A study on properties of PLA/PBAT from blown film process

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Abstract. The aim of this work was to study the properties of films based on PLA/PBAT blend prepared by the reactive compounding. PLA/PBAT blends were prepared at the weight ratio of 80:20 together with peroxide as a reactive agent in a twin screw extruder with temperature profile of 160/170/180/190/210/220/190/175/150ºC from feed to die zone. All blended samples, neat PLA, and neat PBAT were characterized for morphology, mechanical and rheological properties. SEM micrographs showed finely dispersed phases of PBAT in PLA in all cases. The particle sizes of PBAT were around 1 µm. The results indicated that the drawability and toughness properties of PLA were greatly improved when blended with 20%wt PBAT. The interface adhesion, and mechanical properties of PLA/PBAT blends were also improved when adding a very small quantity of peroxide. PLA/PBAT blends were then used to produce films. The film characteristics and mechanical properties were examined. Tensile strength of films was significantly improved in the machine direction in PLA/PBAT/peroxide blends whereas the good optical transparent property were remained the same compared with neat PLA.

1. Introduction

A sustainable use of resources and the pollution prevention are important issues for generations to come. The needs of both renewable and non-renewable feedstocks management are vital. One of the most concerned feedstocks is a fossil, which is normally utilized for energy and as an intermediate for petrochemical industries including plastics. In terms of plastics, most of the conventional plastics are generally fossil-based and can be accumulated in the environment after usage as solid wastes. An alternative approach to replacing the non-biodegradable or/fossil-based plastics is the use of biobased plastics (could be either biodegradable or not), which have been recognized for decades.

Among bio-based polyester [1, 2], polyactic acid (PLA) is very fashionable and one of the most explored bioplastics. Polylactic acid has high modulus and strength comparable to that of petroleum-based plastics, making it an attractive alternative to conventional plastics. The use of PLA not only reduces the dependency on fossil fuels but also offers advantages such as biodegradability and biocompatibility. However, PLA is generally brittle and has low crystallinity, which limits its applications in various industries. To overcome these limitations, the development of compatibilizers and processing techniques has been extensively studied.

Compatibilizers are typically added to enhance the compatibility and interfacial adhesion between different polymer phases. One of the most commonly used compatibilizers is peroxide. Peroxide-based reactive compounding is a technique that allows for the in-situ formation of interfacial layers during melt blending, which can improve the mechanical and physical properties of the resulting blends.

Birefringence and drawability are significant properties that affect the film formation process. Birefringence is a measure of the optical anisotropy of a material, indicating how the material behaves under stress. Drawability, on the other hand, refers to the ability of a material to be stretched without breaking. Improving the drawability of PLA/PBAT blends is crucial for the production of high-quality films.

This study aimed to investigate the properties of PLA/PBAT blends prepared by reactive compounding and the effects of peroxide on their morphology, mechanical, and rheological properties. The focus was on evaluating the influence of peroxide on the drawability and toughness of the blends. The results showed that the addition of a very small amount of peroxide significantly improved the drawability and toughness properties of the blends, making them more suitable for film production.
based plastic [3]. Its tensile strength and elastic modulus are comparable to poly (ethylene terephthalate) (PET) [4]. However, PLA is brittle, possesses low heat distortion temperature (HDT around 60°C), low water vapor, and gas barrier properties [5-7], which limited its applications.

Many methods have been investigated in the literature to improve the toughness of PLA such as plasticization [8], copolymerization [9], and blending with a variety of flexible polymers, elastomers or rubbers. Blending PLA with other biodegradable polymers presents a more practical and economic measure to obtain products with properties not currently attainable [10]. In this sense, improving the brittleness of PLA is considered to be economical as PLA is less expensive when compared to other biodegradable polyesters. PLA/Poly (butylene-adipate-co-terephthalate) (PBAT) blends have been extensively investigated by many researchers [11-17] due to the flexibility of PBAT. In terms of the high toughness PBAT, it is considered to be a good candidate for the improved toughness of PLA [18]. The elongation at break of PLA was increased from 4% to 200% by addition PBAT 20 wt % (Ecoflex®) [19]. However, PLA /PBAT blend are immiscible [19]. In situ compatibilization could be achieved in PLA/PBAT blends in a presence of glycidyl methacrylate (GMA) using dicumyl peroxide (DCP) as a free radical initiator [11]. It led to reducing PBAT domain size and enhanced in their interfacial adhesion [20]. To ensure the material performance and feasibility of production, most of the compounds should be tested for finished products such as films, injection-molded articles and thermoformed items. However, there is very few information on blown film processing of PLA compounded with PBAT. Therefore, in this study we reported the reactive blend between PLA and PBAT with fixed ratio of 80:20. Their rheological, mechanical and morphological properties on reactive compounded polymers were investigated whereas the mechanical and optical properties of the resulting films were fully examined.

2. Experimental

2.1. Materials
PLA (4043D grade) was purchased from Nature Works LLC, USA. PBAT (Ecoflex F blend C1200) was purchased from BASF Chemical Company, Germany. Di (tert-butylperoxyisopropyl) benzene (Paradox® 14-40B-pd) was commercially supplied by Akzo Nobel (Asia) Co., Ltd. (Shanghai, PR China).

Table 1. The composition of reactive blend and the non-reactive blend of PLA/PBAT blends.

| Sample name | PLA | PBAT | Perkadox (phr) |
|-------------|-----|------|----------------|
| Neat PLA    | 100 | 0    | 0              |
| 80/20       | 80  | 20   | 0              |
| P0.002      | 80  | 20   | 0.002          |
| P0.02       | 80  | 20   | 0.02           |
| Neat PBAT   | 0   | 100  | 0              |

2.2. Blending and sample preparation
Before use, both PLA and PBAT resin were dried at 60°C for six h in an oven in order to remove all trace moisture and to prevent potential hydrolytic degradation during melt processing. PLA and PBAT were blended via a twin screw extruder (Labtech engineering, Thailand). The temperature profiles were set from feed zone to die at 160/170/180/210/220/190/175/150°C. The screw speed was maintained at 80 rpm. The weight ratios of PLA, PBAT and reactive agents in this study were shown in table 1. The extrudate was cooled in a water bath, pelletized and dried at 60°C for six h. The pellets were compression-molded into micro-tensile and impact specimens at 180°C for 4 min through a hot compression molding machine (Charcon tut CO., LTD). The films of blends were produced via the single screw extruder blown film (HAAKE); annular die with a 34 mm diameter. The temperatures were set at 160, 170 and 180°C and the temperature of die was set at 190°C. The blow-up ratio (BUR) of the bubble was 2.5:1. This setting produced a bubble with an average thickness of 0.03 mm.
2.3. Characterization and testing

2.3.1. Morphology. The micrographs of the blends were examined using a scanning electron microscope (SEM) operated at 15 KV. The specimens were fractured under cryogenic condition in liquid nitrogen and the fractured surfaces were sputtered with gold.

2.3.2. Rheological property. Shear Viscosity of sample melt were measured by using a capillary rheometer (ROSAND Rh 2200, Rosand (Bohlin Instrument)) at 190°C in a shear rate from 10-5000 s⁻¹, according to ASTM D 3835.

2.3.3. Mechanical properties. Mechanical properties of the specimens were investigated by using tensile and impact testing. The tensile testing was carried out on an Instron machine (High Wycombe, UK) at 23°C, crosshead speed of 10 mm/min on at least five dumbbell-shaped specimens of each material typed V and gauge length of 17 mm, according to ASTM D 638. Tensile modulus, elongation at break, tensile strength and toughness were determined. The Izod impact testing was performed on 5-10 specimens of each material using the impact tester (GT-7016-A2, Gotech Testing Machines, Taiwan) with maximum hammer energy of 4 J. Shape of the specimens conformed to ASTM D256. The tensile testing of blown film sample was carried out according to ASTM D882 via a universal testing machine. The crosshead speed of the test was set at 10 mm/min. This test was recorded for both machine and transverse directions (MD and TD).

2.3.4. Optical properties. Optical properties of films were investigated by using Hazemeter (Haze-gard plus, BYK additives and instruments, USA), according to ASTM D1003.

3. Results and discussion

PLA/PBAT (80:20) with and without peroxide were first compounded in a twin screw extruder. Neat PLA and PBAT were also processed at the same conditions for comparison. The morphology, mechanical and rheological properties were then examined for further film processing.

3.1. Morphology of the blends

SEM micrographs of PLA and PLA/PBAT blends were shown in figure 1. The cryo-fractured surface of the neat PLA was fairly smooth (not shown here). In the case of PLA/PBAT 80/20 blend, PBAT phase was finely dispersed in PLA matrix. PBAT particles were less than 1 µm. They could be considered as a partially compatible blend at this ratio. For PLA/PBAT/Perkadox reactive blends with adding Perkadox as less as 0.002 phr, finer morphology of the blend was achieved (figures 1(b)-1(c)) and the particle size of dispersed phases was reduced. The in situ free radical reaction of peroxide improved the compatibility of PLA/PBAT blend, providing better interfacial adhesion between PLA and PBAT phases.

![Figure 1](image-url) Scanning electron microscopy (SEM) images of the cryo-fractured surfaces of (a) PLA/PBAT 80/20, (b) P0.002 and (c) P0.02.

3.2. Rheological property of the blends
Rheological properties of neat PLA, PLA/PBAT blends, and neat PBAT were evaluated as shown in figure 2. All samples showed that shear viscosity were reduced with increasing shear rate, and this was generally corresponded to shear thinning effect of the polymer. For neat PLA, the effect of shear thinning was more pronounced where its shear viscosity was dropped more rapidly for the shear rate above 1000 s$^{-1}$. The shear viscosity at the shear rate between 100 and 5000 s$^{-1}$ were presented in figure 3. At the shear rate of 100 s$^{-1}$, PLA showed the highest shear viscosity whereas at the shear rate of 5000 s$^{-1}$ PLA exhibited the lowest shear viscosity. In the case of PLA/PBAT blend with and without peroxide, its viscosity was close to that of neat PLA for the shear rate of 100 s$^{-1}$ while its viscosity was close to that of PBAT for shear rate of 5000 s$^{-1}$. The addition of PBAT 20 wt. % could change the rheology properties of PLA. In the case of the reactive blends of PLA/PBAT/Perkadox, upon increasing the peroxide contents, the shear viscosity of the blends were increased and higher peroxide content (P0.002) exhibited the highest shear viscosity. These results confirmed that there was the possible interaction at the interface between PLA and PBAT. However, when adding Perkadox 0.021 phr, the shear viscosity was decreased when compared to that of PLA/PBAT blend without peroxide probably due to chain scission from free radicals. At high shear rate region (5000 s$^{-1}$), the viscosity of all samples except neat PLA was very close. Thus, it could be concluded that PLA/PBAT blends remained processable when compared with neat PLA even at the high shear processing.

Figure 2. Shear viscosity versus shear rate (at 190°C) for PLA/PBAT blends.

Figure 3. Shear viscosity of the blends at shear rate (a) 5000 s$^{-1}$ and (b) 100 s$^{-1}$.

3.3. Mechanical properties of neat polymers and blends
Table 2 showed the mechanical properties of neat PLA, neat PBAT and reactive and non-reactive PLA/PBAT films. The results showed that the tensile strength and modulus of PLA/PBAT blend were insignificantly improved when adding peroxide. The elongation at break and impact strength of neat PLA, neat PBAT and PLA/PBAT blends were increased. PLA/PBAT with Perkadox 0.02 phr had the highest elongation at break. The impact strength of the blends was insignificantly changed when increasing Perkadox content.
Table 2. Mechanical properties of the blends.

| Sample name | Tensile strength (MPa) | Modulus (MPa) | Elongation at break (%) | Impact strength (KJ/m²) |
|-------------|------------------------|---------------|-------------------------|------------------------|
| Neat PLA    | 90.6±6.3               | 1470±101      | 10.6±2.1                | 3.3±0.4                |
| 80/20       | 66.1±4.6               | 1087±75       | 157.7±11.0              | 6.4±0.9                |
| P0.002      | 67.2±5.3               | 1095±70       | 180.4±35.9              | 6.0±1.2                |
| P0.02       | 63.6±2.5               | 1126±59       | 288.9±23.1              | 6.1±0.9                |
| Neat PBAT   | 14.1±1.0               | 44±2          | >300                    | Not break              |

Figure 4 demonstrated the stress-strain relationship of neat PLA and PLA/PBAT blends. The toughness of the samples could be determined by the area under the stress-strain curve. All blends had a characteristic of drawability curve. Neat PLA yielded the tensile strength of about 90 MPa and elongation at break of about 10%. It showed very weak drawability and poor toughness property. The tensile strength and modulus of all blends decreased to about 60 MPa, but the elongation at break was increased to about 290%. However, PLA/PBAT with peroxide (P0.002 and P0.02) exhibited better strength tensile strength and modulus. The elongation at break was improved when adding peroxide to the blends. A lot of research of immiscible PLA blends with other polymers occurring the dispersed phase indicated that having defect lead to poor mechanical properties [21]. The improved drawability of reactive PLA/PBAT blends could correspond to the better interfacial adhesion between the two polymers as represented by fine dispersion morphology discussed earlier in SEM.

![Stress-strain curves of the blends with peroxide contents.](image)

Figure 4. Stress-strain curves of the blends with peroxide contents.

![Comparison of the illustration between a) Neat PLA, b) P0.02 and c) Neat PBAT.](image)

Figure 5. Comparison of the illustration between a) Neat PLA, b) P0.02 and c) Neat PBAT.

3.4. Blown film processing
The blown film machine was then used to convert the compounds (neat polymers and blends) into films. The physical appearance and film properties were evaluated. Figures 5(a)-(c) showed blown film processing of neat PLA, PBAT and the reactive blend of PLA/PBAT (P0.02). Blowing neat PLA was difficult, and the bubble shape was unstable due to low melt strength of PLA. The resulting film had a large variation of dimension and thickness. The film was transparent as PLA was amorphous and had low crystallization rate. In the case of neat PBAT film processing, it was easier to blow. The shape of PBAT bubble was dominated by a long neck champagne similar to that of HDPE bubble. However, the PBAT film was stick together after conveying into the nip roll. In the case of
PLA/PBAT blends with and without peroxide, the films could be processed more easily when compared to neat PLA. The bubble shape was tubular similar to that of LDPE blown film.

3.5. Mechanical properties of films
Table 3 showed mechanical properties of PLA/PBAT (80/20) and P0.02 films in both machine and transverse directions. In the machine direction, in the case of P0.02, the tensile strength, elongation at break and secant modulus were all improved and more than those of non-reactive PLA/PBAT (80/20). On the other hand, in the transverse direction, the tensile strength, elongations at break and secant modulus of P0.02 were decreased when compared with PLA/PBAT (80/20). Figure 6 showed the stress-strain curve of machine direction film samples.

| Sample name | Direction | Tensile strength (MPa) | Modulus (MPa) | Elongation at break (%) |
|-------------|-----------|------------------------|---------------|-------------------------|
| Neat PLA    | MD        | 51.8±3.7               | 4068±525      | 4.9±0.9                 |
|             | TD        | 37.9±6.3               | 3813±367      | 5.1±1.2                 |
| 80/20       | MD        | 36.4±4.0               | 3274±130      | 87.7±29.9               |
|             | TD        | 40.5±6.9               | 2949±587      | 209.6±30.3              |
| P0.002      | MD        | 24.1±5.0               | 2497±391      | 123.1±27.2              |
|             | TD        | 42.3±5.9               | 3514±212      | 219.9±15.9              |
| P0.02       | MD        | 41.9±4.2               | 3515±90       | 199.1±11.2              |
|             | TD        | 26.1±2.6               | 3099±240      | 9.3±3.8                 |
| Neat PBAT   | MD        | 16.3±1.1               | 287±12        | >300                    |
|             | TD        | 13.2±1.1               | 290±12        | >300                    |

Figure 6. Stress-strain curve of the blends with film samples in machine direction.

3.6. Optical properties
Table 4 showed results from haze testing of neat polymers and the blends. Neat PLA had a low haze whereas PBAT had a high haze values that contrary to PBAT, PLA is transparent. All blends despite the different phase morphology (SEM), also showed low haze values indicated that upon adding...
PBAT, the optical clarity (figure 7) remained unaffected due to finely dispersed phases of PBAT. The addition of peroxide did not influence the haze values.

| Table 4. Haze values of films. |
|--------------------------------|
| Sample name | Haze (%) |
| Neat PLA | 0.46±0.16 |
| 80/20 | 6.27±0.72 |
| P0.002 | 5.95±0.82 |
| P0.02 | 5.49±0.77 |
| Neat PBAT | 61.2±1.31 |

4. Conclusions

PLA/PBAT blends were prepared at the weight ratio of 80:20 with two concentrations of peroxide (0.02 and 0.0002 phr) as a reactive agent. The improvement of the drawability obtained with 0.02 phr of peroxide was due to the improved interfacial adhesion between PLA and PBAT phases. Neat PLA, neat PBAT, and PLA/PBAT blends showed similar shear thinning effect of the polymer. The shear viscosity of neat PLA was dropped more rapidly at the shear rate above 1000 s⁻¹. Adding PBAT 20 wt. %, PBAT could change the rheological properties of PLA at high shear rate (above 1000 s⁻¹). All of the blends non-reactive and reactive PLA/PBAT blends had the same rheology properties. The tensile strength and modulus of PLA/PBAT blend were insignificantly changed when adding Perkadox. PLA/PBAT with 0.02 phr peroxide had the highest elongation at break (288.9%). The impact strength of the blends was insignificantly changed when increasing peroxide contents. PLA/PBAT with peroxide could improve drawability.

For blown film processing, neat PLA was difficult to keep the tubular profile shape due to low melt strength. The PLA/PBAT film with or without peroxide could be better processed by blown film. For mechanical properties of the films in the machine direction, in the case of P0.02, the tensile strength, elongation at break and secant modulus were improved more than those of PLA/PBAT (80/20). The optical properties of PLA had a low haze, but PBAT had a high haze.

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