
พอลิเมอร์ผสมที่มีการเติมสารเสริมสภาพพลาสติกของเซลลูโลสอะซิเตทบิวทิเรทและพอลิบิวทิลีนซัคซิเนท
สำหรับการใช้งานเป็นพลาสติกที่ย่อยสลายได้ตามธรรมชาติ

Plasticized Polymer Blends of Cellulose Acetate Butyrate and Poly(butylene Succinate)
as Biodegradable Plastics

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บทคัดย่อ

ในการศึกษาครั้งนี้ พอลิเมอร์ผสมที่มีเซลลูโลสอะซิเตทบิวทิเรท (CAB) และพอลิบิวทิลีนซัคซิเนท (PBS) เป็นองค์ประกอบได้ถูกเตรียมขึ้นมาโดยเทคนิคหล่อขึ้นรูปแบบใช้ตัวทำละลาย สารละลายผสมที่มีร้อยละโดยน้ำหนักของ PBS ที่แตกต่างกันไป (0-100% w/w) ได้ถูกเตรียมในคลอโรฟอร์ม จากนั้นจึงทำการหล่อขึ้นรูปโดยการเทลงบนจานเพาะเชื้อแก้ว สารเสริมสภาพพลาสติกบางชนิด ได้แก่ โคพอลิเมอร์แบบสลับของสไตรีนและมาเลอิกแอนไฮไดรด์ (PSMA) กลีเซอรอล (GCR) และพอลิไวนิลอะซิเตท (PVA) ได้ถูกเลือกมาใช้เพื่อปรับปรุงสภาพความเข้ากันได้และคุณสมบัติเคมีเชิงกายภาพของพอลิเมอร์ผสม การใช้เทคนิควิเคราะห์ทางกายภาพและทางสเปกโทรสโกปีแสดงให้เห็นว่า ความเป็นเนื้อเดียวกันของฟิล์มขึ้นอยู่กับส่วนประกอบในของผสม อุณหภูมิการหล่อขึ้นรูป และการเติมสารเสริมสภาพพลาสติก ทั้งนี้เมื่อองค์ประกอบของ PBS ในของผสมเพิ่มขึ้น แผ่นฟิล์มที่ได้จะมีเสถียรภาพทางความร้อนที่สูงขึ้นแต่จะมีความโปร่งใสลดลงยิ่งไปกว่านั้น ฟิล์มผสมที่มี PBS อยู่ร้อยละ 20 โดยน้ำหนัก แสดงค่าความทนต่อแรงดึงสูงสุดที่สุด คือ 39 MPa ในขณะที่แผ่นฟิล์มผสมที่มี PBS อยู่ร้อยละ 40 โดยน้ำหนัก จะมีค่าความยืดสูงสุด ณ จุดขาดสูงสุดที่สุด คือ 126% นอกจากนี้ยังพบว่าสารเสริมสภาพพลาสติก PSMA สามารถทำให้ฟิล์มผสมที่มี 40% PBS มีค่าความยืดสูงสุด ณ จุดขาดเพิ่มขึ้นจาก 126% ไปเป็น 171% อีกด้วย ดังนั้น ระบบพอลิเมอร์ผสมที่มีการเติมสารเสริมสภาพพลาสติกนี้ จัดได้ว่าเป็นวัสดุทางเลือกอีกอันหนึ่ง ที่มีความเป็นไปได้ในการนำมาใช้ผลิตพลาสติกที่มีความเป็นมิตรต่อสิ่งแวดล้อม

คำสำคัญ: พอลิเมอร์ผสม เซลลูโลสอะซิเตท การเสริมสภาพพลาสติก พลาสติกที่ย่อยสลายได้ตามธรรมชาติ

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In this study, the polymer blends consisting of cellulose acetate butyrate (CAB) and poly (butylene succinate) (PBS) were prepared by using a solution casting technique. The blend solutions, containing different weight percentages of PBS (0-100% w/w), were prepared in a chloroform, prior to casting onto the glass petri-dish. Some plasticizers, including poly (styrene-alt-maleic anhydride) (PSMA), glycerol (GCR) and poly (vinyl acetate) (PVA), were chosen to mix with the blends to improve their compatibility and physicochemical properties. A combined use of both physical and spectroscopic techniques indicated that the film homogeneity depended on the blend composition, casting temperature and the addition of the plasticizer. As the PBS content in the blends was increased, the resultant films showed improved thermal stability, but decreased transparency. Furthermore, the blend film of 20% PBS achieved the maximum tensile strength of 39 MPa, while the 40% PBS film reached the highest elongation at break of around 126%. Additionally, the most pronounced plasticization effect was observed in the 40% PBS blend with the PSMA addition, as evidenced by the increased elongation at break from 126% to 171%. This plasticized blend system is, thus, one of promising candidates with high potential for the manufacture of environmentally friendly plastics.

Keywords : Polymer blend, Cellulose ester, Plasticization, Biodegradable plastics

Introduction

Petroleum-based plastics are attractive man-made materials that are widely used in many applications due to their excellent properties such as low cost, strong but light weight, ease of fabrication, tunable properties for different applications and durability. Despite these advantages, these plastics also cause serious environmental problems because of their long-lasting in nature. Thus, there is a need to develop alternative sources of material that can be naturally decomposed and can reduce greenhouse-gas emission by replacing and reducing the uses of crude-oil. Biodegradable plastics have long been suggested as a promising candidate for the substitution of the traditional ones. They are designed to be readily decomposed in natural aerobic and anaerobic environments and produce inert humus-like non-toxic materials after degradation. The benefits of using biodegradable plastics include decreasing of landfills, ground water and air pollution, requiring less energy to produce and improving of the soil structure (Smith, 2005). Among all available biodegradable materials, celluloses have received much attention for the manufacture of renewable bioplastics due to their abundant, good tensile properties, water-resistance and degradability under appropriate conditions (Buchana, Gardner & Komarek, 1993; Komarek, Gardner, Buchanan & Gedon, 1993). Despite these advantages, it is generally insoluble in all organic solvents thus, limiting its use in practical applications. Cellulose acetate butyrate (CAB) is one of the most widely used cellulose derivatives with better mechanical properties, water-resistance and processability than cellulose. CAB, esterified by acetyl and butyryl groups, is a brittle and transparent material. It has been applied to a wide range of applications including as a photo-film, coating material, a thin film packaging and as a plasticizer for some thermoplastics. CAB with low degree of substitution (DS) was reported to be biodegradable at a reasonable rate, while that of a relatively high substituted was at very slow rate of degradation (Edgar, Buchanan, Debenham, Rundquist,

Seiler, Shelton & Tindall, 2001). This somehow limits potential use of the polymer as biodegradable plastics. Blending of CAB with other polymers is one of the good ways to tailor its biodegradability. Generally, blending is convenient, economic and is possible to produce a range of materials with properties completely from those of the blend constituents.

Poly (butylene succinate) (PBS), the most widely used aliphatic polyester, has recently received much attention for a development of biodegradable packaging. PBS resins are resistant to heat and water, biodegradable by some microorganisms and can be processed into different injection molded products (Vert, 2005; Ray, Okamoto & Okamoto, 2003). It has been applied as agricultural mulch sheets to protect against insects, slow-release materials, thin film packaging and other green products (Ray, Okamoto & Okamoto, 2003; Tachibana, Giang, Ninomiya, Funabashi & Kunioka, 2010). Likewise other polyesters, PBS could form miscible blends with variety of thermoplastics including CAB (Edgar, Buchanan, Debenham, Rundquist, Seiler, Shelton & Tindall, 2001). The blends are generally stable, amorphous transparent and exhibit improved mechanical properties. Previous study revealed that CAB/PBS blend film at 10% CAB content exhibited maximum strain at break and tensile strength values. A further addition of CAB deteriorated the films properties and at 80% CAB, the blend film became very brittle (Tachibana, Giang, Ninomiya, Funabashi & Kunioka, 2010). In order to extend practical limit use of CAB/PBS blend as well as to enhance compatibility of the two components, some plasticizers are needed.

In this study, glycerol (GCR), poly (styrene-alt-maleic anhydride) (PSMA) and poly (vinyl acetate) (PVA) were used as a plasticizer to mix with CAB/PBS blends to improve their performance. To achieve the optimal casting conditions, a number of parameters were studied through a combined use of physical and analytical techniques. Various properties of the blends including optical transparency, surface morphology, thermal and

mechanical properties were investigated as a mean to evaluate their structural integrity, miscibility as well as their feasible use as biodegradable thin film packaging.

Materials and Methods

Cellulose acetate butyrate (CAB) type 500-5 of number-average molecular weight 57,000 was obtained from Eastman Chemical Company (Kingsport, Tennessee, USA). The CAB polymer consists of hydroxyl groups (1%), acetyl groups (4%) and butyryl groups (51%). Poly(butylene succinate) (PBS) pellets were received as a gift from PTT Public Company Limited (PTT), Thailand. Chloroform was purchased from Labscan (Asia, Thailand). Glycerol (GCR), poly(styrene-*alt*-maleic anhydride) (PSMA) and poly(vinyl acetate) (PVA) were purchased from Ajax Finechem (NSW, Australia), Sartomer and Aldrich, respectively. All chemicals were used as received.

A solution casting method was employed to prepare the PBS/CAB blend films. Briefly, various blends at different PBS contents (0-100 percent by weight) were dissolved in a chloroform to obtain a homogeneous blend solution. After that, the plasticizer (GCR, PSMA or PVA) was added into the blend solution prior to casting onto a glass petri-dish. The thin films were finally obtained after incubation at either 25°C or 50°C for 24 hr. The amount of plasticizer used in each formulation was around 1% by weight of the blend.

The transparency (%T) of the resultant films was measured by using the UV-Vis Spectrophotometer (Genesys 20, Thermo) at 600 nm. All measurements were performed in triplicate. The polymer compatibility was evaluated through the uses of the Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer), Differential Scanning Calorimetry (DSC, Mettler Toledo) and Thermogravimetric Analysis (TGA, Mettler Toledo). For DSC and TGA tests, a nitrogen flow rate and a heating scan of 20 mL/min and 10°C/min were employed, respectively. Surface morphology of the blend films was investigated by using the Scanning Electron Microscopy (SEM, LEO 1450VP). The

tensile measurement was performed on the machine (INSTRON-5566) and the method used was adapted from the ASTM D638-03. The crosshead speed was 10 mm/min and the initial gauge length was 30 mm.

Results and Discussion

Film Transparency

In this study, the optical transparency (%T) of the casted films was measured as a mean to evaluate the compatibility between CAB and PBS. As can be observed in Figure 1, the %T of all blend films casted at 25°C is generally lower than that casted at 50°C. This suggests a high impact of energy input on the polymer compatibility and so the optical transparency of the resultant films. The increased temperature may dissociate both inter- and intramolecular CAB-CAB bonding thus, suppressing the formation of CAB spherulite within the sample (Suttiwittitpukdee, Sato, Zhang, Hashimoto & Ozaki, 2011). This enhances intermolecular interactions between CAB and PBS in the amorphous region of the blend. Similar behavior was also observed in many cellulose ester blend systems (El-Shafee, Saad & Fahmy, 2001; Ogata, Tatsushima, Nakane, Sasaki & Ogihara, 2002). At higher PBS contents (> 60%), the transparency of the blend films, casted at elevated temperature, decrease to below 50%. This is due to a macroscopic phase separation in the samples. Thus, there is a certain limit of which PBS can be incorporated without causing a phase separation. For the neat PBS film, the polymer-polymer interaction becomes energetically favorable after solvent evaporation. This causes PBS molecules to collapse and adapt themselves into larger particles that eventually scatter the incident light. The effect of plasticizer on the film transparency is shown in Figure 2. As noticed, all plasticized 20% and 40% PBS blend films display the %T values of more than 85%, similarly to those of the unplasticized ones. This suggests a good compatibility of GCR, PSMA and PVA in the blend systems.

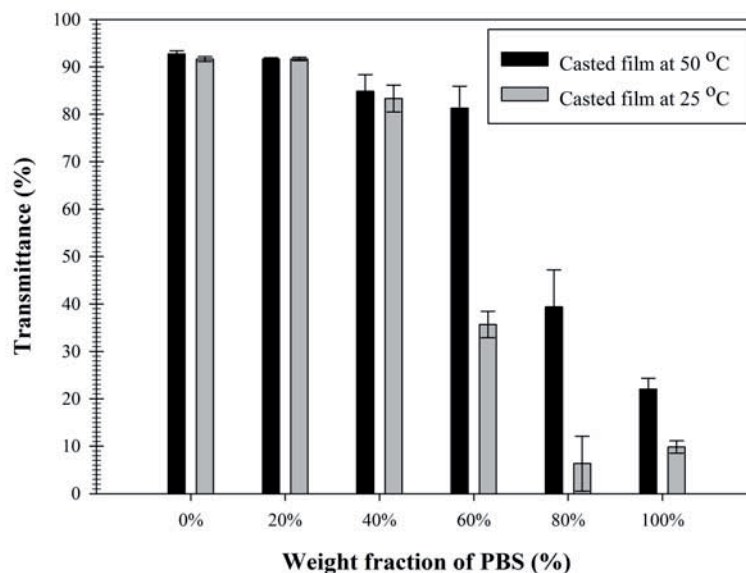


Figure 1 Transparency (%T) of the films containing different PBS contents (% w/w) casted at either 25°C or 50°C.

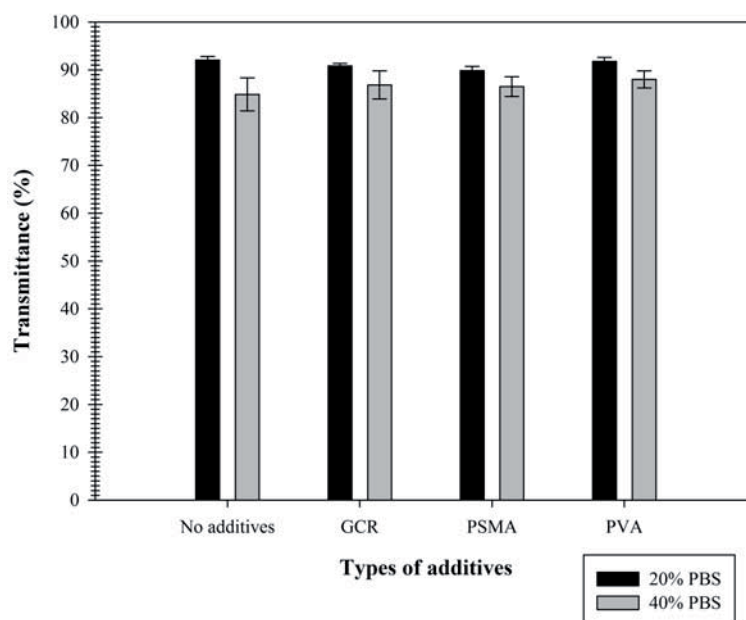


Figure 2 Transparency (%T) of the blend film containing either 20% or 40% (w/w) PBS content in the presence of different plasticizers. All films were casted at 50°C.

Structural Analysis

Figure 3 shows the IR spectra of the casted films containing 0%, 20%, 40%, 60%, 80% and 100% PBS contents. As noticed, there is a difference between the peak position of the carbonyl group (C=O), appeared

between 1600–1800 cm^{-1} , of CAB and that of PBS. As the mass fraction of PBS in the blends is increased, the corresponding C=O peak is slightly shifted towards that of the pure PBS. This finding illustrates the existence of PBS in the blends. Figure 4 shows IR spectra in the OH

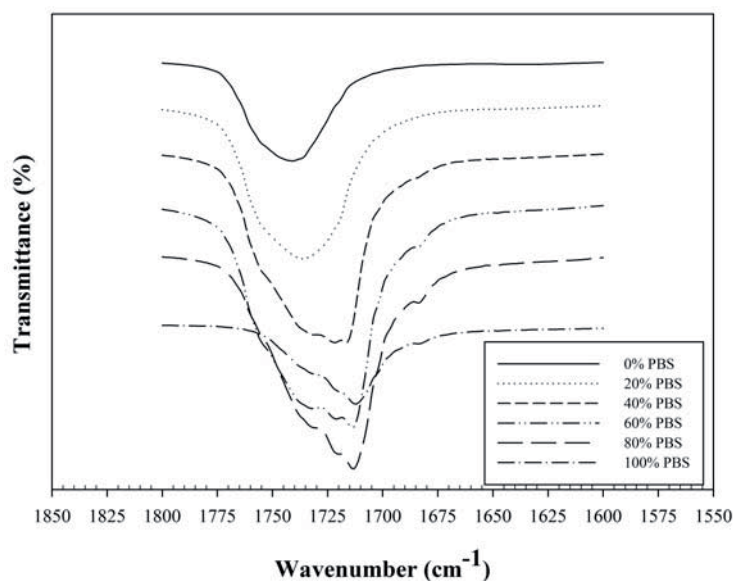


Figure 3 FTIR-Spectra of the casted films containing different PBS contents showing the C=O absorption peak between 1600–1800 cm^{-1} . All films were casted at 50°C.

stretching region between 4000–3200 cm^{-1} of the 20% PBS blend films with and without the addition of the plasticizer. The unplasticized blend film displays a broad absorption band at 3480 cm^{-1} and two weak shoulders at 3540 and 3638 cm^{-1} . The band at 3480 cm^{-1} indicates the OH stretching mode of inter-chain hydrogen bonding (C=O---H-O) occasionally defined as the *inter* CAB-CAB,

while the band at 3540 cm^{-1} may be ascribed to the *intramolecular* hydrogen bonding in CAB (*intra* CAB-CAB). The band at 3638 cm^{-1} is believed to arise from the free O-H groups because it appears at the highest wavenumber (Suttiwijitpukdee, Sato, Zhang, Hashimoto & Ozaki, 2011). For the blend films plasticized by GCR, PSMA and PVA, these three characteristic O-H stretching bands are

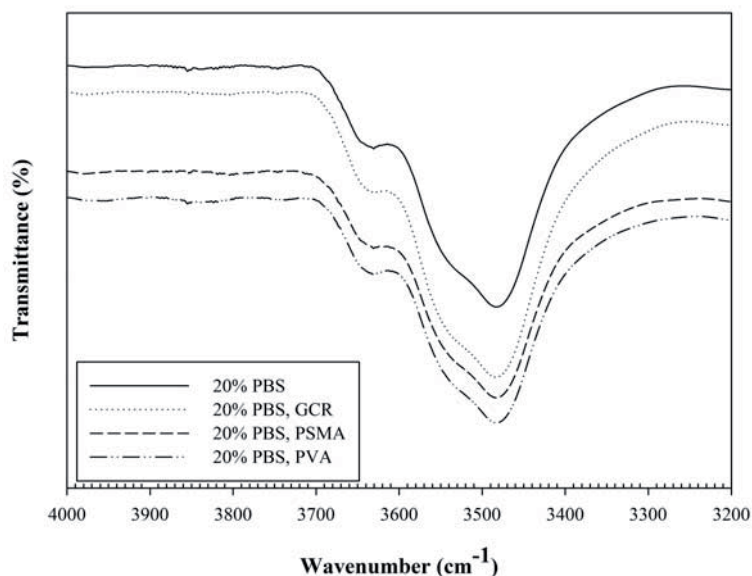


Figure 4 FTIR spectra in the O-H stretching region of the unplasticized and plasticized (GCR, PSMA or PVA) 20% PBS films. All films were casted at 50°C.

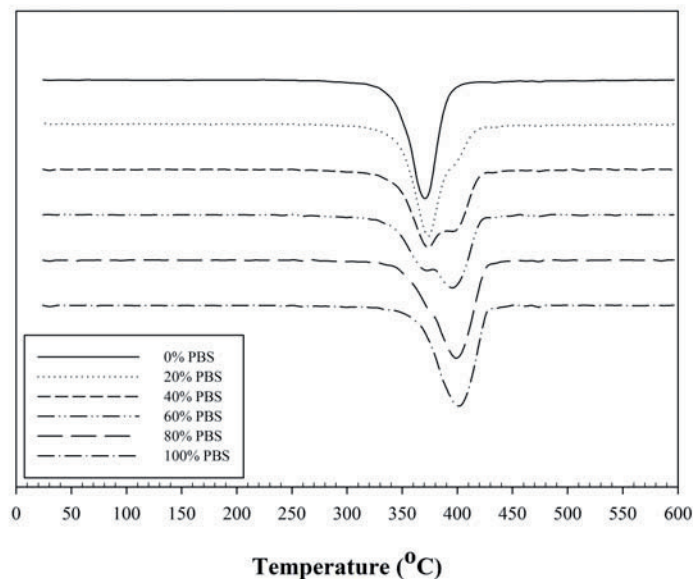


Figure 5 1st-Derivative plots of TGA thermograms of the blend films containing different PBS contents. All films were casted at 50°C.

found to maintain at the same wavenumbers, suggesting that the interaction of such plasticizers and CAB may not occur through the hydrogen bonding formation. Additional experiments would be needed to further clarify this matter.

Thermal Properties

Thermal degradation of the films was evaluated by examining their mass loss during heating. The 1st-derivative plots of the TGA thermograms and their $T_{d,max}$ values are present in Figure 5 and Table 1, respectively. The value is defined as a temperature at the maximum weight-loss rate.

As seen in Figure 5, the neat CAB (0% PBS) and PBS (100% PBS) exhibit a single thermal degradation pattern. The neat CAB film displays the T_d value of around 371°C, less than that of the neat PBS film (419°C) (see Table 1). This implies the greater intermolecular chain interactions and thus, thermal stability in PBS than in CAB. As expected, the T_d value of the blend films increases with the weight fraction of PBS. For example, the incorporation of 60% PBS into the blend system raises the T_d of the neat CAB by 15°C. This highlights the efficacy

of using PBS to modulate the film properties for a wider range of practical applications.

Table 1 Degradation temperature of the unplasticized films containing different PBS contents (% w/w) and casted at 50°C.

Films	$T_{d,max}$ (°C)
0% PBS	371.15
20% PBS	376.92
40% PBS	380.39
60% PBS	386.00
80% PBS	398.08
100% PBS	419.23

The addition of GCR, PSMA and PVA proves to be able to enhance thermal properties of the 40% and 60% PBS blend films, as confirmed by the increased T_d values of the plasticized films comparing to that of the unplasticized ones. This effect is more pronounced for the case of the 60% PBS film, whereby the addition of PSMA raises the T_d of the blend from 386°C (unplasticized) to

Table 2 Degradation temperature of the plasticized blend films containing different PBS contents (% w/w) and casted at 50°C.

Films	T _{d,max} (°C)
20% PBS (unplasticized)	376.92
20% PBS, GCR	371.56
20% PBS, PSMA	373.34
20% PBS, PVA	374.19
40% PBS (unplasticized)	380.39
40% PBS, GCR	382.35
40% PBS, PSMA	384.31
40% PBS, PVA	382.35
60% PBS (unplasticized)	386.00
60% PBS, GCR	388.00
60% PBS, PSMA	392.00
60% PBS, PVA	388.00

392°C (Table 1-2). The work finding thus, indicates the preferential interactions among the plasticizers, CAB and PBS within the blend systems. For the 20% PBS film, the addition of the plasticizers lowers the T_d value of the blend from 376.92°C (Table 1) to 371.56°C (GCR), 373.34°C

(PSMA) and 374.19°C (PVA), see Table 2. The molecules of GCR, PSMA or PVA may disperse between the polymer chains, disrupt and the n, weaken their associative forces. The plasticization behavior of the additive thus, varies from one system to another.

Mechanical Properties

The stress-strain curves of different blend films casted at 50°C are shown in Figure 6. Their tensile properties are also summarized in Table 3.

As observed in Figure 6, the 20% PBS film shows a clear yield point which is a characteristic of plastic deformation (Tatsushima, Ogata, Nakane & Ogihara, 2004). The tensile stress and the elongation at break of the 20% PBS film are found to be around 39.0 ± 3.1 MPa and 32.3 ± 4.9%, respectively (Table 3). These imply a hard and strong characteristic of the material. The 40% and 60% PBS blend films show similar stress-strain behavior. They show an impressive high elongation at break of more than 80%, but lower yield strength as compared to the 20% PBS. The result suggests that the 40% and 60% films are a soft and tough, rather than a hard and strong material.

The effect of the plasticizers, GCR, PSMA and PVA, on the mechanical characteristics of the blend films can be illustrated in Figure 7 and Table 3. It is found that

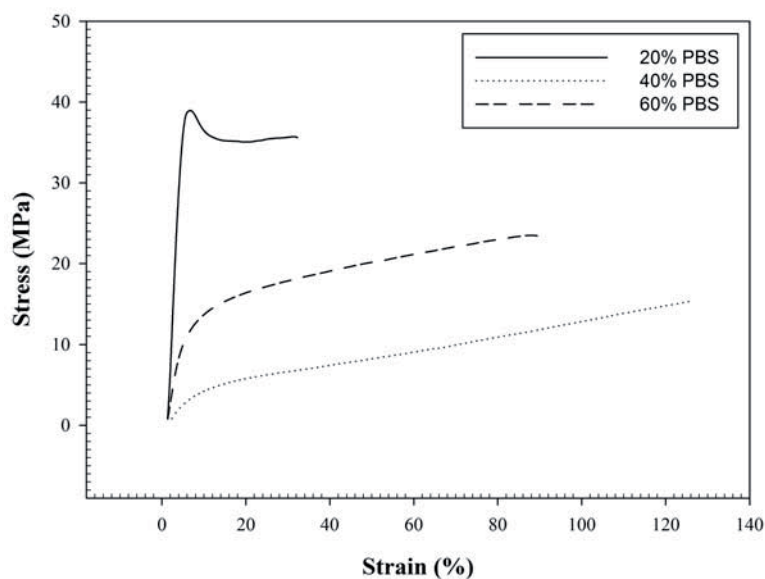


Figure 6 Stress-strain curves of the blend films at different PBS contents (20%, 40% and 60%) casted at 50°C.

Table 3 Mechanical properties of the unplasticized and plasticized blend films containing different PBS contents (%w/w) and casted at 50°C.

Samples	Tensile stress at break (MPa)	Elongation at break (%)
20% PBS	39.0 ± 1.1	32.3 ± 4.2
40% PBS	15.3 ± 1.3	125.7 ± 6.2
60% PBS	23.5 ± 2.2	88.0 ± 1.9
20% PBS, GCR	30.7 ± 3.1	52.6 ± 2.5
20% PBS, PSMA	39.1 ± 2.7	46.9 ± 1.7
20% PBS, PVA	36.8 ± 1.9	50.2 ± 1.5
40% PBS, GCR	13.3 ± 3.2	99.8 ± 3.9
40% PBS, PSMA	9.9 ± 2.7	170.7 ± 3.1
40% PBS, PVA	15.7 ± 1.9	101.8 ± 1.5

the added PSMA significantly increases the elongation at break of the unplasticized 40% PBS film from 125.7 ± 6.2% to 170.7 ± 3.1 % (Table 3), illustrating the plasticizing effect of the copolymer in this blend system. Additionally, PSMA could also increase the elongation at break of the 20% PBS blend, but less pronounced than in the 40% PBS system, suggesting the more favorable interactions of PSMA with PBS than with CAB. This is supported by the enhanced thermal stability in the 60% PBS blend

comparing to that in the 20% PBS previously discussed (see Table 2).

Surface Morphology

Scanning electron microscopy (SEM) was used to investigate surface morphology of the films. As seen in Figure 8, the neat CAB (0% PBS) and the unplasticized 20% PBS blend films display smooth surface even at high (500x and 1000x) magnifications, confirming the absence of a microscopic phase separation and a good compatibility

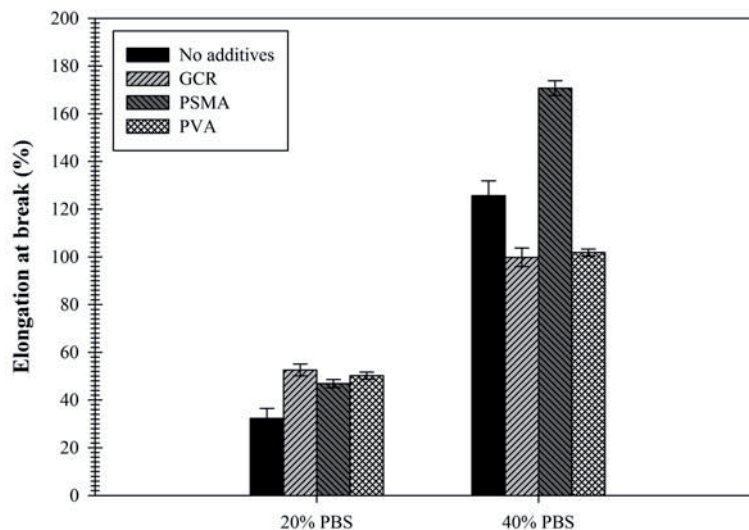


Figure 7 Elongation at break (%) of the 20% and 40% PBS blend films with and without the addition of the plasticizer (GCR, PSMA or PVA). All films were casted at 50°C.

Blend films	Magnifications		
	50x	500x	1000x
0% PBS			
20% PBS			
20% PBS, GCR			
20% PBS, PSMA			
20% PBS, PVA			
100% PBS			

Figure 8 SEM images of the neat CAB (0% PBS), PBS (100% PBS), unplasticized and plasticized 20% PBS blend films. The films were casted in chloroform at 50°C. Images were taken at magnifications of 50x, 500x and 1000x.

of the two components. Our results by the TGA, %T and mechanical measurements were earlier proven that GCR, PSMA and PVA are compatible with the CAB/PBS blends. This is also confirmed by the appearance of a clean and smooth surface of the plasticized 20% blend observed by the SEM micrographs shown in Figure 8. For the case of the neat PBS film, the polymer molecules aggregate to some extents to form a stable configuration as seen in Figure 8 (100% PBS). Such aggregation is believed to minimize their local contact with chloroform and explains the reduced transparency of the neat film in Figure 1.

Conclusion

The CAB and PBS blend film could be prepared in chloroform by the solution casting. It was found that the optical transparency (%T), thermal and mechanical properties of the films depend on the casting temperature, blend composition and the addition of the plasticizer. At some specific blend compositions (0-60% PBS

contents) and at the casting temperature of 50°C, the PBS/CAB films with good structural and physicochemical characteristics were obtained. The incorporation of PBS increased the thermal decomposition temperature of CAB, depending on the PBS content. Nonetheless, this induced a microscopic phase separation within the film and hence, the reduction of their compatibility. Among all blend films, the 20% PBS film showed a characteristic of plastic deformation with a clear yield point of 39 MPa and the elongation at break of around 32%. The 40% PBS film achieved a maximum elongation at break of around 126% and this was significantly increased to around 171% by the addition of PSMA. The enhanced tensile properties of the 40/60 (PBS/CAB) blend indicated the preferential intermolecular interactions among the three components and the most pronounced plasticizing effect of PSMA in the blend system. The plasticized PBS/CAB blends have thus, demonstrated its potential uses for a development of new biodegradable plastics.

References

- Buchana, C.M., Gardner, R.M. & Komarek, R.J. (1993). Aerobic biodegradation of cellulose acetate. *Journal of Applied Polymer Science*, 47, 1709-1719.
- Edgar, Kevin J., Buchanan, Charles M., Debenham, John S., Rundquist, Paul A., Seiler, Brian D., Shelton, Michael C. & Tindall, Debra (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, 26, 1605-1688.
- El-Shafee, E., Saad, G.R. & Fahmy, S.M. (2001). Miscibility, crystallization and phase structure of poly (3-hydroxybutyrate)/cellulose acetate butyrate blends. *European Polymer Journal*, 37, 2091-2104.
- Komarek, R.J., Gardner, R.M., Buchanan, C.M. & Gedon, S. (1993). Biodegradation of radiolabeled cellulose acetate and cellulose propionate. *Journal Applied Polymer Science*, 50, 1739-1746.
- Ogata, N., Tatsushima, T., Nakane, K., Sasaki, K. & Ogihara, T. (2002). Structure and physical properties of cellulose acetate/poly(L-lactide) blends. *Journal Applied Polymer Science*, 85, 1219-1226.
- Ray, S.S., Okamoto, K. & Okamoto, M. (2003). Structure-property relationship in biodegradable poly (butylene succinate)/layered silicate nanocomposites. *Macromolecules*, 36, 2355-2367.
- Smith, R. (2005). *Biodegradable Polymers for Industrial Applications*, Cambridge, Woodland Publishing, CRC Press.
- Suttiwijitpukdee, N., Sato, H., Zhang, J., Hashimoto, T. & Ozaki, Y. (2011). Intermolecular interactions and crystallization behaviors of biodegradable polymer blends between poly (3-hydroxybutyrate) and cellulose acetate butyrate studied by DSC, FT-IR and WAXD. *Polymers*, 52, 461-471.
- Tachibana, Yuya, Giang, N.T., Ninomiya, F., Funabashi, M. & Kunioka, M. (2010). Cellulose acetate butyrate as multifunctional additive for poly (butylene succinate) by melt blending: Mechanical properties, biomass carbon ratio, and control of biodegradability. *Polymer Degradation and Stability*, 95, 1406-1413.
- Tatsushima, T., Ogata, N., Nakane, K. & Ogihara, T. (2004). Structure and physical properties of cellulose acetate butyrate/poly (butylene succinate) blend. *Applied Polymer Science*, 96, 400-406.
- Vert, Michel (2005). Aliphatic polyesters: Great degradable polymers that cannot do everything. *Biomacromolecules*, 6, 538-546.