

Melt Characteristics, Mechanical, and Thermal Properties of Blown Film from Modified Blends of Poly(butylene adipate-*co*-terephthalate) and Poly(lactide)

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ABSTRACT: Blown films from poly(butylene adipate-*co*-terephthalate) and poly(lactide) (PLA) blends were investigated. The blends were prepared in a twin-screw extruder, in the presence of small amounts of dicumyl peroxide (DCP). The influence of DCP concentration on film blowing, rheological, mechanical, and thermal properties of the blends is reported in this article. Rheological results showed a marked increase in polymer melt strength and elasticity with the addition of DCP. As a consequence, the film homogeneity and the stability of the bubble were improved. The modified blend films, compared with the unmodified blend, showed an improvement in tensile strength and modulus with a slight loss in elongation.

Fourier transform infrared and gel results revealed that chain scission and branching were more significant than crosslinking when the DCP loadings in the blends were not higher than 0.7%. A reduction in melt temperatures of PLA was observed due to difficulty in chain crystallization. The concentrations of DCP strongly affected the melting temperatures but had an insignificant effect on the decomposition behavior of the blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4986–4992, 2012

Key words: films; poly(lactide); poly(butylene adipate-*co*-terephthalate); blends; reactive extrusion

INTRODUCTION

Blown-film extrusion is an important processing method widely used in producing a variety of packaging films and bags. In such a process, the polymer melt is shaped in the form of a bubble by air blowing. The molten blown film is then cooled down and crystallization occurs in a short period of time. Therefore, suitable polymers for film making should have characteristics of high melt strength, good thermal stability, and high crystallization rate. Polyethylene (PE) is one of the ideal polymers for blown-film applications. Several tons of PE packaging films are produced annually.

In recent years, increased emphasis has been made on developing biodegradable products to replace existing non-biodegradable materials to overcome the landfill crisis and environmental problems. Poly(butylene adipate-*co*-terephthalate) (PBAT) is a commercially available biodegradable aliphatic-aromatic *co*-polyester, produced from fossil resources. PBAT has high flexibility and toughness.¹ With the

aid of enzymes, it can fully degrade within a few weeks.² Therefore, it is one of the candidates for biodegradable packaging materials. However, its low modulus, high water vapour transmission rate and high cost limit its application. Poly(lactide) (PLA) is a biodegradable polymer which is derived from 100% renewable resources. It is produced by polymerization of lactide (or lactic acid) which is a product from microbial fermentation of agricultural by-products such as corn starch or other starch-rich substances.^{3,4} Compared with PBAT, PLA has higher modulus and strength but lower elongation at break and much lower cost. Therefore, combining the high toughness PBAT with the high stiffness PLA may overcome some of the limitations of each material and could result in biodegradable blends of balanced properties. Blending of these two polymers has been investigated by a number of researchers.^{5–13} The research works in this area were mainly focused on the binary blends where PLA forms a matrix phase with PBAT as a minor phase. The content of PBAT commonly used for improving the elongation at break and impact strength of PLA is in the range of 5–20 wt %.^{5–9} The properties of the resulting blends are influenced by a variety of factors like blend composition, processing conditions, and compatibility between the two components. A considerable amount of the literature describes efforts made to improve the compatibility between the two

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components.⁵⁻⁷ Zhang et al. found both better miscibility and more shear yielding in the toughening of PLA/PBAT (70/30) blends containing a random terpolymer of ethylene, acrylic ester, and glycidyl methacrylate compatibilizer (T-GMA).⁶ Yuan et al. reported the effectiveness of maleic anhydride (MA) as a compatibilizer in this system.⁷ Ultrasound irradiation was recently applied to the PLA/PBAT blends during melt mixing to enhance adhesion between the PLA matrix and the PBAT domains.⁸ A drastic reduction of the PBAT particle size was clearly observed after irradiation for 30 s. At longer irradiation times, the PBAT phase underwent flocculation. Whereas several studies on biodegradable blends of PLA and PBAT can be found in the literature, published work on film blowing of these is very rare.

In this study, we attempted to investigate the modification of PBAT/PLA blends through the use of a small amount of organic peroxide; i.e., dicumyl peroxide (DCP), to obtain a properly modified biodegradable blend for blown-film processing. The effects of DCP addition on melt characteristics of the blends were investigated using a parallel-plate rheometer, a melt flow index (MFI) tester, and a melt strength tester. The effects of DCP concentrations on film homogeneity, tensile, and thermal properties of blown-film products are discussed. The changes in polymer structure brought about by peroxide addition were analyzed using Fourier transform infrared (FTIR) spectroscopy. Reaction mechanisms are proposed.

EXPERIMENTAL

Materials

PBAT, Ecoflex FBX 7011, was purchased from BASF. It has a M_w of 105,000 g/mol and M_n of 47,000 g/mol as determined by gel permeation chromatography (GPC) analysis. PLA 4042 D was from NatureWorks LLC (Minnetonka, MN) with a M_w of 201,000 g/mol and M_n of 101,000 g/mol (GPC analysis). DCP was purchased from Aldrich Chemical Co. (Milwaukee, Switzerland) and used without purification.

Blend preparation and blown-film extrusion

Before compounding, both PBAT and PLA pellets were dried under vacuum at 80°C for 12 hr to remove moisture. PBAT/PLA blends in the fixed weight ratio of 70/30 were prepared in a TSE16 intermeshing co-rotating twin-screw extruder (Prism, Staffordshire, UK). DCP in the concentrations of 0–0.5 wt % was added to the blends during melt mixing. A temperature profile of 135, 180, 160, 160, and

150°C from feed zone to die and a screw speed of 60 rpm were carefully controlled.

Biodegradable films were prepared using a blown-film extrusion process. The melt temperatures of the extruder (Haake Rheomex Film Blowing Machine, Karlsruhe, Germany) were set in the range of 135–155°C. A screw speed of 40 rpm was used. A spiral flow blown-film die with a diameter of 30 mm was used. The die temperature was set at 150°C. The blow-up ratio of the bubble was 3 : 1. This setting produced a bubble with an average film thickness of 60 μm (0.06 mm).

CHARACTERIZATION AND TESTING

Extraction test

Soxhlet extraction tests were performed on the blends to determine the crosslink fraction or gel that might occur as a result of peroxide addition. Approximately 0.3 g of each sample was wrapped in a 120 mesh stainless steel cage and extracted for 6 hr in refluxing xylene containing 1% of antioxidant (Irganox 1010, Ciba-Geigy). After extraction, the samples were dried in a vacuum oven until constant weight. The gel fraction was calculated as the weight of the dried extracted sample divided by the original sample weight.

Melt characteristics

Rheological properties of various PBAT/PLA blends were studied using a parallel-plate rheometer (Physica MCR 500, Stuttgart, Germany) with a 25-mm diameter parallel-plate. The samples of 1-mm thick, cut from compression-moulded sheets, were loaded between the parallel plates and melted at 180°C. A frequency sweep test was subsequently performed to determine the dynamic properties of the blends. The strain and frequency range used were 5% and 0.1–200 rad/s, respectively.

Changes in MFI of PBAT/PLA blends brought about by peroxide were determined using a Kayness D-7053 melt flow indexer. The samples were melted at 190°C. The melt was driven through a capillary die using a 2.16 kg piston. The weights of extrudate were measured at 10-min intervals.

Melt strength measurements were performed on a Ceast Rheologic 5000 capillary rheometer (Turin, Italy) equipped with a drawing system. The details of Rheologic 5000 capillary rheometer set up for melt strength tester were reported earlier by Xu et al.¹⁴ The blend particles were placed into the barrel and heated at 180°C. The molten polymer strands were forced through the capillary die by the piston and then drawn down by the two counter rotating wheels. The tensile force applied to the wheels (F_b)

and the draw rate at break (v_b) allowed calculation of the melt strength (σ_b) as follow.

$$\sigma_b = F_b v_b / A_0 v_0$$

where A_0 is the initial cross-section of molten string at the die outlet.

In this study, the capillary diameter was 2 mm with a length to diameter ratio of 40. The piston speed (v_0) was 0.07 mm/s.

FTIR spectroscopy

The FTIR measurements were performed on a Perkin Elmer System 2000 (Waltham, MA). Spectra were recorded in transmission mode at room temperature with a resolution of 4 cm^{-1} over the range of $4000\text{--}400 \text{ cm}^{-1}$. Film samples for the FTIR measurement were prepared by solution casting directly onto a KBr disc, using chloroform (CHCl_3) as a solvent.

Film homogeneity

All blown-film samples were measured for their thickness. The measurements were carried out at 20 positions at a distance of 5 cm from each other along the machine direction. The average film thickness (h) and the standard deviation (s) were then calculated. The inhomogeneity of the film, or inhomogeneity index (r), for a given machine parameter is described by the ratio of s and h . The better the homogeneity of a film, the smaller the r value.¹⁵

Tensile testing

The tensile testing was performed using an Instron Model 5566 tensile tester, equipped with a 1 kN load cell. Rectangular samples of 10-mm wide and 100-mm long were cut from the blown-film samples. The test was conducted at a cross-head speed of 50 mm/min and gauge length of 45 mm. All reported results are the averages of at least five test specimens.

DSC and TGA

The thermal properties of neat PBAT, PLA, and their blends were measured by a Perkin Elmer DSC7 (Waltham, MA) differential scanning calorimeter. All specimens were weighed about 6–12 mg and a temperature range of $50\text{--}200^\circ\text{C}$ was used. The heating and cooling rate used was $10^\circ\text{C}/\text{min}$ for all samples. The thermal stabilities of the samples were investigated using a Mettler Toledo TGA/SDTA 851 thermal gravimetric analyzer (Schwerzenbach, Switzerland). The sample was heated from 100 to 800°C at a

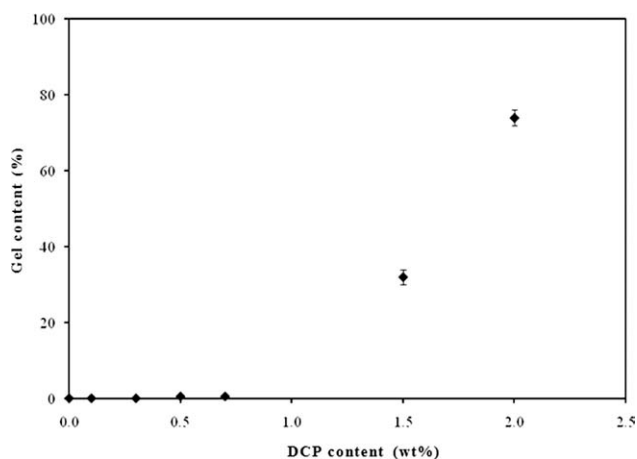


Figure 1 Gel content of various PBAT/PLA (70/30) blends modified with different loadings of DCP.

heating rate of $20^\circ\text{C}/\text{min}$. Nitrogen was used as a purge gas with a flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Solvent extraction results

During the reactive blending of PBAT and PLA in the presence of peroxide, gels may be formed as a result of degradation and crosslinking of the polymer chains. For blown-film processing, the presence of gels in the materials is unacceptable since gels are aesthetically displeasing and they may act as stress concentrators that would lead to premature failure of the blown-film products. In the first stages of this study, the crosslink portion or gel in the PBAT/PLA blends was analyzed. Figure 1 shows the content of gel in the blends as a function of DCP concentration. The addition of DCP in the range of 0.1–0.7 wt % shows a negligible amount of gel in the blend products. Increased DCP loadings between 1.5 and 2.0% lead to a significant rise in the gel content. Gel contents of 37% and 75% were observed in the blends with 1.5 and 2.0% DCP, respectively. During extrusion of these two samples, high processing torques were observed and the extrudates showed melt fracture characteristics. This is indicative of poor flow properties of these high viscosity materials. From these results, the DCP contents of materials used in our further investigation were kept in the range of 0–0.5 wt %, to minimize the crosslink reactions and to produce modified blends that are free of gels.

Flow properties and melt strength

Figure 2(a,b) show the plots of complex viscosity (η^*) and storage modulus (G') as a function of angular frequency for pure PBAT, pure PLA, and their 70/30 blends with and without DCP addition.

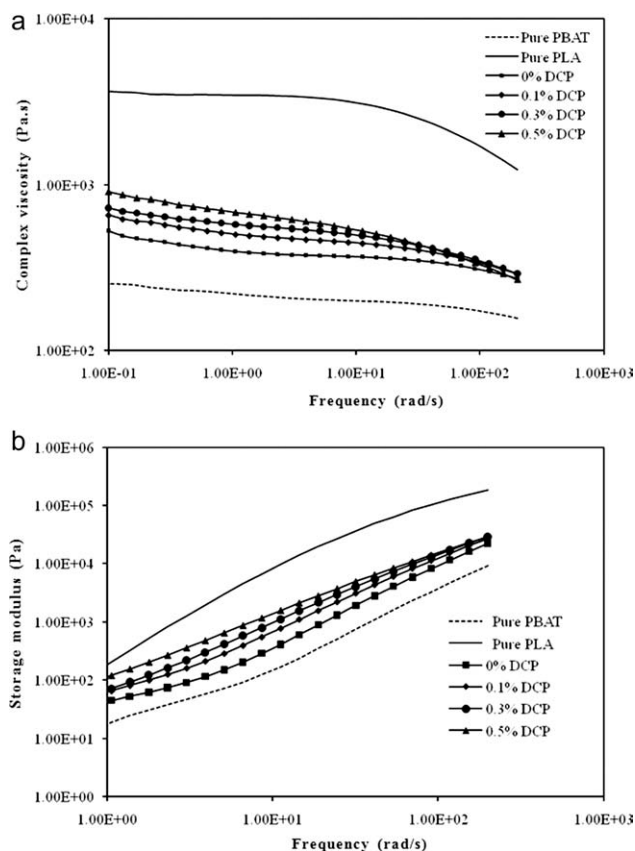


Figure 2 Complex viscosity (a), and storage modulus (b) as a function of angular frequency of various PBAT/PLA blends.

Compared with PBAT, PLA shows a greater frequency dependence of viscosity. A frequency-independent viscosity is observed only for PLA in the lower frequency region (<10 rad/s). Beyond 10 rad/s, the melt flow behavior of PLA changes from Newtonian to shear thinning. PLA also shows a much higher viscosity than PBAT. This is possibly due to the higher molecular weight of PLA (201,000), which is nearly twice that of PBAT (105,000). In the case of PBAT/PLA blends, the complex viscosities of all blends are in between those of the two main components as expected. DCP shows a strong effect on blend viscosity, especially in the low frequency region (<10 rad/s). The magnitude of the viscosity increment varies systematically with the content of DCP in the blends. The storage moduli, reflecting the elasticity of the materials are shown in Figure 2(b). An improvement of elasticity is clearly seen in the blends modified by DCP. The storage modulus becomes less sensitive to frequency as the DCP loading increases. These rheological results indicate changes in polymer structure upon DCP addition. In this context, chain branching and/or crosslinking may occur during the reactive blending process. For the samples used in this study (with 0.1–0.5% DCP), crosslinks between chains seem unlikely since the

extraction test showed that no gel existed. Therefore, polymer chain branching after peroxide addition is believed to be the major reaction in these systems. Chain branching will restrict the polymer chain mobility and, so induce an increase in polymer viscosity and elasticity. Another explanation for the observed increment in the complex viscosity in the modified blends could be an increased bonding between the two phases. The work of Lee et al.⁸ showed that the viscosity of PLA/PBAT (50/50) blends was increased by ultrasonic irradiation. A strong interaction such as transesterification was believed to be the cause. Also, in a similar system, the addition of T-GMA compatibilizer led to an increase in the molecular interactions in the blend, so hindering the movement of the polymer chains.⁶

The effects of DCP on the rheological properties of the blends can be seen also in the MFI and melt strength (Table I). The unmodified blend has a MFI of 8.5 g/10 min at 190°C. A dramatic reduction in the MFI values is observed after the addition of DCP to the blends. These MFI results are in agreement with those of complex viscosity. With the addition of 0.5% DCP, the MFI value drops down to 0.32 g/10 min.

Melt strength is another important property of blown-film materials. This is a measure of the polymer resistance to extensional deformation. Due to the low melt strength of the unmodified PBAT/PLA blend, the melt strands fractured very soon after leaving the capillary die. Therefore, the value of the melt strength could not be detected and is reported as zero in Table I. This is the principal reason why good film blowing of this material is difficult to achieve. The addition of DCP in small amounts of 0.1–0.5 wt % improves the melt strength of all the blends. According to Yuan et al.,⁷ the melt strength of PLA/PBAT (90/10) blends increased correspondingly with the use of increased of MA crosslinking comonomer in the systems.

FTIR results

Figure 3 shows the FTIR spectra of pure PBAT, pure PLA, and their corresponding blends with and

TABLE I
Melt Flow Index (MFI), Melt Strength, and Film Inhomogeneity Index of Various PBAT/PLA (70/30) Blends Modified with Different Loadings of DCP

DCP loading (%)	MFI (g/10 min)	Melt strength (N/m ²)	Inhomogeneity index (%)
0.0	8.52 ± 0.44	0.0	4.3
0.1	4.67 ± 0.32	4.5	3.9
0.3	2.39 ± 0.36	6.7	2.3
0.5	0.32 ± 0.04	7.4	3.5

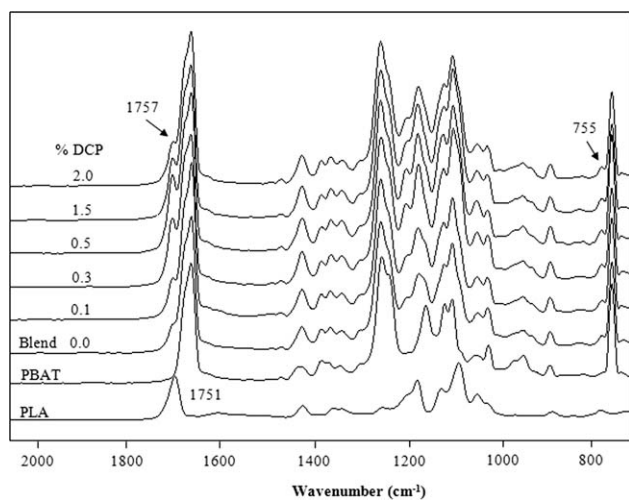


Figure 3 FTIR spectra of various PBAT/PLA blends modified with different loadings of DCP.

without DCP. The peak band wave number and assignments are listed in Table II. The spectra show characteristic ester absorption peaks at 1104, 1120, 1165, and 1269 for the stretching vibration of the C—O of PBAT and at 1087, 1129, 1184, and 1268 for the stretching vibration of the C—O of PLA. The carbonyl peak of PLA shifts slightly from 1751 cm^{-1} for pure PLA to 1757 cm^{-1} for the PBAT/PLA blends. This is an evidence of hydrogen bonding between PBAT and PLA in the blends. The peak bands of PLA, ascribed to the carbonyl (at 1757 cm^{-1}) and —CH— bending (at 755 cm^{-1}) vibrations, change greatly when the DCP concentration varies from 0.0 to 2.0 wt %. The intensities of these peaks increase systematically when the DCP loading is increased from 0.1 to 0.5%, but then drop drastically when the DCP content is increased further to 1.5 and 2.0%. These results indicate that some chemical reactions have taken place during the reactive blending process. Three possible reactions are chain scission, branching, and crosslinking. Figures 4 and 5 demonstrate reactions between PBAT and PLA in the presence of peroxide. The chain reaction starts with the decomposition of peroxide, giving primary free radi-

TABLE II
IR Peak Assignments for PBAT and PLA

Assignment	Peak position (cm^{-1})	
	PBAT	PLA
—OH bending	1047	1047
—C=O stretching	1715, 1732	1751
—CH ₃ bending	1453	1455
—C—O—stretching	1269, 1165, 1120, 1104	1268, 1184, 1129, 1087
—C—C—stretching	—	926, 868
—CH—bending	—	871, 755
—CH ₂ —stretching	2957, 2874	—
—CH ₂ —rocking	729	—

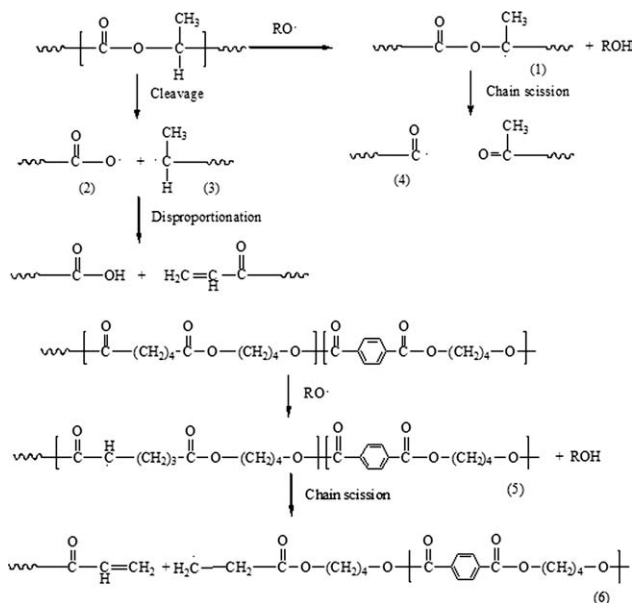
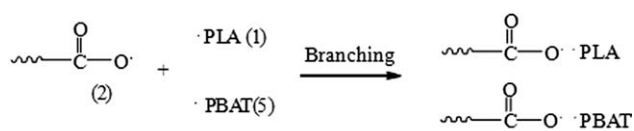


Figure 4 Proposed reactions for the chain scission of PLA and PBAT in the presence of peroxide.

icals. Then hydrogen abstraction from PBAT and PLA takes place, producing PBAT and PLA macroradicals. These radicals may cause scission, chain branching, or crosslink reactions. In the presence of low level of peroxide (0–0.7%), chain scission and branching dominate. The extraction results show no crosslink gel in those samples. With DCP content increasing beyond 0.7%, a marked decrease in the intensities of the carbonyl peak of PLA is observed. Under these conditions, a large number of radicals are generated and these combination of macroradicals causes crosslinking. The solvent extraction tests reveal a gel content as high as 37% and 75% in the blends with 1.5 and 2.0% DCP, respectively.

Blown-film properties

The properties of blown-film products are dependent on many factors.¹⁶ Film homogeneity is an important property for many applications. However,



The radicals could be (2) or (3) or (4) or (6).

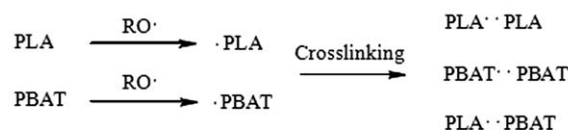


Figure 5 Expected reaction for the branching and crosslinking of PBAT and PLA in the blends.

TABLE III
Effect of DCP Loadings on Tensile Modulus, Strength, and Elongation at Break of PBAT/PLA Blown Films

Sample	DCP (%)	Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Pure PBAT	0.0	0.03 ± 0.00	18.77 ± 1.63	388.24 ± 44.81
Pure PLA	0.0	1.77 ± 0.24	44.08 ± 7.30	6.04 ± 2.75
Blend film	0.0	0.37 ± 0.04	23.79 ± 1.99	363.58 ± 24.34
	0.1	0.53 ± 0.06	27.05 ± 2.45	289.48 ± 30.75
	0.3	0.47 ± 0.02	30.32 ± 1.19	264.67 ± 19.58
	0.5	0.50 ± 0.04	26.71 ± 1.58	278.30 ± 33.92

analytical investigation of this property is very rare. For blown-film processing, the homogeneity of film correlates to the stability of bubble in the process.¹⁷ Any pulsation of the bubble affects the film homogeneity. In this study, the homogeneity of the prepared films is reported in the term of an r value where r is the inhomogeneity index. A lower r value means higher film homogeneity. As shown in Table I, all the modified blend films have r values below 4.0% which are lower than those of the unmodified blend. This confirms that DCP can improve polymer melt strength and can enhance bubble stability in the film blowing process. Munstedt et al.,¹⁵ reported that the best homogeneity of linear low density PE films has r of 7% for a film with the thickness of 31 μm . However, their investigations found no general relationship between the homogeneity of the film thickness and the bubble stability. This finding is in contrast to that reported by Fleissner.¹⁷

The tensile results of the unmodified and modified PBAT/PLA blends are shown in Table III. The unmodified blend (without DCP) shows a modulus of 0.37 GPa with a tensile strength of 23.79 MPa and an elongation of approximately 360%. The addition of peroxide in the range from 0.1 to 0.5% leads to a slight improvement in tensile strength and modulus with a slight loss in elongation. However, for processing productivity, the modified samples are easily blown into films since bubbles are very stable and

plastic wastage during film blowing is rather small. On average, the tensile strength and modulus of the modified samples are about 17 and 35% greater than those of the unmodified blends.

Figure 6 demonstrates the DSC thermograms of pure PBAT, pure PLA and their blends. PBAT shows a broad melting endotherm from 70 to 150°C. This has been explained as being due to the random structure of the copolymer, which cannot crystallize easily.¹⁸ In the case of PLA, a sharp melting peak at 150°C is clearly seen. In the unmodified blend (0% DCP), two separate melting peaks are observed. A broad melting peak in the lower temperature region (around 90–140°C) belongs to the main PBAT phase whereas a sharp peak at 148°C is the melting of the PLA crystals. According to Zhao et al.,⁵ blending of PBAT with PLA has no effect on the melting temperature of PLA. In that work, blends showed a melting temperature around 150°C.⁵ In this work, changes in the PBAT melting characteristics brought about by DCP addition are difficult to verify due to its broad melting range. Nevertheless, a systematic reduction in the PLA melting peak with an increase in the DCP concentration is clearly observed. The plot of PLA melting temperature versus amount of DCP in the blends is shown in Figure 7. It clearly reveals a linear relationship with the R^2 of 0.97. The formation of chain branching in the modified blends reduces polymer chain organization and crystallization. As

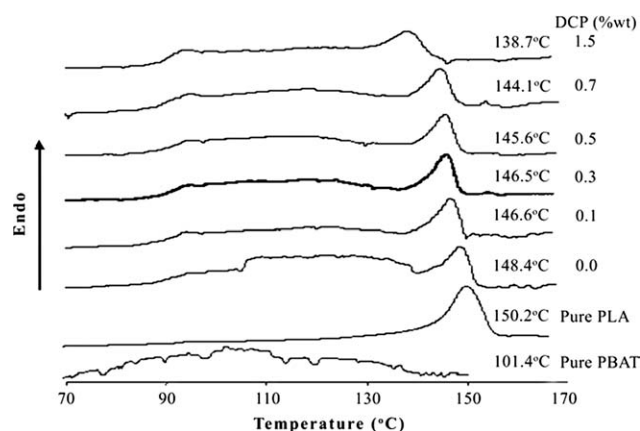


Figure 6 DSC heating thermograms of PBAT/PLA (70/30) blends modified with different loadings of DCP.

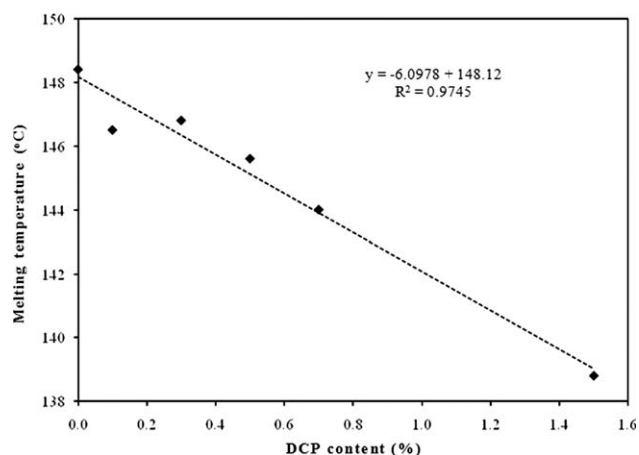


Figure 7 Melting temperature of PLA in the blends as a function of DCP concentration.

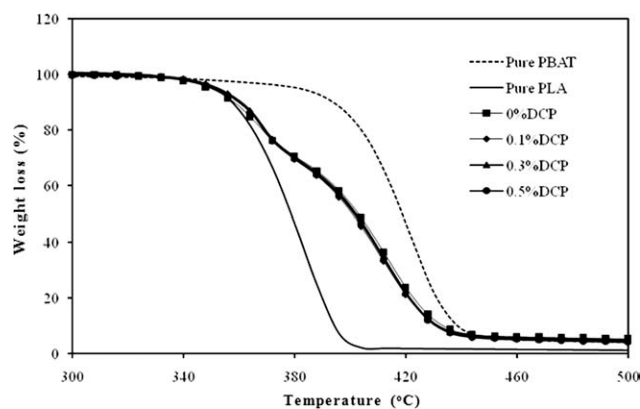


Figure 8 TGA thermograms of various PBAT/PLA (70/30) blends.

a result, smaller and less perfect crystals are formed and this causes a decrease in the melting temperatures.

Figure 8 shows the TGA thermograms of pure PBAT, pure PLA, and their blends with and without DCP addition. Pure PBAT shows the onset of thermal degradation at 370°C, with a central degradation temperature at 450°C. PLA has less thermal stability than PBAT, with the onset of degradation at 340°C and with a central degradation temperature at 410°C. Two degradation steps are observed for the PBAT/PLA blend sample. The first degradation step at 357°C is the decomposition of PLA, while the degradation at 415°C is the thermal decomposition of PBAT. The addition of DCP in the range of 0–0.5% insignificantly affects the decomposition behavior of the two polymer components. Our earlier study found that incorporation of DCP in the higher amounts of 1.5 and 2.0 wt % resulted in a significant drop in the decomposition temperature of PLA in the blends.¹⁹

CONCLUSION

Reactive blending of PBAT and PLA in the weight ratio of 70/30 was performed in a twin-screw extruder in the presence of peroxide. The blends were blown into films with a thickness of approximately 60 μm and were then characterized. The content of DCP showed strong effects on the polymer structure and the properties. Gel was observed in blends with the DCP content higher than 0.7%. With a low

loading of DCP, chain branching occurred predominately. The formation of chain branching in the modified blends causes a difficulty in polymer chain crystallization. As a result, the crystals of smaller sizes or less perfection are formed and leads to blends with decreased melting temperatures. The addition of DCP significantly increased the elasticity and viscosity of the blends. Considering film blowing, the reactive blends were easily blown into films due to their good melt strength. The increase in melt strength of the blends was systematic with the increase in DCP loading. A slight improvement in tensile strength and modulus with a slight loss in elongation was observed after DCP addition. TGA results revealed that the blends had two degradation steps at 357 and 415°C, corresponding to the decompositions of PLA and PBAT components, respectively. DCP content in the range 0–0.5% insignificantly affected the decomposition behavior of the blends.

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