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ORIGINAL PAPER

Effect of secondary forces in the compatibility of two incompatible biodegradable polymers

P. M. Chou · M. Mariatti · A. Zulkifli · M. Todo

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Abstract Poly(ethylene adipate) (PEA) and polytetramethylene ether glycol (PTMEG) were used as compatibilizers in the biodegradable polymer blend of poly(L-lactic acid)/poly(butylene succinate-*co*-L-lactate) (PLLA/PBSL). The compatibilizers of various contents were incorporated into the blend using a Haake internal mixer. The compatibilization between PEA and PTMEG on the blends was measured using thermogravimetric analysis (TGA), flexural test, field emission scanning electron microscopy (FESEM), and Fourier transform infrared (FTIR) spectroscopy. From the TGA results, it was found that the thermal stability of the blend improved with the addition of PEA. The flexural strength showed a dependency on the extent of the secondary forces interaction between PEA and PTMEG with the blends. This observation corresponded well with the FESEM micrographs. Based on the FTIR analysis, the physical interaction between PEA and PLLA/PBSL was due to the presence of secondary forces.

Keywords Poly(butylene succinate-*co*-L-lactate) (PBSL) · Poly(L-lactic acid) (PLLA) · Compatibilization · Blend · Interfacial adhesion · Strength

Introduction

Poly(L-lactic acid) (PLLA) is an aliphatic polyester that can be produced from renewable agricultural resources such as corn starch and beet sugar [1]. Recently,

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P. M. Chou · M. Mariatti (✉) · A. Zulkifli
School of Materials and Mineral Resources Engineering, Engineering Campus,
Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia
e-mail: mariatti@eng.usm.my

M. Todo
Research Institute for Applied Mechanics, Kyushu University,
6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

PLLA has been studied extensively due to its biodegradability, biocompatibility, and processability. In addition, its mechanical properties are comparable to those of petroleum-based polymers, making it suitable for biomedical applications, such as controlled-release devices, absorbable sutures, and orthopedic implants [2]. However, its low toughness and impact resistance, poor thermal stability, and high production cost have limited its applications.

In this context, polymer blending is a simple and cheap yet effective method of obtaining new materials with desired properties [3]. The blending of PLLA with polymers that exhibit ductile impact fracture behaviors, such as poly(ε-caprolactone) (PCL) [4], poly(3-hydroxybutyrate) (PHB) [5], poly(butylene succinate) (PBS) [6], poly(butylene succinate-*co*-L-lactate) (PBSL) [7], poly(vinyl alcohol) (PVA) [8], and poly(hydroxyl ester ether) [9], have shown to contribute toughness and flexibility to PLLA. Regarding the PLLA/PBSL blend, Shibata et al. [7] reported that the elongation at break and the isothermal and non-isothermal crystallization of the PLLA component are enhanced by the addition of a small amount of PBSL. Nevertheless, the PLLA/PBSL blend is immiscible, and the poor interfacial adhesion between the two phases reduces the flexural strength and fracture toughness of the blend. The miscibility of an immiscible blend can be improved by using a compatibilizer, which is usually a block copolymer containing blocks that are chemically identical to the constituting polymers of the blend [10]. A compatibilizer of similar chemical structure should allow for the formation of a good interaction, either physically or chemically, between both polymers in the blend, thereby improving the miscibility of the blend. This has been the general strategy in designing suitable compatibilizers to improve several immiscible blends [11–13]. Examples of the compatibilizers used in PLLA/PBSL blends are diglycerine tetraacetate [14], lysine triisocynate (LTI) [15], and polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) triblock copolymer [16]. According to Vilay et al. [15], LTI results in a chemical bonding with PLLA and PBSL, whereas in the case of the PEO–PPO–PEO triblock copolymer, there is a physical bonding between the copolymer and the PLLA/PBSL blend, which involves secondary forces, such as hydrogen bonding and hydrophobic interaction [16]. Both chemical and physical bonds improve the miscibility of the PLLA/PBSL blend. The role of secondary forces in enhancing the miscibility of polymer blends has been clearly documented by Mekhilef and Hadjiandreou [17], Shafee [18], Kim and Kim [19], and Naveen Kumar et al. [20].

In this study, poly(ethylene adipate) (PEA) and polytetramethylene ether glycol (PTMEG) were used as compatibilizers for the PLLA/PBSL blend to modify the immiscible morphology and mechanical properties of the PLLA/PBSL blend. No study on the compatibilization of the PLLA/PBSL blend with these two materials has been reported yet. Both PEA and PTMEG contain hydroxyl groups (at both ends of the molecules), ether bonds, and repeating methylene units. However, PEA contains carbonyl groups that are not present in PTMEG. The former is expected to affect a different level of interaction between PLLA and PBSL in the blend. The effectiveness of compatibilization between the two compatibilizers (i.e., PEA and PTMEG) and the blend was assessed by Fourier transform infrared (FTIR) spectroscopy, flexural test, and field emission scanning electron microscopy (FESEM).

Experimental

Materials

PLLA pellets (Lacty 5000) with a weight-average molecular weight of 1.45×10^5 and PBSL pellets with a weight-average molecular weight of 1.47×10^5 were obtained from Shimadzu Co. Ltd. and Mitsubishi Chemical Corp., respectively. PEA with a weight-average molecular weight of 10,000 and PTMEG with a number-average molecular weight of 650 were purchased from Sigma Aldrich. The chemical structures of PLLA, PBSL, PEA, and PTMEG are shown in Fig. 1.

Blend preparation

PLLA and PBSL pellets were melt mixed with either PEA or PTMEG (2, 4, and 6 phr) for 7 min using a Haake internal mixer with a twin screw speed of 50 rpm at 170 °C. To minimize degradation due to hydrolysis, PLLA and PBSL pellets were oven dried for 24 h at 80 °C before mixing. After blending, the solidified blends were hot pressed for 5 min at 180 °C and 10 MPa. This was followed by cooling to room temperature. The specimens were then sealed in plastic bags and kept in a desiccator for characterization.

Thermogravimetric analysis (TGA)

A Pyris Diamond thermogravimetric analyzer (TGA) was used to measure the thermal stability and decomposition temperature of the test samples. This was conducted by monitoring the weight change that occurred as a specimen was heated. Measurements were carried out in an inert atmosphere, and weight loss was recorded as a function of increasing temperature. TGA was run from 30 to 600 °C at a heating rate of 10 °C/min.

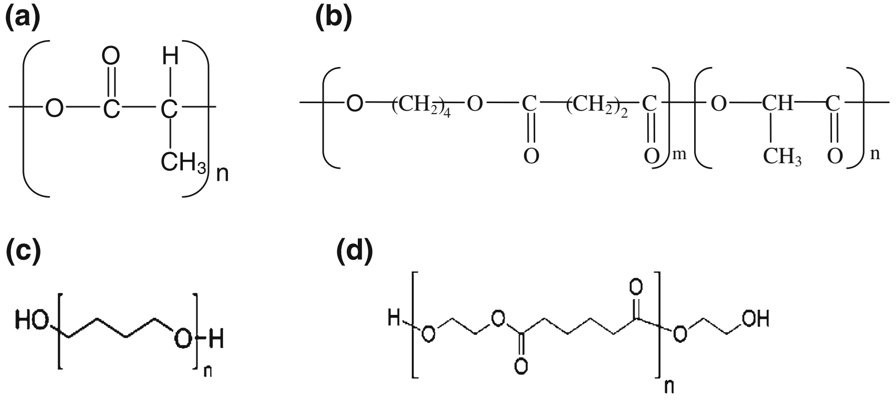

Fig. 1 Chemical structures of **a** PLLA, **b** PBSL, **c** PTMEG, and **d** PEA

Flexural test

Flexural test was performed according to the standard ASTM D790-03 using the Instron Universal Testing Machine Model 3366. Specimens of rectangular bars with dimensions of 100 × 12.7 × 3 mm^3 were prepared for the mechanical test. A cross-head speed of 10.00 mm/min and a span length of 50 mm were employed in the test. The flexural strengths and moduli were computed based on the average results of the five specimens tested.

Morphological study

Cryofractured surfaces of the PLLA blends were examined using a field emission scanning electron microscope (FESEM) Model Supra 35 VP Zeiss. The specimens were prepared by immersing the flexural test bars in liquid nitrogen for about 30 min. The fracture surfaces were sputtered with gold before the examination.

Fourier transform infrared (FTIR) spectroscopy

A Perkin-Elmer Spectrum One FTIR spectrometer was used to obtain the FTIR spectra of the PLLA/PBSL blends containing different compatibilizers. The analysis was conducted with four scans at a range of 550–4,000 cm^{-1}.

Results and discussion

Thermogravimetric analysis (TGA)

Figures 2 and 3 display the TGA and DTG thermograms of PLLA/PBSL blends added with varying contents of PEA, respectively. As shown in Fig. 2, the onset decomposition temperature of the blend decreased with increasing PEA content in the blend. However, the decomposition temperature at weight loss of 50% ($T_{d50\%}$) of the blend containing PEA is slightly higher than that of the uncompatibilized blend. It is observed that $T_{d50\%}$ of the 75/25 blend is approximately 364 °C whereas $T_{d50\%}$ of the blends added with 2, 4, and 6 phr of PEA are 372, 371, and 365 °C, respectively. This suggests that the PLLA/PBSL blend decomposed slower above 365 °C in the presence of PEA. In other words, addition of PEA improved the thermal stability of the PLLA/PBSL blend. This is evidenced by the shifting of peaks to higher temperature with increasing PEA content in DTG curves as depicted in Fig. 3. In Fig. 3, the doublet found in the DTG curve of uncompatibilized PLLA/PBSL blend indicates that the sample experienced two steps of thermal degradation, wherein the first peak corresponds to the decomposition of PLLA while the second peak is attributed to the decomposition of PBSL. It is observed that the doublet coalesced with each other after adding PEA into the blend system. This suggests that PEA improved the miscibility of the PLLA/PBSL blend, resulting in a single step of thermal decomposition. Apart from that, the weight loss of a polymer as a function of temperature which is commonly determined by TGA, can reflect the

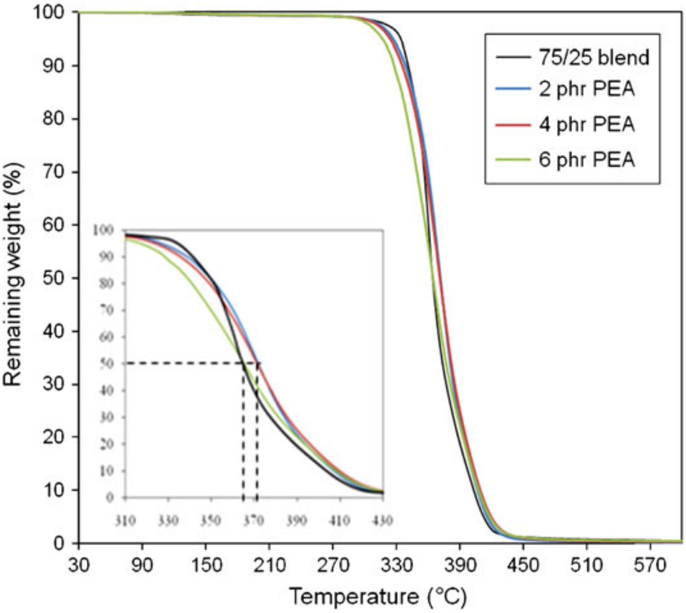

Fig. 2 TGA curves of 75/25 blends added with varying contents of PEA

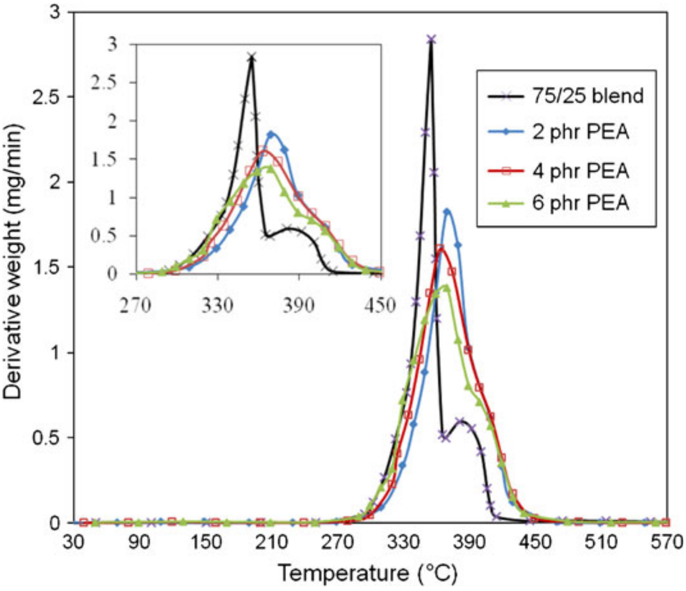

Fig. 3 DTG curves of 75/25 blends added with varying contents of PEA

thermal degradation behaviors of the polymer. Weight loss of a polymer due to thermal degradation is an irreversible process. This thermal degradation is largely related to oxidation whereby the molecular bonds of a polymer are attacked by

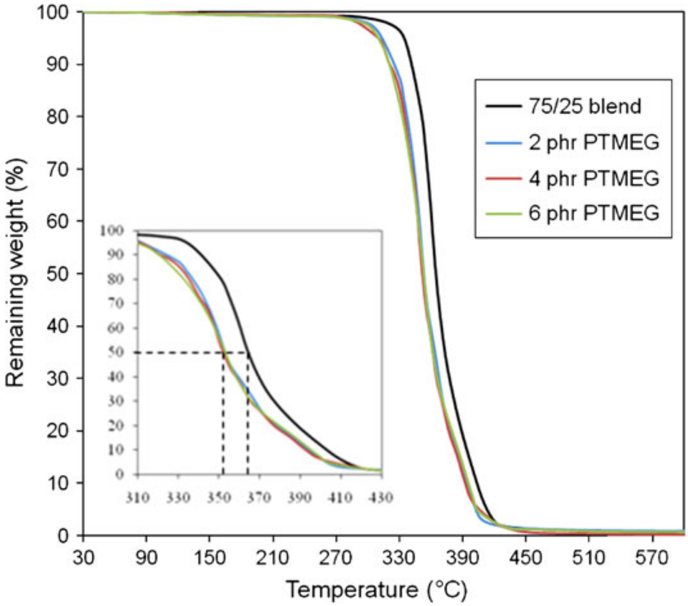

Fig. 4 TGA curves of 75/25 blends containing different contents of PTMEG

oxygen molecules [21]. It is found that the char yield of all the samples beyond 570 °C was very little, indicating the polymer blends decomposed almost completely at 570 °C.

Figures 4 and 5 present the TGA and DTG thermograms of PLLA/PBSL blends containing different contents of PTMEG, respectively. Apparently, all of the blends containing PTMEG exhibited lower decomposition temperature range compared to the uncompatibilized 75/25 blend, as shown in Fig. 4. The decomposition temperature at weight loss of 50 % ($T_{d50\ \%}$) of the blend containing PTMEG was about 11 °C lower than that of the uncompatibilized blend, indicating that the addition of PTMEG reduced the thermal stability of the PLLA/PBSL blend. This is probably due to the relatively low molecular weight of PTMEG as compared to PEA. According to Murariu et al. [22], high volatility of the low molecular weight of additive contributed to the decrease in thermal stability of the polymer blend. Moreover, it is found that char yield of the blends containing PTMEG is identical to that of blends containing PEA. In Fig. 5, it is worth noting that DTG curve pattern of the blend containing PTMEG are similar to that of uncompatibilized PLLA/PBSL blend, which exhibited two peaks. This implies that PTMEG is not an effective compatibilizer for PLLA/PBSL blend. This is probably because PTMEG contains hydroxyl (–OH) functional group only, which is insufficient in forming good polar interaction with PLLA and PBSL. Therefore, miscibility of the PLLA/PBSL blend remained unchanged, whereby two steps of thermal degradation was found in the blend system.

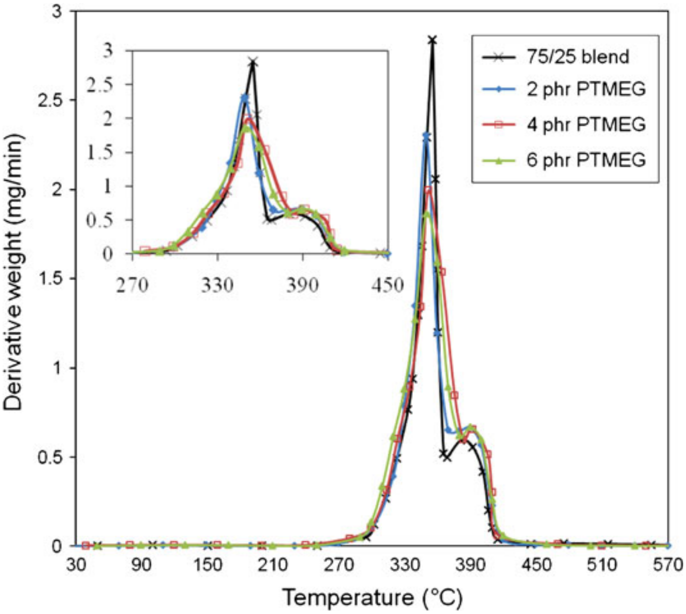

Fig. 5 DTG curves of 75/25 blends containing different contents of PTMEG

Flexural properties

Figure 6 shows the flexural strength and modulus of the PLLA/PBSL blends as a function of compatibilizer content. The flexural strength value of the PLLA/PBSL containing 2 phr of PEA is almost similar to that of the blend without the compatibilizers, whereas the addition of 2 phr of PTMEG resulted in an approximately 20 % drop in flexural strength. Beyond 2 phr of either PEA or PTMEG, the flexural strength of the blend reduced monotonically. It is found that the reduction in flexural strength of the blend containing PEA is less than PTMEG. This is attributed to the formation of good polar interaction between the carbonyl group of PEA and the carbonyl group of PLLA and PBSL components, as seen in the FTIR analysis in the following section. Unlike PEA, there is no good polar interaction occurs between PTMEG and the blend components due to the absence of carbonyl group in PTMEG. As a result, the interfacial bonding between PLLA and PBSL phases is relatively weak as compared to that of PLLA/PBSL blend compatibilized with PEA. This weak interfacial bonding is responsible for the decrease in flexural strength of the blend system. When higher stress was applied to the sample having weak interfacial bonding, the sample could not sustain higher stress and failed prematurely. This is in agreement with the result reported by Sarazin et al. [23] in their study on the binary and ternary blends of polylactide, polycaprolactone, and thermoplastic starch. The addition of 2 phr of PEA resulted in a slight increase in the flexural modulus; the flexural modulus of the sample containing 2 phr of PTMEG did not change significantly as compared with the pure blend. Modulus is an intrinsic property that does not change much if the chemical

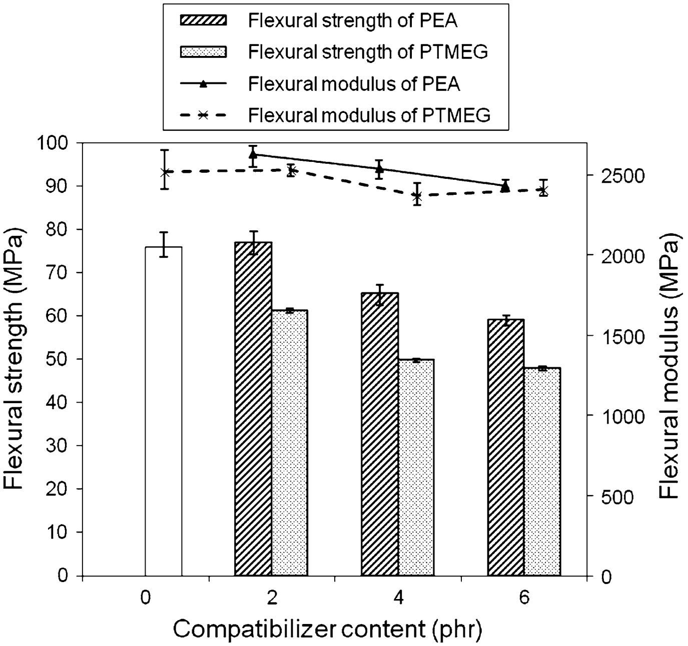

Fig. 6 Effect of PEA and PTMEG content on flexural strength and modulus of PLLA/PBSL blend

structures of the blend components are similar. Therefore, there is an insignificant change in the modulus of the blend with the addition of PEA and PTMEG.

Figure 7 depicts the stress–strain curves of the PLLA/PBSL blends without and with varying contents of PEA and PTMEG. It is found that the area under the curves reduced with increasing amount of PEA and PTMEG. However, the reduction in

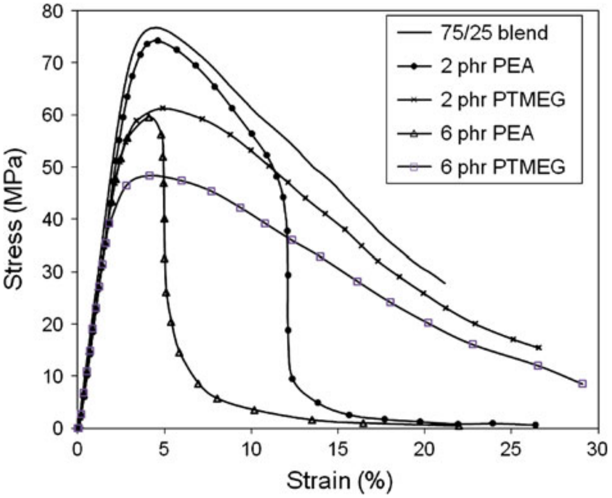

Fig. 7 Stress–strain curves of PLLA/PBSL blend containing various contents of PEA and PTMEG

area is less in the PTMEG system. Furthermore, the blends compatibilized with PEA showed a relatively abrupt drop in stress as the strain increased compared with the blends compatibilized with PTMEG, which displayed a gradual decrease in stress at higher strains. The deformation behavior of the latter is notably similar to that of the PLLA/PBSL blend without a compatibilizer. This implies that PTMEG acts as a plasticizer rather than a compatibilizer in the PLLA/PBSL blend. This is corroborated by the FESEM micrographs of the morphology of the PLLA/PBSL blends with and without the compatibilizers as shown in Fig. 8.

Observations of cryofractured surfaces of the blend

Based on the FESEM observations in Fig. 8, all samples comprised of two phases, namely the continuous PLLA and the dispersed PBSL spherical-phases. It is observed that cryofractured surface of the PLLA/PBSL blend without any compatibilizer exhibited almost no microvoids but only some degree of phase separation between the two phases. With the addition of 2 phr of PEA, the cryofractured surface became flatter and smoother, as compared to the unmodified PLLA/PBSL blend. In addition, it is observed that the spherical dispersed phases of PBSL were embedded into the PLLA matrix phase. However, as the PEA content increased up to 6 phr, the phase separation between the PLLA and PBSL phases increased, as shown in Fig. 8f. This proves that the interfacial bonding of the blend was improved by adding small amount of PEA.

In the case of PTMEG, at 2 phr content, there is an apparent phase separation with some PBSL globules embedded into the PLLA matrix phase, and some cavities formed by the detachment of the PBSL phase. As the PTMEG content increased up to 4 phr, phase separation became more prominent. Further addition of PTMEG up to 6 phr resulted in major removal of the PBSL phase from the PLLA matrix, as seen in Fig. 8g. This observation is probably due to the presence of tetramethylene $(CH_2)_4$ sub-units in PTMEG, which favors a good hydrophobic interaction with the similar sub-units in PBSL. However, the $(CH_2)_4$ sub-units do not present in PLLA, and therefore, the hydrophobic interaction does not occur between PLLA and PTMEG. In other words, PTMEG interacts preferentially with PBSL, thus inducing phase separation between the PLLA and PBSL phases. This is consistent with the flexural test results presented in the previous section.

FTIR analysis

The FTIR spectra of PLLA/PBSL blend with blending ratio of 75/25 containing various amount of PEA are shown in Fig. 9a. In Fig. 9, the carbonyl (C=O) groups of PLLA and PBSL are represented by the peaks at 1,748 and 1,722 cm^{-1}, respectively. With the addition of PEA, there was a slight change in the spectrum, notably in the region of 1,700 and 1,800 cm^{-1}. As observed in Fig. 9b, the uncompatibilized PLLA/PBSL blend exhibited a doubled peak in the region of 1,700 and 1,800 cm^{-1}, corresponding to the carbonyl group of the PBSL (1,722 cm^{-1}) and PLLA (1,748 cm^{-1}). This is due to the difference in bonding motion of the PLLA and PBSL. At 2 phr of PEA, the doubled peak appeared

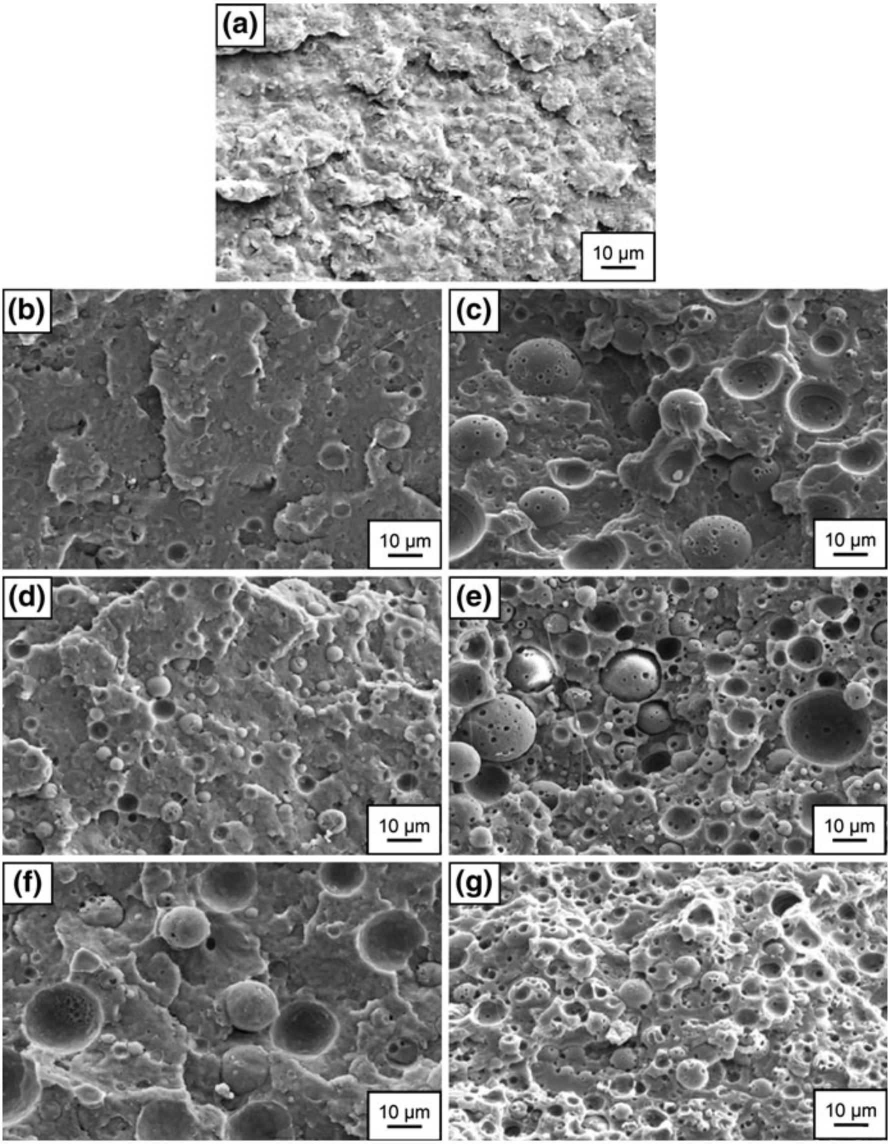

Fig. 8 FESEM images of the cryofractured surfaces of the PLLA/PBSL blend **a** without compatibilizer, **b** containing 2 phr PEA, **c** 2 phr PTMEG, **d** 4 phr PEA, **e** 4 phr PTMEG, **f** 6 phr PEA, and **g** 6 phr PTMEG

slightly coalesced. This coalescence appeared more prominent at 6 phr of PEA. This observation indicates that, at 6 phr of PEA, the carbonyl bonds of PLLA and PBSL were vibrating synchronically as unit entities, suggesting the good interaction between PLLA and PBSL in the presence of PEA.

On the contrary, the FTIR spectra of the blend added with varying content of PTMEG are almost identical to those of the blend that was not compatibilized, as

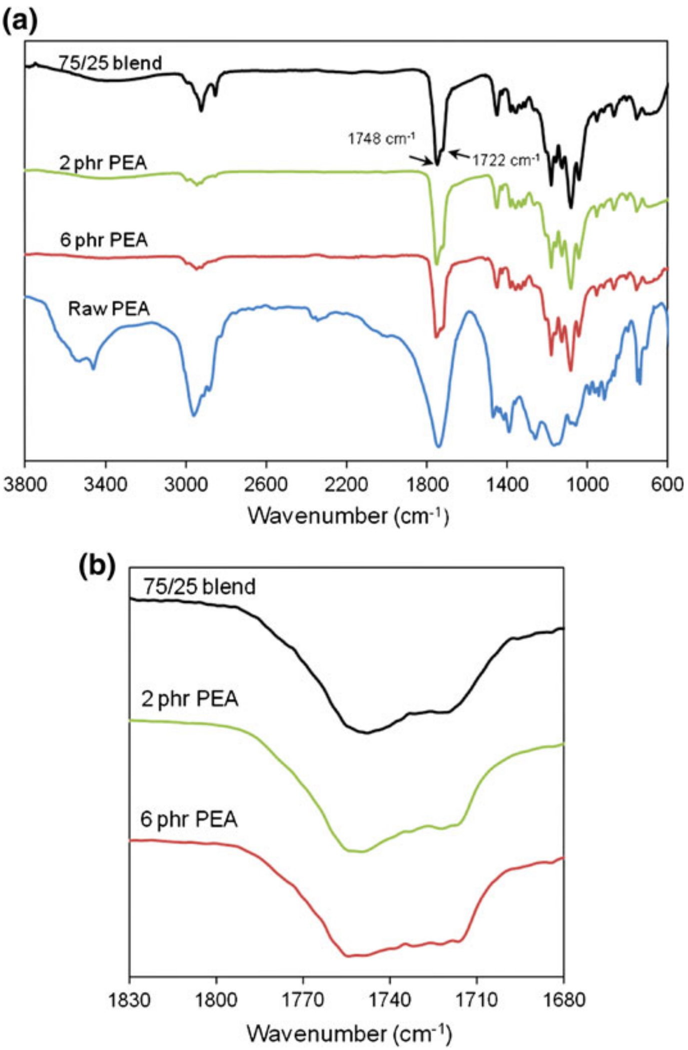

Fig. 9 FTIR spectra of **a** PLLA/PBSL blends containing different contents of PEA, and **b** magnified portion at region between 1,680 and 1,830 cm^{-1}

displayed in Fig. 10a. This implies that there is no interaction between the molecular chains of the PTMEG and the PLLA/PBSL blend. In Fig. 10b, at 2 and 6 phr of PTMEG, the doubled peak in the region of 1,700 and 1,800 cm^{-1} remained, indicating that the carbonyl groups of the PLLA and PBSL were vibrating as different groups. This represents a comparably poorer interaction between PBSL and PLLA. There have been several references proving that the change in the peak intensity of the FTIR spectrum represents the occurrence of interaction between molecular chains [24, 25].

The secondary forces present in the blend system accounted for the good interaction between the PEA and the PLLA/PBSL blend. PEA contains carbonyl groups that apparently introduce polar interaction with the blend components.

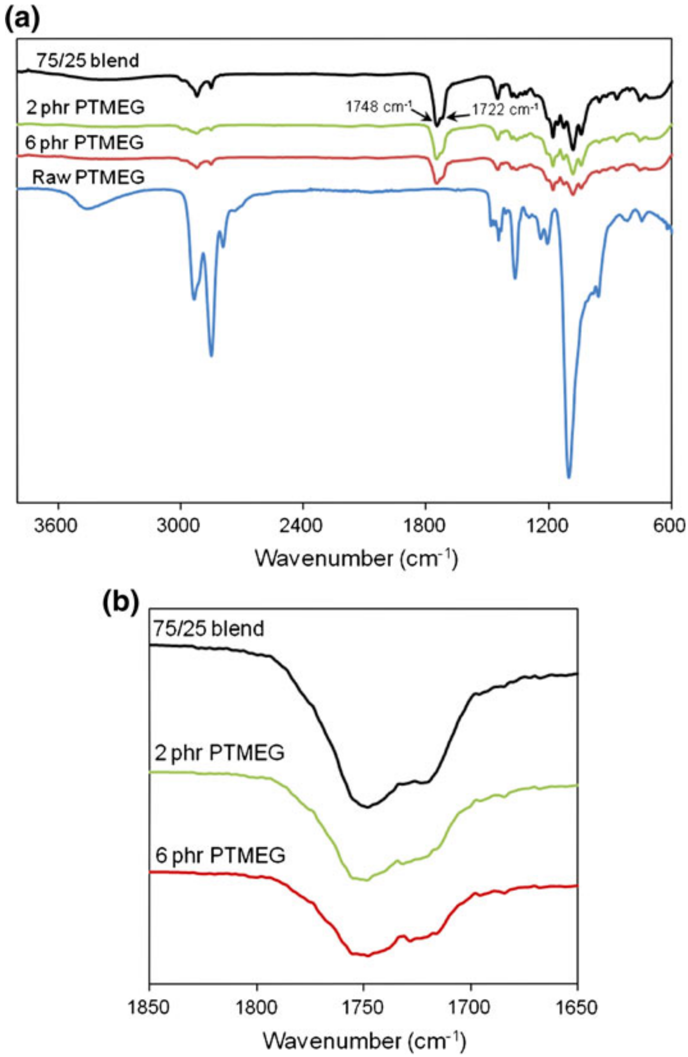

Fig. 10 FTIR spectra of **a** PLLA/PBSL blends containing different contents of PTMEG, and **b** magnified portion at region between 1,650 and 1,850 cm^{-1}

However, in the case of PTMEG, no such interaction occurs because it is devoid of carbonyl functionality. Figure 11 depicts the proposed interaction between PLLA and PBSL in the presence of PEA. The chain structure was minimized using Dreiding force-field to yield a linear chain conformation which is arranged parallel to each other. Their interchain distance was about 2.624 Å. It is observed that, a carbonyl oxygen of PEA aligned at a closed proximity to one of the carbonyl carbon of PLLA while the next carbonyl oxygen of PEA aligned at closed proximity to the carbonyl carbon of PBSL. Their distances were about 1.593 and 1.749 Å, respectively. The distances were within the range for polar interaction to happen

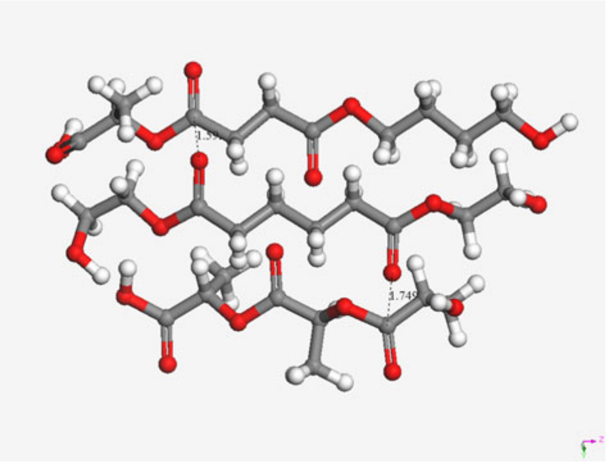

Fig. 11 Schematic diagram of the chemical interaction of PEA with PLLA and PBSL

[26]. In their geometrical arrangement, the PEA functions to establish a good interaction between the PBSL and PLLA thus forming good miscibility between the two chains. This polar interaction is responsible for the improved flexural properties of PEA incorporated system. The lack of carbonyl group in PTMEG incorporated system disfavors for any good interchains interaction, which results in weak interfacial bonding between the PLLA and PBSL phases, and consequently causes an inferior mechanical property.

Conclusion

Only the sample containing 2 phr of PEA exhibited a slight improvement in flexural strength and modulus compared with the virgin PLLA/PBSL blend. However, PTMEG incorporated system did not show any improvement in flexural properties. The presence of ether and carbonyl bonds in PEA induced a good polar interaction with ester bonds in both PLLA and PBSL. In contrast, PTMEG did not act as a good compatibilizer in the PLLA/PBSL blend. Therefore, the general strategy of designing an effective compatibilizer is to introduce a chemical structure that is identical to those of the blend components.

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