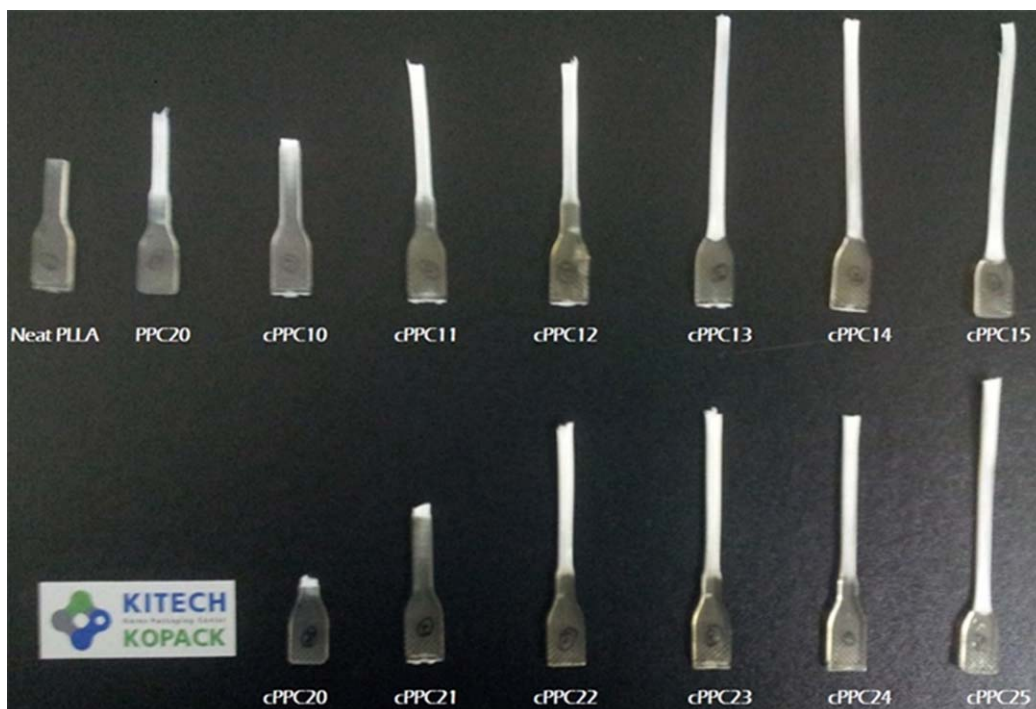


Figure 5. PLLA and PLLA/PPC blend samples after the tests. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

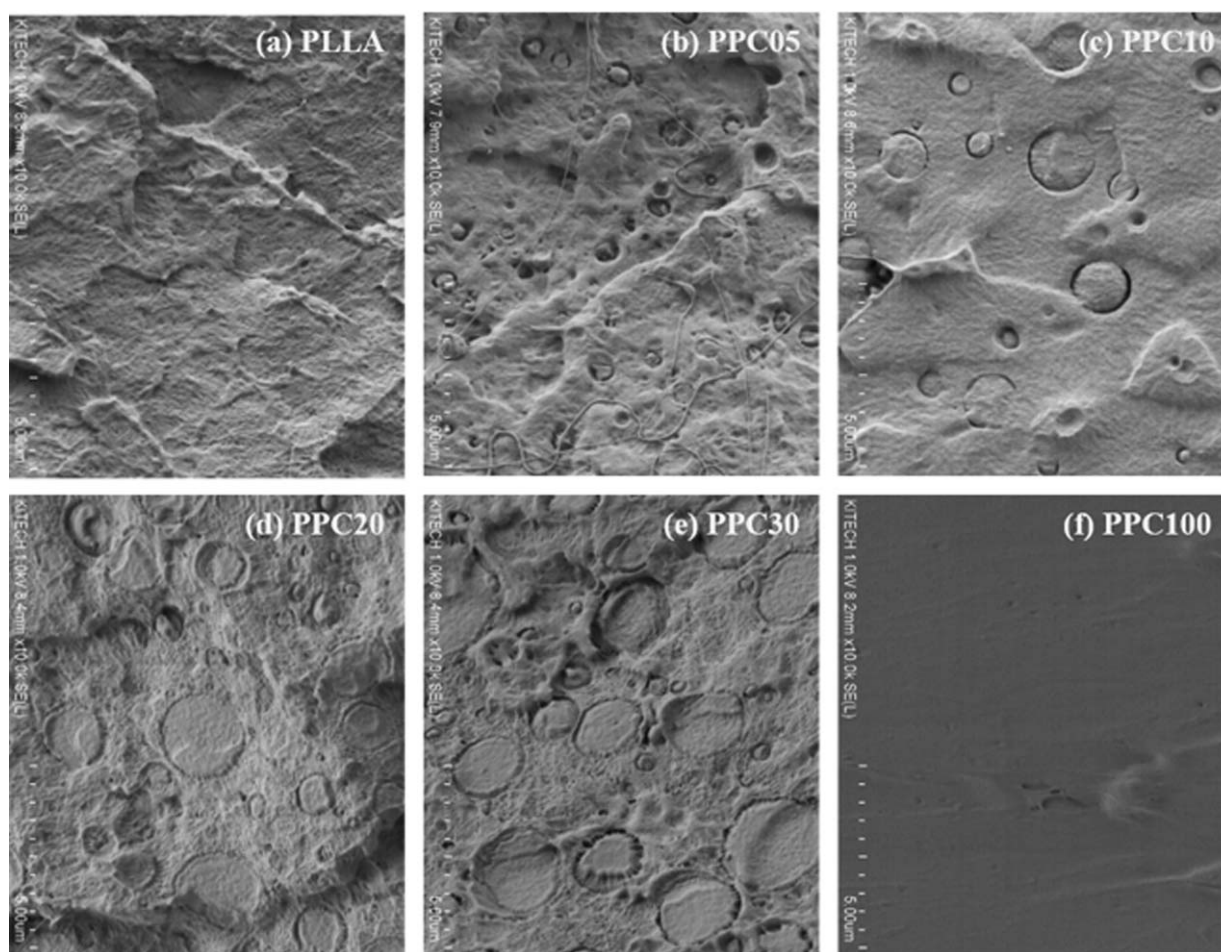


Figure 6. SEM micrographs of the PLLA/PPC blend samples.



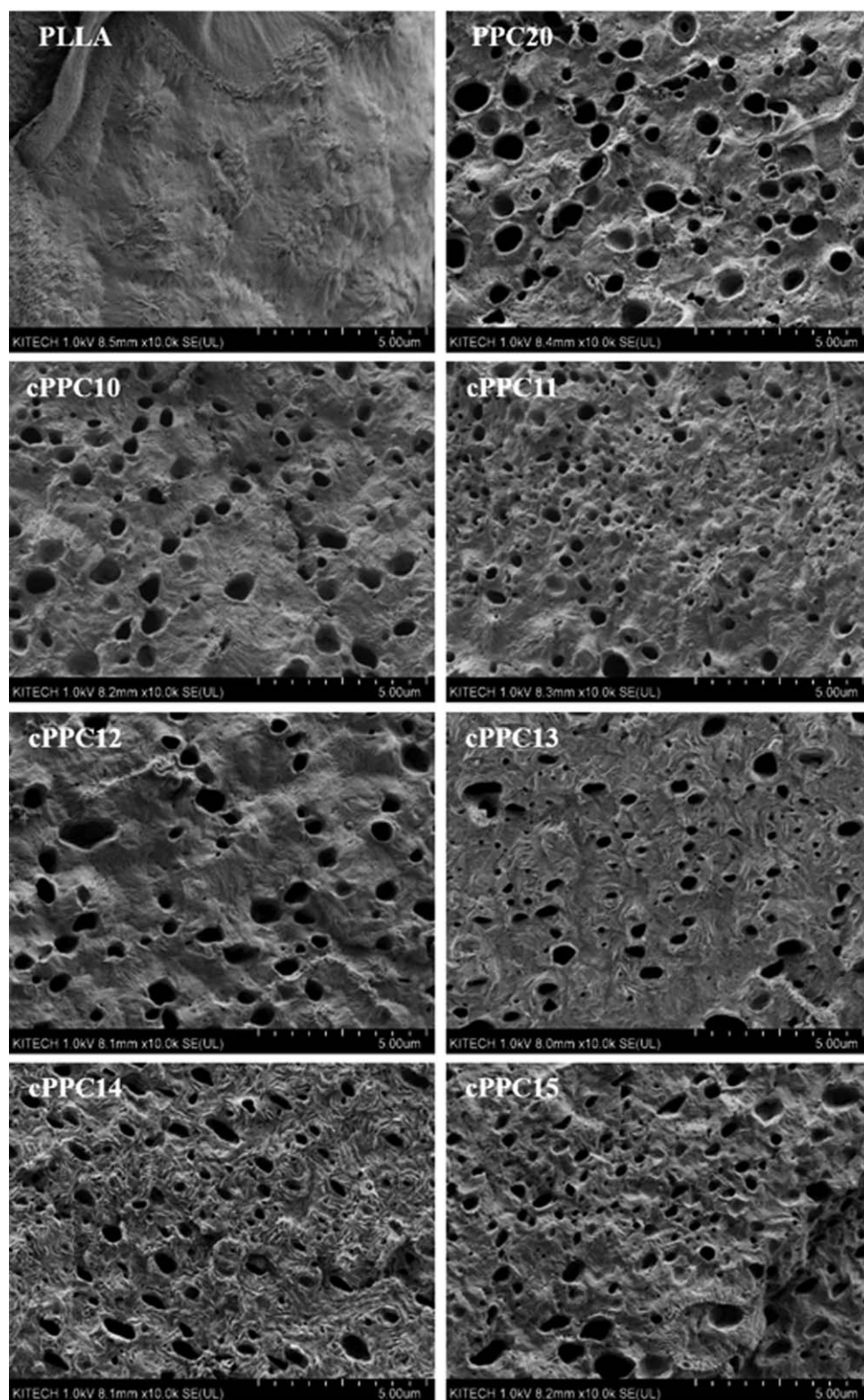
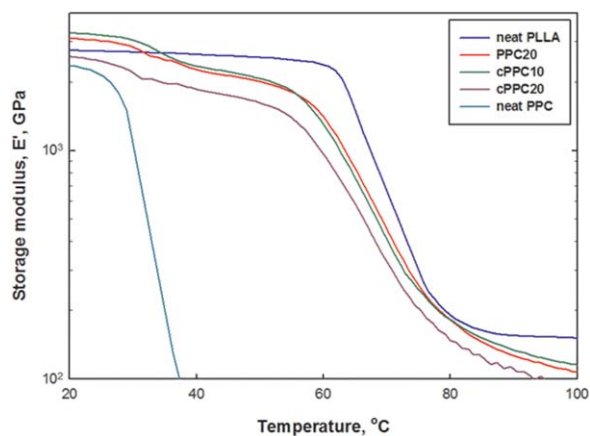


Figure 7. SEM micrographs of the compatibilized PLLA/PPC blend samples.

the elastic modulus for cPPC the blends as compared to PPC20 because of the plasticizing effect of MA. Yao *et al.*<sup>14</sup> also investigated a PLA/PPC blend with MA and found that elastic properties and thermomechanical stability of the blend were reduced with the addition of MA.

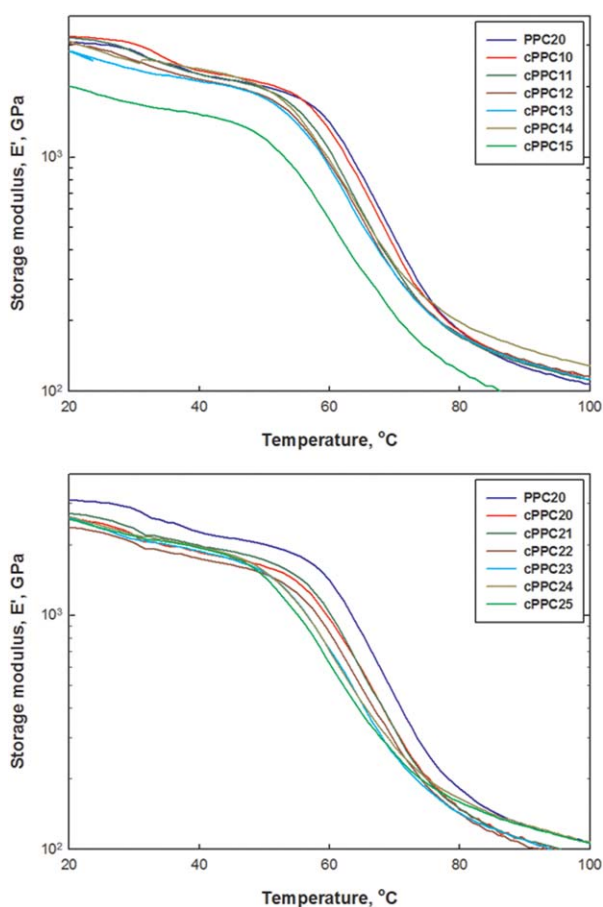
#### Rheological Properties

Figures 10 and 11 present the dynamic storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) of the simple PLLA/PPC and cPPC blends at 190 °C. Ray *et al.*<sup>18</sup> investigated the master curves of a PLLA melt at a low frequency; a terminal region could be described with

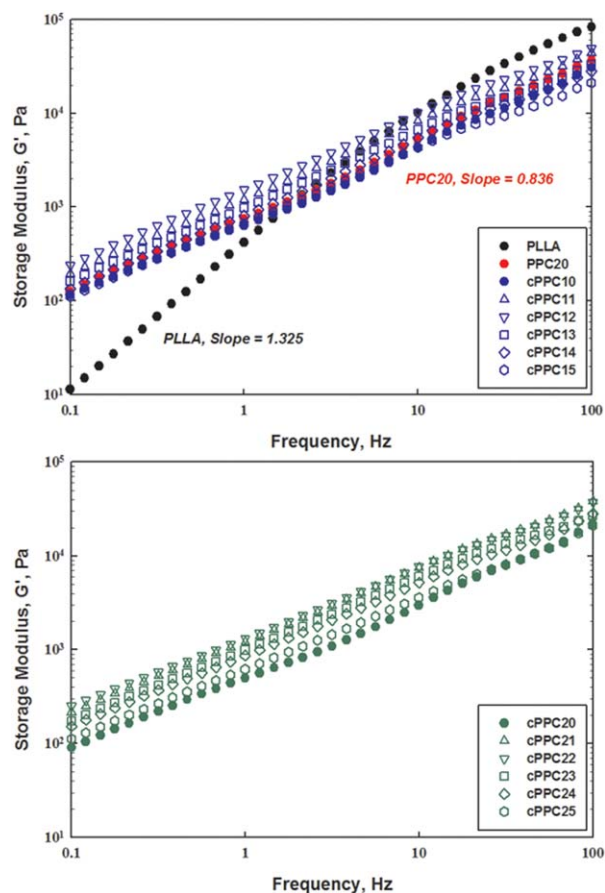


**Figure 8.**  $E'$  values of the PLLA and PLLA/PPC blend samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the power laws  $G'(\omega) \propto \omega^2$  and  $G''(\omega) \propto (\omega)$ , where  $\omega$  is angular frequency and similar behavior was observed in the homopolymer melts having narrow molecular weight distributions. The slope of  $G'$  in the low-frequency region ( $<1$  Hz) of PLLA was found to be 1.325; this was lower than that of previous study, which showed a



**Figure 9.**  $E'$  values of the compatibilized PLLA/PPC blend samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 10.**  $G'$  values of the PLLA and compatibilized PLLA/PPC blend samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value of around 1.6.<sup>19,20</sup> This difference could have been due to the different experimentation techniques. The slope of PPC20 was found to be 0.836; this was much lower than that of PLLA, and this lower value indicated a higher elasticity and chain entanglement, which led to solidlike behavior in the blends. Therefore, the addition of PPC with more chain flexibility to form the chain entanglement had a great effect on improving the elasticity of the PLLA/PPC binary blend. The slope of the cPPC blends did not show much difference from that of PPC20, but the addition of up to 2.0-phr MA further increased the  $G'$  values of the blend because of the improved interfacial adhesion. However, the plasticizing effect of residual MA was also observed when the usage of MA was over 3.0 phr. We found that the PLLA showed almost Newtonian behavior in the 0.1–1-Hz frequency range, and shear thinning, a typical pseudo-plastic behavior, was observed at a higher frequency region ( $>1$  Hz). The addition of PPC induced very strong shear-thinning tendency, and this tendency was independent of the addition of L101 and MA. PPC is an amorphous polymer and has more flexibility; therefore, under low shear rate, PPC could exist as a random coil structure, whereas the PPC polymer chain could be oriented to the flow direction at the high shear rate; this resulted in the reduction of  $\eta^*$ . However, as observed in the  $G'$  results,  $\eta^*$  improved considerably with the addition of up to 2.0-phr MA in the blend. This confirmed that the enhanced



interfacial adhesion between PLLA and PPC was accomplished from the reactive compatibilization process.

### Barrier Properties

Table IV shows the  $O_2$  permeability of the PLLA, PPC, and PLLA/PPC blends. It is widely known that the PPC had excellent  $O_2$ -barrier properties ( $0.45\text{--}0.6\text{ cc}\cdot\text{mm}/\text{cm}^2\cdot\text{day}\cdot\text{atm}$ ).<sup>21</sup> In this study, neat PPC showed a  $5.4 \pm 0.2\text{ cc}\cdot\text{mm}/\text{cm}^2\cdot\text{day}\cdot\text{atm}$  of  $O_2$  permeability value, that is, one order magnitude higher than the reported value. It is widely known that various factors can affect the barrier properties; these include the polymer internal structure, molecular weight,  $X_c$ , molecular chain entanglement, and polymer processing techniques. The morphology of the compression-molded film samples of the blends was differentiated from that of extrusion-cast film. In addition, the two-step processing of PPC could result in the thermal degradation of PPC and increased the  $O_2$  permeability of neat PPC. The addition of PPC to PLLA had the effect of reducing the permeability, and it was found that L101 and MA did not have much effect on the permeability of the PLLA/PPC blend. This reduction of permeability was also correlated with increased crystallinity in the blend samples (Table II). In case of 0.1-phr L101, an excess MA circumstance, an increase in the permeability was found, and this could have been due to the increase in the free volume resulting from the MA branching and chain scission of

**Table IV.**  $O_2$  Permeability of the PLLA, PPC, and PLLA/PPC Blends

Sample	$O_2$ permeability ( $\text{cc}\cdot\text{mm}/\text{cm}^2\cdot\text{day}\cdot\text{atm}$ )	Sample	$O_2$ permeability ( $\text{cc}\cdot\text{mm}/\text{cm}^2\cdot\text{day}\cdot\text{atm}$ )
Neat PLLA	$19.2 \pm 0.2$	—	—
PPC20	$14.6 \pm 1.3$	cPPC20	$15.5 \pm 2.9$
cPPC10	$12.8 \pm 0.2$	cPPC21	$12.5 \pm 0.7$
cPPC11	$13.8 \pm 0.4$	cPPC22	$12.0 \pm 0.7$
cPPC12	$13.3 \pm 1.9$	cPPC23	$11.8 \pm 0.9$
cPPC13	$13.3 \pm 2.4$	cPPC24	$11.8 \pm 1.3$
cPPC14	$14.5 \pm 3.7$	cPPC25	$12.0 \pm 1.3$
cPPC15	$17.5 \pm 6.4$	Neat PPC	$5.4 \pm 0.2$

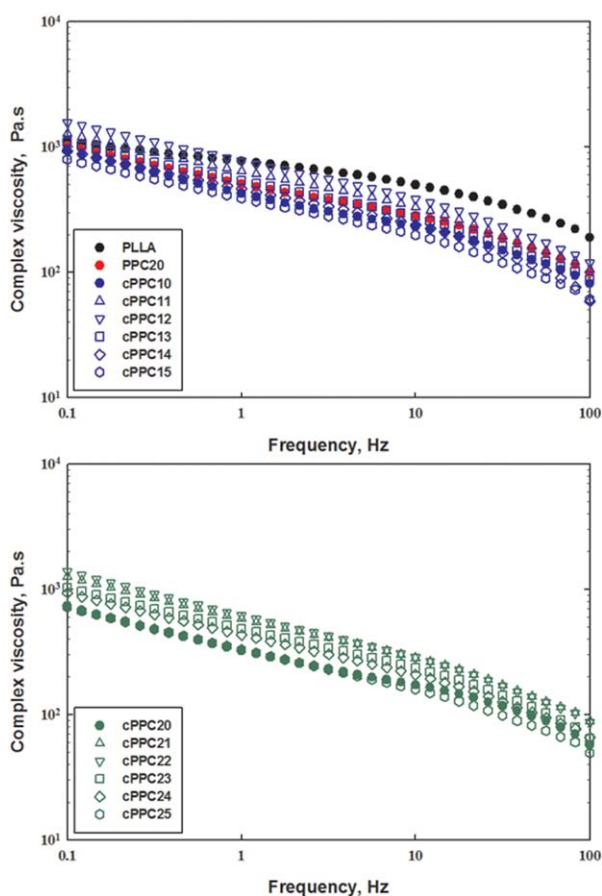
PPC. PLLA is normally considered as a relatively low  $O_2$ -barrier polymer, and a permeation-controllable polymer with biodegradability could be fabricated with the combination of PLLA with PPC, and this approach would increase the potential for food packaging applications.

### CONCLUSIONS

Simple PLLA/PPC blends were investigated, and the slight shift in the  $T_g$  values of PLLA and PPC in the blend, and the FTIR spectra results revealed that there were specific interactions between the chains of PLLA and PPC. The tensile strength and modulus showed a decreasing tendency with the addition of ductile PPC. This showed the poor interfacial adhesion between two polymers. The effect of reactive compatibilization on the PLLA/PPC (80/20) blends was also assessed, and we found that it improved the interfacial adhesion between PLLA and PPC. This resulted in a profound increase in the elongation at break. Although excess MA was found to act as a plasticizer; this made the tensile strength decrease. The use of up to 2.0-phr MA worked well in the blend to give it balanced mechanical properties. From the rheological results, we found that PPC had a great effect on the transition from liquidlike to solidlike behavior of the PLLA/PPC blends, and  $G'$  and  $\eta^*$  were enhanced with the use of up to 2.0-phr MA. The increased crystallinity may have had an effect on the slight improvement in the oxygen-barrier properties of the blends, and their potential as a packaging materials with biodegradability was confirmed.

### REFERENCES

1. Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.
2. Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, *4*, 835.
3. Wang, Y.; Hillmyer, M. A. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2755.
4. Reddy, N.; Nama, D.; Yang, Y. *Polym. Degrad. Stab.* **2008**, *93*, 233.
5. Iannace, S.; Ambrosio, L.; Huang, S. J.; Nicolais, L. *J. Appl. Polym. Sci.* **1994**, *54*, 1525.



**Figure 11.**  $\eta^*$  values of the PLLA and compatibilized PLLA/PPC blend samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

6. Chen, C.-C.; Chueh, J.-Y.; Tseng, H.; Huang, H.-M.; Lee, S.-Y. *Biomaterials* **2003**, *24*, 1167.
7. Hwang, S. W.; Shim, J. K.; Selke, S.; Soto-Valdez, H.; Rubino, M.; Auras, R. *Macromol. Mater. Eng.* **2013**, *298*, 624.
8. Song, P. F.; Xiao, M.; Du, F. G.; Wang, S. J.; Gan, L. Q.; Liu, G. Q.; Meng, Y. Z. *J. Appl. Polym. Sci.* **2008**, *109*, 4121.
9. Wang, S. J.; Du, L. C.; Zhao, X. S.; Meng, Y. Z.; Tjong, S. C. *J. Appl. Polym. Sci.* **2002**, *85*, 2327.
10. Tao, J.; Song, C.; Cao, M.; Hu, D.; Liu, L.; Liu, N.; Wang, S. *Polym. Degrad. Stab.* **2009**, *94*, 575.
11. Luinstra, G. A.; Borchardt, E. In *Synthetic Biodegradable Polymers*; Rieger, B., Künkel, A., Coates, G. W., Reichardt, R., Dinjus, E., Zevaco, T. A., Eds.; Springer: Berlin, **2012**; Chapter 126.
12. Zeng, S.; Wang, S.; Xiao, M.; Han, D.; Meng, Y. *Carbohydr. Polym.* **2011**, *86*, 1260.
13. Wang, X. L.; Du, F. G.; Jiao, J.; Meng, Y. Z.; Li, R. K. Y. *J. Biomed. Mater. Res. B* **2007**, *83*, 373.
14. Yao, M.; Deng, H.; Mai, F.; Wang, K.; Zhang, Q.; Chen, F.; Fu, Q. *Express Polym. Lett.* **2011**, *5*, 937.
15. Fischer, E. W.; Sterzel, H. J.; Wegner, G. *Colloid Polym. Sci.* **1973**, *251*, 980.
16. Ma, X.; Yu, J.; Wang, N. *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 94.
17. Peng, S.; An, Y.; Chen, C.; Fei, B.; Zhuang, Y.; Dong, L. *Polym. Degrad. Stab.* **2003**, *80*, 141.
18. Sinha Ray, S.; Yamada, K.; Okamoto, M.; Ueda, K. *Polymer* **2003**, *44*, 857.
19. Gu, S.-Y.; Zhang, K.; Ren, J.; Zhan, H. *Carbohydr. Polym.* **2008**, *74*, 79.
20. Hwang, S. W.; Shim, J. K.; Selke, S. E. M.; Soto-Valdez, H.; Matuana, L.; Rubino, M.; Auras, R. *Polym. Int.* **2012**, *61*, 418.
21. Empower Materials Inc. (2010) QPAC poly(alkylene carbonate) copolymers. <http://www.empowermaterials.com> Accessed June 2014.