

Novel Polymer Blends from Polyester and Bio-Based Cellulose Ester

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ABSTRACT: A strategy to reduce the dependence on petroleum-based building blocks and the disposal concerns of solid wastes was proposed by developing a novel polymer blend from bio-based cellulose acetate butyrate (CAB) and poly(trimethylene terephthalate) (PTT). The thermodynamic immiscibility and the thermal behaviors of the polymer melt blends were investigated. The interfacial properties were analyzed to provide the theoretical guidance to improve the compatibility of blends. A reactive compatibilizer, poly(trimethylene terephthalate)-graft-(ma-

leic anhydride) (PTT-g-MA) was prepared from melt reaction and characterized with FTIR. The compatibilizer was melt blended into the CAB and PTT blends. The effects of different compatibilizers on the phase morphologies and mechanical properties of blends were characterized and the interfacial interactions were studied. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2302–2309, 2011

Key words: polymer blends; cellulose acetate butyrate (CAB); interfacial properties; reactive compatibilizer

INTRODUCTION

Polyesters are widely involved in our modern life, ranging from disposable bottles for carbonated soft drinks and water, to fibers for textiles and apparels, as well as photographic films and recording tapes.¹ However, there are two serious concerns on the sustainability of these materials. One is the basic building blocks for the above polyesters are all made from finite and nonrenewable petroleum resources.² The other is on the disposal of the petroleum-based polyester solid wastes. Although all aromatic polyesters degrade eventually, with hydrolysis being the dominant mechanism, the degradation rate is expected to be decades, depending on the exposed contact surface area of polyesters, crystallinity of polyesters and specific environmental factors such as humidity, pH and temperature.^{1,3–5} Thus, it becomes increasingly important to replace the current building blocks of polyesters with renewable and biodegradable materials.

Cellulose esters, a kind of polysaccharide, are prepared from the esterification of renewable and biodegradable cellulose derived from abundant plant residues, trees, dry grasses, and agriculture wastes, materials referred to as "Biomass."^{6,7} They are con-

sidered as potentially useful thermoplastic polymers in biodegradable applications. However, cellulose esters, by themselves, have severe limitations in applications due to their poor processibility and brittleness. The high melt viscosities and instability in the molten state of cellulose esters lead to difficulties in thermoplastic processing. In addition, yellowing often occurs at high temperature.⁸ Furthermore, although cellulose esters have high tensile strength and modulus, the impact strength and elongation at break are relatively low compared with petroleum-based polyesters. To improve the thermoplasticity and impact resistance of cellulose esters is a great challenge in extending their applications.

Many research activities on incorporating biodegradable polymers, such as poly(3-hydroxybutyrate) (PHB), poly(hydroxybutyrate-co-valerate) (PHBV), polycaprolactone (PCL) or poly(tetramethylene glutarate) (PTG) with polyesters or cellulose esters have been carried out.^{9–26} Various strategies for such incorporation, such as copolymerization and melt blending have been employed. With the incorporation of these polymers, the biodegradability of polyesters, the rheological properties as well as impact strength of cellulose esters can be improved. The overall mechanical properties of modified polymers were, however, significantly decreased due to the linear chain structure of the incorporated aliphatic polyesters.

A novel polymer blend from petroleum-based polyester and cellulose ester with improved

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mechanical and biodegradable properties would be of great importance to the material world, not only as a solution to make the best use of renewable and biodegradable cellulose resources and unhook widespread dependence on petroleum, but also as a solution of reducing the growing environmental pollution. Aimed at solving the above problems, we studied novel polymer blends of bio-based cellulose esters-cellulose acetate butyrate (CAB) with petroleum-based polyesters-poly (trimethylene terephthalate) (PTT). The morphology and thermal degradation behavior of the melt blends were characterized and analyzed. The strategy to improve the compatibility of the blends are discussed with the synthesis of a compatibilizer, poly(trimethylene terephthalate)-graft-(maleic anhydride) (PTT-g-MA).

EXPERIMENTAL

Materials

Poly (trimethylene terephthalate) PTT was kindly supplied by Shell Chemicals L P, USA. Cellulose acetate butyrate (CAB; butyryl content 35–39%) was purchased from the Acros Chemical Co. Initiator (2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (Luperox 101), maleic anhydride(MA) polyethylene glycol (PEG) and poly (butylene glutarate) were obtained from Aldrich Chemicals Co.

Reactive melt mixing of PTT

The mixture of premeasured PTT and MA with initiator Luperox 101 was premixed. The resulting mixture was fed into a mixer at temperature 240°C for 5 min at a speed of 100 rpm.

Melt mixing of PTT/CAB and PTT/CAB/PTT-g-MA

Mixtures of PTT/CAB or PTT/CAB/PTT-g-MA at different weight ratios were blended in a mixer (Plasticorder ATR, C.W. Brabender, USA) for 5 min. The screw speed was 100 rpm. The temperature was 240°C.

Measurement and characterization

To clearly demonstrate the morphology, the blends were fractured and immersed in the acetone at room temperature for 1 h to remove the CAB component. The fracture surfaces of the blends were observed using a Philips XL30 Scanning Electron Microscope (SEM). The thermal behaviors and thermal degradation of PTT/CAB blends were determined with thermal gravimetric analysis (TGA) (TGA-50, Shimadzu, Columbia, USA) at a heating rate of 10°C/min under a nitrogen atmosphere.

The chemical structures of maleic anhydride grafted PTT (PTT-g-MA) were analyzed with Nicolet 6700 FT-IR (Thermo Electron Corp.).

The mechanical properties of the extruded blends were performed on Instron Tensile Tester 4465. The diameter of the extruded blend rods is 2 mm.

RESULTS AND DISCUSSION

Morphology of PTT/CAB blends prepared from melt mixing

The miscibility of polymer blends plays an important role in determining the appearance, thermal behaviors, mechanical, and biodegradable properties of blends.²⁷ Several reports indicate that cellulose acetate butyrate (CAB) could form miscible or partially miscible blends with several aliphatic polyesters, such as poly (3-hydroxybutyrate), poly(hydroxybutyrate-co-valerate), poly (tetramethylene glutarate) and poly (caprolactone).^{15–26} To probe the miscibility of the CAB with PTT, the SEM images of the fracture surfaces of PTT and CAB blends, in the composition range of 0, 10, 20, and 40% CAB, prepared by the melt mixing, are shown in Figure 1. The CAB phases were etched out with acetone as a solvent, leaving the empty holes in the PTT matrix, suggesting that PTT and CAB were thermodynamically immiscible. It can be found that the CAB was evenly dispersed as small spheres within the PTT matrix. The average sizes of spheroid CAB phase increased from 0.6 μm to 2.5 μm as the CAB content was increased in the range of 0–40%.

Thermal behavior of PTT/CAB blends prepared from melt mixing

Figure 2 shows TG-DTG curves of the CAB, PTT, PTT/CAB blends in compositions of 20 and 40% CAB at a heating rate of 10°C in nitrogen. Table I lists the onset thermal degradation temperature (T_d), maximum degradation temperature (T_{dm}), char yield at 400°C and kinetic parameters. The CAB showed the lowest thermal degradation temperature with the beginning of debutyrylation and deacetylation around 339°C, and thermal pyrolysis of cellulose skeleton with the maximum weight loss rate at 385°C. The thermal degradation of PTT involves the hydroxyl end group initiated the depolymerization at 368°C, and the thermal degradation of the small fragments with the maximum degradation temperature of 418°C. The onset thermal degradation temperatures of PTT/CAB blends were between the pure PTT and CAB, at 349°C and 347°C, for blends containing 20 and 40% CAB, respectively. As the amount of the CAB increased, two maximum degradation temperatures appeared, centered at 372°C and 414°C for 40% CAB blends, suggesting that the

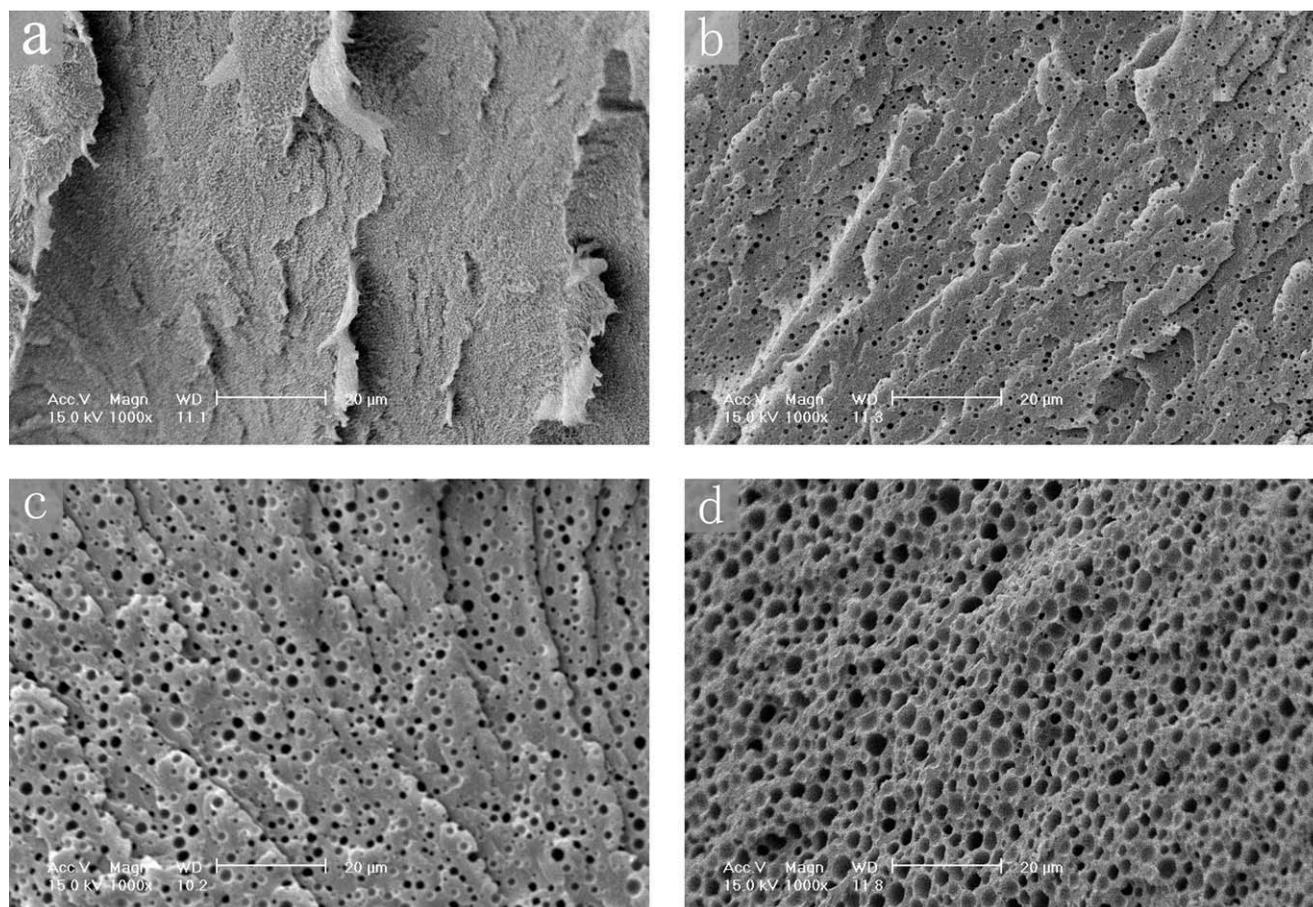


Figure 1 SEM images of PTT/CAB blends prepared from melt mixing. All samples were immersed in acetone for 1 h to etch away the CAB matrix. (a) PTT, (b) PTT/CAB = 90/10, (c) PTT/CAB = 80/20, (d) PTT/CAB = 60/40. (a–d) Scale bar: 20 μm .

thermal stability of both CAB and PTT components in the blends slightly decreased after blending. It may be attributed to the acetyl or butyryl groups released from the CAB which could accelerate the breakage of the ester groups in PTT.²⁸ The results, however, revealed that the thermal stability of the blends was better in comparison to the pure CAB. The char yields of PTT/CAB blends at 400°C were higher than that of the CAB alone, but lower than PTT. With increasing the amount of the CAB in the blends, the char yields decreased. Furthermore, the weight loss rates of the blends were even lower than that of both CAB and PTT, demonstrating the blends as a new class of materials may have better thermal properties than CAB alone.

Analysis of interfacial properties between PTT and CAB blends

Unlike small molecules, it is very hard to obtain polymer blends miscible at chain segmental or molecular scale. For immiscible polymer blends, the concept of compatibility is introduced, referring to interfacial adhesion and desirable properties of poly-

mer blends. The overall physical and mechanical properties of the blends are dependent on the proper interfacial tension between two polymers, which could generate small phase size for the dispersed phase and strong interfacial adhesion. The interfacial adhesion could transmit applied stresses between the two components. To develop the strategy to compatibilize the PTT/CAB blends, the analysis of the interfacial adhesion between polyesters and cellulose esters are very important. The interfacial tension and adhesion between polymer blends can be expressed based on the Harmonic-Mean equations as follows.²⁹

$$W_{12} = \frac{4 \cdot \gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4 \cdot \gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (1)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12} \quad (2)$$

where W is the work of adhesion, γ is the surface tension, γ^d its dispersive component and γ^p its polar component. The subscripts 1 and 2 correspond to the two polymer materials.

On the basis of the equations, the curved surfaces of interfacial tension and work of adhesion of blends with either PTT or CAB as a matrix were fitted with

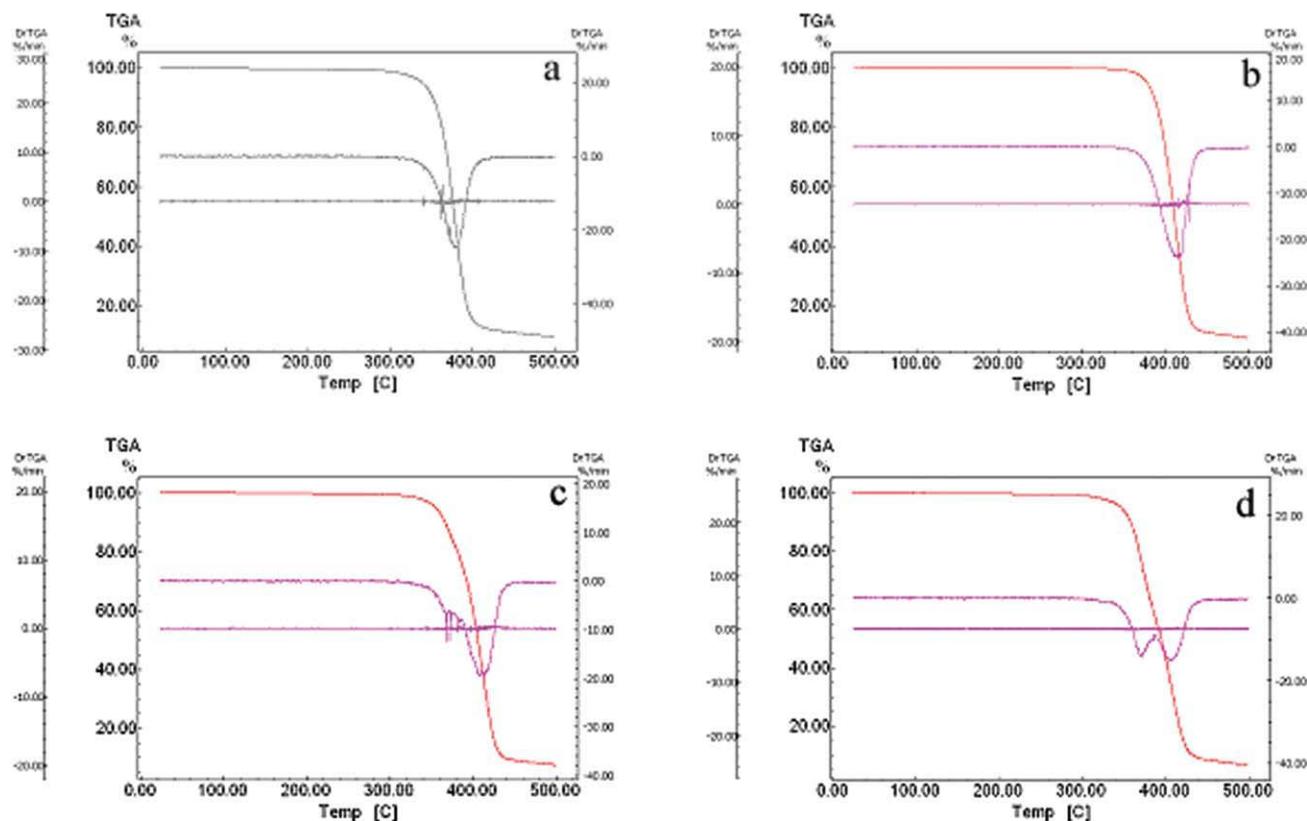


Figure 2 TG-1st DTG curves of CAB, PTT, and PTT/CAB blends. (a) 1st CAB, (b) 1st PTT, (c) PTT/CAB = 80/20, (d) PTT/CAB = 60/40. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a Matlab software, respectively, as indicated in Figures 3 and 4. The lower interfacial tension and higher work of adhesion are desired to improve the compatibility of the polymer blends. The increases in the dispersive component γ^d and polar component γ^p resulted in the higher work of adhesion. But it was not the case for the interfacial tension. The value of γ^p has a significant influence on the interfacial tension when γ^d is above 30. Lower interfacial tension could be obtained when γ^p is in the range of 10–15. The overall calculation results indicated that the component phase with γ^d above 30 mJ/m^2 and γ^p ranging from 10 to 15 mJ/m^2 will favor the interfacial adhesion and compatibility, in good agreement with the previous reports of the miscibility of CAB with the aliphatic polyesters, like poly(butylene succinate-co-adipate) (PBSA) with γ^d and γ^p of 43 and 14 mJ/m^2 as well as polycaprolactone (PCL) having γ^d and γ^p of 41 and 11 mJ/m^2 .^{12–23,27} The analysis

results were also consistent with the observation of the obvious phase separations of PTT and CAB blends due to the lower γ^d of 33 and γ^p of 9.7 mJ/m^2 for CAB. Typically, two approaches could be employed to enhance the interfacial adhesion between two components. One is to physically add compatibilizers into the PTT/CAB blends with the interfacial analysis as guidance. The other one is to chemically graft the maleic anhydride which could react with the hydroxyl group in the CAB at interfaces to PTT backbone by melt free radical grafting to form a reactive compatibilizer.

FTIR spectrum of PTT-g-MA and PTT/CAB/PTT-g-MA blends

Studies on polypropylene grafted with maleic anhydride PP-graft-MA have been reported before. There were, however, few reports about the melt grafting

TABLE I
Thermal Degradation Data of CAB, PTT, and Blends

Sample	T_d (°C)	T_{dm} (°C)	Char yield at 400°C (%)	$d\alpha/dt$ (%/min)
CAB	339	385	14	23.9
PTT	368	418	71	23.7
PTT/CAB = 80/20	349	420	60	18
PTT/CAB = 60/40	347	372 (414)	43	15.1

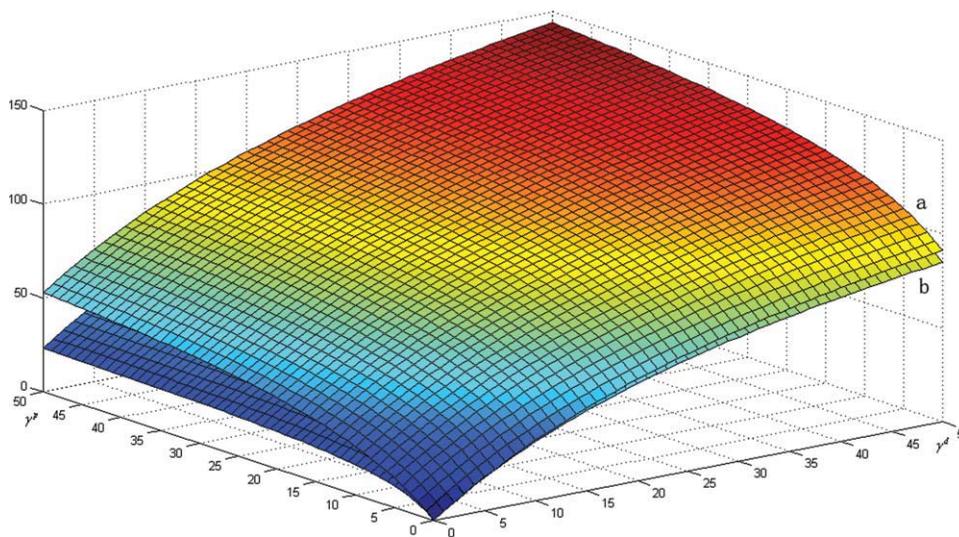


Figure 3 Response surface curve of work of adhesion W_{12} vs. γ_d and γ_p , (a) CAB (b) PTT as matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the PTT-g-MA. The typical melt grafting mechanism is as follows. The peroxide initiator could break into two radicals upon heating. The radicals will then extract hydrogen atoms from the backbone of the molten polymers to generate the macromolecular radicals which could initiate the grafting of the vinyl groups of MA. The grafting of the MA onto the PTT was confirmed by FTIR, as shown in Figure 5. The appearance of two absorption bands centered at 1778 and 1840 cm^{-1} are assigned to the symmetric and asymmetric stretching of the carbonyl groups in the grafted anhydride, respectively. The intense absorption band at 1721 cm^{-1} is characteristic of the ester group from the PTT.

Figure 6 shows the O—H stretching region in the FTIR spectrum of the PTT/CAB and PTT/CAB/

PTT-g-MA blends. The PTT/CAB absorption band centered at 3441 cm^{-1} , which is very broad, is indicative of the intramolecular hydrogen bonding of hydroxyls. With the addition of the PTT-g-MA, the broad band shifted to the lower wave number of 3432 cm^{-1} , which could be attributed to the formation of the intermolecular hydrogen bonding between anhydride and hydroxyl groups in the CAB.¹⁵

Effect of compatibilizers on morphology of the blends

To study the effects of the different compatibilizers, SEM images of the fracture surfaces of blends of PTT/CAB (80/20), PTT/CAB with polycaprolactone

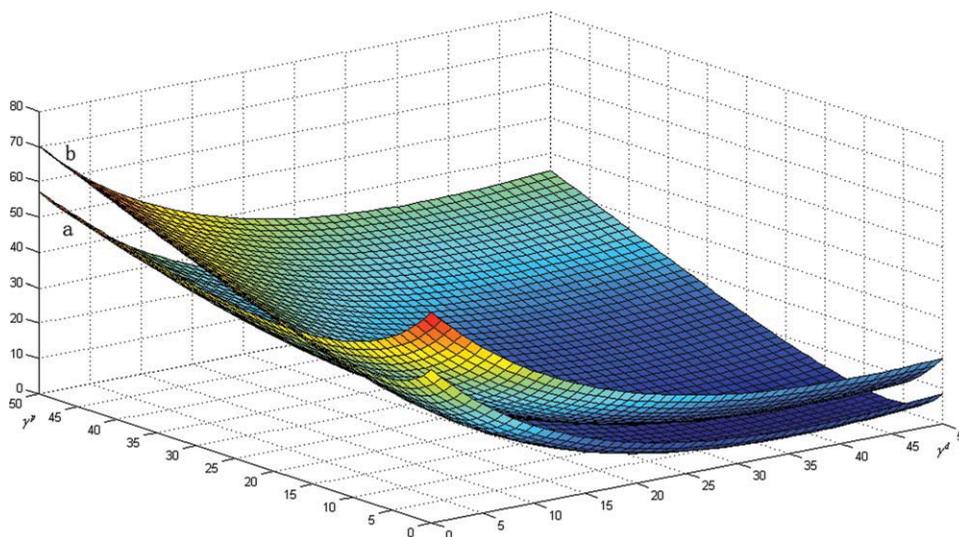


Figure 4 Response surface curve of interfacial tension γ_{12} vs. γ_d and γ_p , (a) CAB, (b) PTT as matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

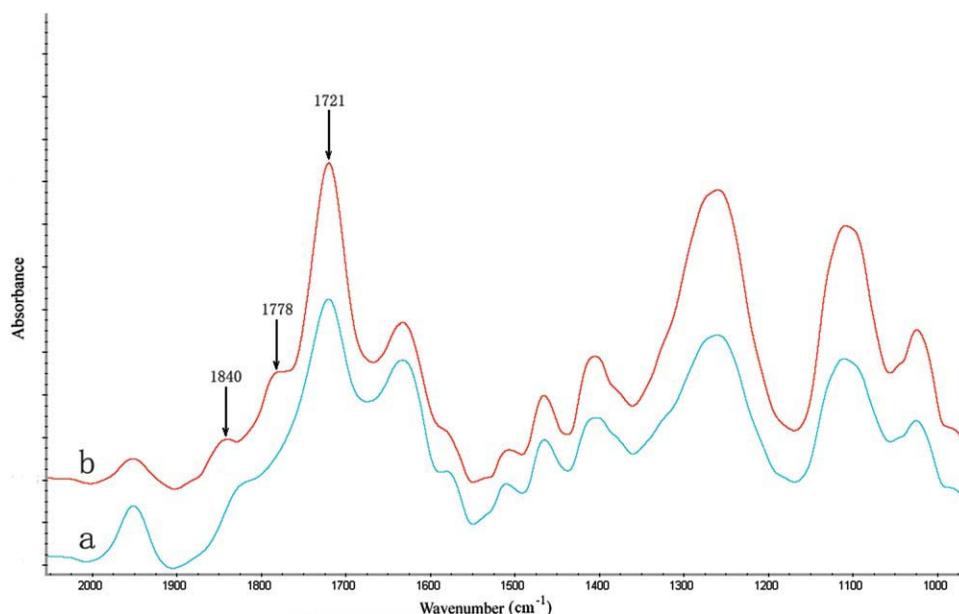


Figure 5 FTIR spectra of (a) PTT (b) PTT-g-MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(PTT/CAB/PCL), PTT/CAB with poly(1, 4-butylene glutarate) (PTT/CAB/PBG), PTT/CAB/MA, PTT/CAB/PEG 3400 and PTT/CAB/PTT-g-MA with a composition of 80/20/10 are shown in Figure 7(a–f). To clearly demonstrate the difference, the blends were immersed in acetone to remove the CAB phase. The CAB minor phases existed inside the PTT matrix in spherical forms. The PEG 3400 resulted in the slightly decreased sizes of minor phases and improved compatibility. The PCL, however, made the sizes of the minor phases even larger than those of the blends without it. The effect of the PBG was also negligible. It could be analyzed with the interfacial analysis. The CAB has relatively stronger work of adhesion and lower interfacial tension with PCL and PBG compared with the interactions with PTT. As a result, the added PCL and PBG may enrich in the CAB phase, instead of staying at the interfaces between PTT and CAB and acting as the compatibilizer. Considering the fact that PCL could be dissolved in acetone, the larger minor phases etched out should include CAB and enriched PCL. On the other hand, the compatibilizer of PEG 3400, having comparable interfacial interactions between PEG 3400/CAB and PEG3400/PTT, is slightly better. But it could be found that the effect of physically blending on the compatibility is very limited. The incorporated small molecules, maleic anhydride (MA) could react with free hydroxyl groups in the CAB through immigration to the interfaces, which could slightly reduce the sizes of minor phases. A reactive and amphiphilic compatibilizer containing one end compatible with PTT, and the other end reactive with CAB, such as PTT-g-MA, would be highly desirable. In fact, the

addition of the synthesized PTT-g-MA significantly reduced the sizes of the minor phases, shown in Figure 7(f), strengthened the interfacial adhesion.

Rheological properties of the blends

Figure 8 presents the variation of apparent viscosities with apparent shear rates for PTT, CAB, PTT/CAB = 80/20 and PTT/CAB/PTT-g-MA = 80/20/10 at 240°C. The increase in the apparent shear rate led to a decrease in the apparent shear viscosity, which implies PTT, CAB, and their blends are non-Newtonian fluids and follow shear-thinning

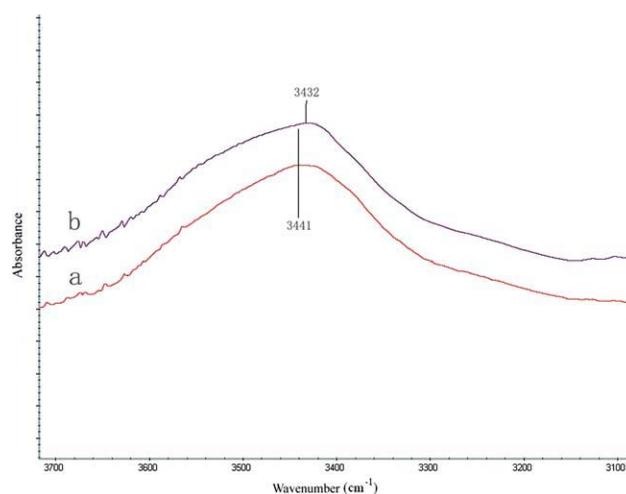


Figure 6 FTIR spectra of (a) PTT/CAB = 80/20 blend (b) PTT/CAB/PTT-g-MA = 80/20/10 blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

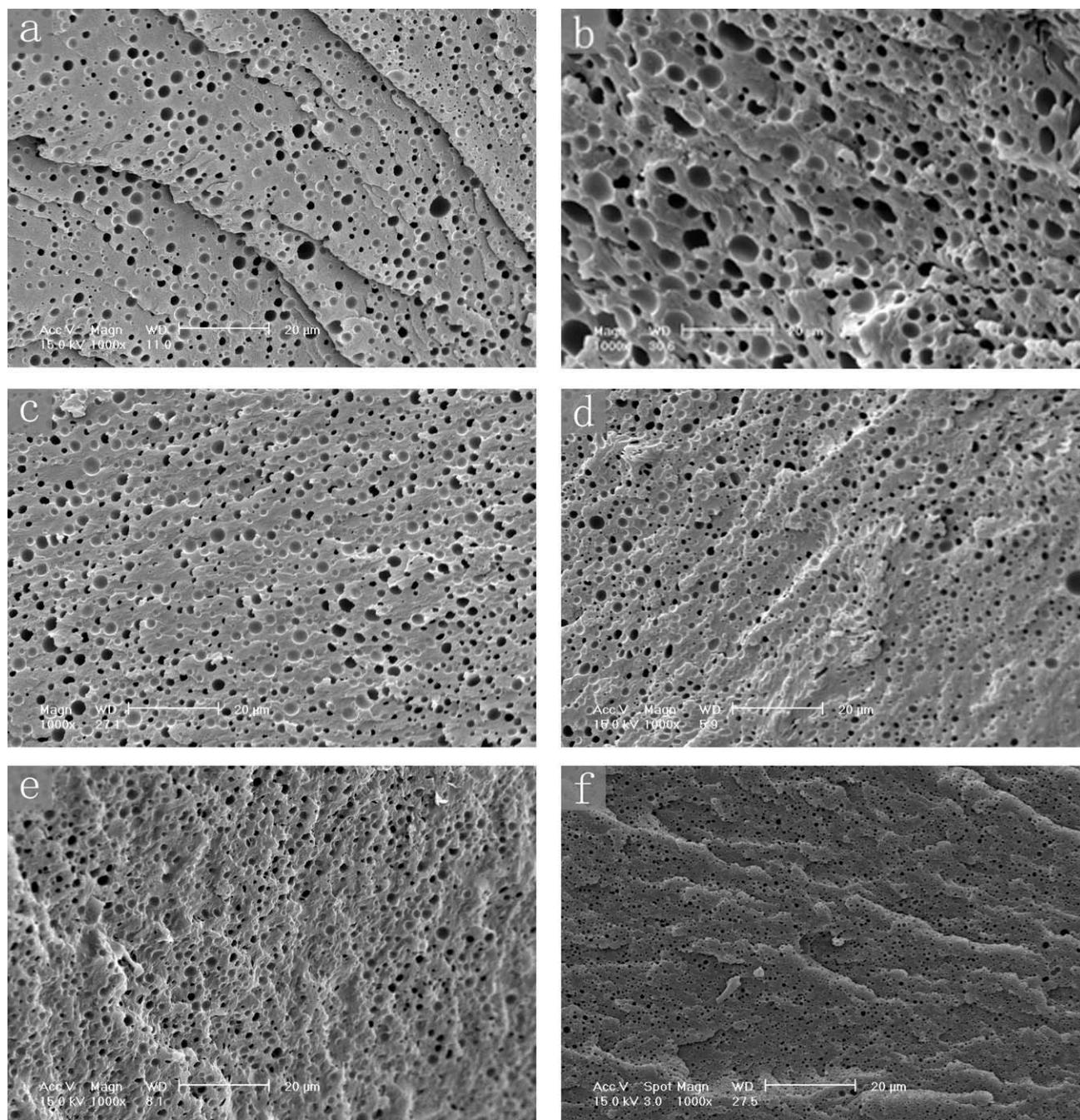


Figure 7 SEM images of PTT/CAB/compatibilizer blends prepared from melt mixing. All samples were immersed in acetone for 1 h to etch away the CAB matrix. (a) PTT/CAB = 80/20, (b) PTT/CAB/PCL = 80/20/10, (c) PTT/CAB/PBG = 80/20/10, (d) PTT/CAB/Maleic Anhydride (MA) = 80/20/10, (e) PTT/CAB/PEG3400 = 80/20/10, (f) PTT/CAB/PTT-g-MA=80/20/10. (a–f) Scale bar: 20 μm .

behavior. It should be noted that the viscosity of PTT/CAB/PTT-g-MA (80/20/10) was higher than that of PTT/CAB (80/20). The increase could be a result of the reaction or interaction of anhydride group on PTT-g-MA with free hydroxyl group on CAB at interface and the formation of crosslinked structure, consistent with the observations from the FTIR spectrum and SEM results in Figures 6 and 7(f).

Mechanical properties of the blends

The tensile strength and elongation at break of CAB, PTT, and their blends are listed in Table II. Compared with the original of CAB and PTT, the tensile strength of the PTT/CAB blends decreased due to the introduction of the interfacial defects resulting from the immiscibility. With an increase in the amount of CAB in the polymer blends, the tensile strength increased from

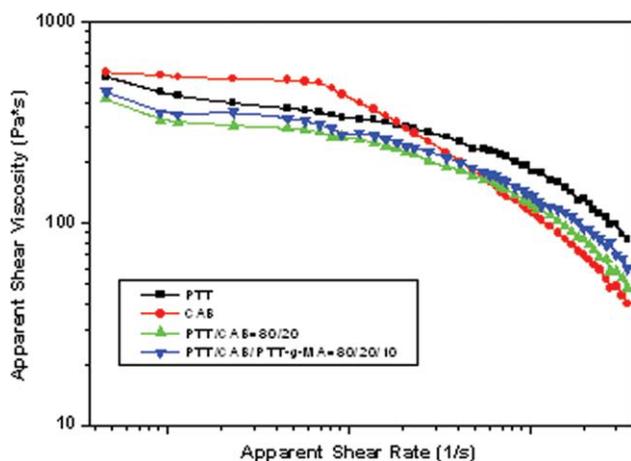


Figure 8 Apparent shear viscosity of PTT, CAB, PTT/CAB = 80/20 and PTT/CAB/PTT-g-MA = 80/20/10 versus apparent shear rate at 240°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

40.04 ± 3.82 to 46.41 ± 2.32 MPa. As the amount of the CAB was above 20%, the elongation at break decreased sharply, even lower than that of the original CAB. The addition of the compatibilizer, PTT-g-MA to the blends resulted in the significant increase in the tensile strength and elongation at break, 47.28 ± 2.26 MPa and 234%, respectively. It could be explained by the strengthening of the interfacial adhesion between PTT-g-MA and the hydroxyl groups in the CAB at the interfaces.

CONCLUSIONS

A novel polymer blend from bio-based cellulose acetate butyrate (CAB) and poly(trimethylene terephthalate) (PTT) were prepared by melt mixing. The SEM images of etched fracture surfaces of PTT/CAB blends indicated that the PTT and CAB were thermodynamically immiscible. With increasing amount of CAB, the sizes of minor phases increased in the blends. The thermal gravimetric analysis results showed that the thermal stability of PTT/CAB

TABLE II
Mechanical Properties of Polymer Blends

	Tensile strength (MPa)	Elongation at break (%)
PTT/CAB = 100/0	50.46 ± 2.34	390
PTT/CAB = 80/20	40.04 ± 3.82	194
PTT/CAB/PTT-g-MA = 80/20/10	47.28 ± 2.26	234
PTT/CAB = 70/30	42.27 ± 2.63	80
PTT/CAB = 50/50	44.93 ± 3.04	60
PTT/CAB = 30/70	45.80 ± 2.14	20
PTT/CAB = 20/80	46.41 ± 2.32	6
PTT/CAB = 0/100	53.85 ± 2.43	72

blends were better than the CAB alone. PTT-graft-MA was synthesized via melt reactive mixing process. The effects of reactive compatibilizer, PTT-g-MA and physically added compatibilizers, PEG 3400, PBG, MA, PCL on the morphologies and interfacial interactions of blends were investigated. Among them PTT-g-MA could give better compatibility characteristic of significantly reduced phases sizes, the strong interfacial interactions and improved mechanical properties.

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