

Synergistic Efficiency of Tricresyl Phosphate and Montmorillonite on the Mechanical Characteristics and Flame Retardant Properties of Polylactide and Poly(butylene succinate) Blends

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Abstract The main aim of this research was to investigate the synergistic influence of additives and poly(butylene succinate) (PBS) in improving both the mechanical and flame retardant properties of polylactide (PLA) blends. Tricresyl phosphate (TCP) and montmorillonite (MMT) were the additives used to improve the mechanical characteristics and fire resistance of PLA. Differential scanning calorimetry (DSC) thermograms revealed that the addition of TCP and MMT significantly affected their thermal behaviors. The results of the mechanical and morphological characterizations were in agreement with the changes in thermal behavior. The impact strength and limiting oxygen index (LOI) value of PLA significantly increased with the presence of PBS. The failure mode of the blends as evidenced by scanning electron microscopy (SEM) changed from brittle to ductile. The addition of TCP and MMT produced excellent anti-dripping and self-extinguishing behaviors of the blends, achieving V-0 rating. For the PLA/PBS blends, the synergistic combination of PBS and additives led to an acceleration of cold crystallization, a significant increment of flexibility and impact toughness, and an improvement of flame retardancy.

Keywords Polylactide; Poly(butylene succinate); Blend; Flame retardant; Impact toughness

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INTRODUCTION

Over the past decades, aliphatic biodegradable polyesters have attracted academic interest due to their outstanding biocompatibility and biodegradability^[1, 2]. Polylactide (PLA), one of the most promising biodegradable polyesters for reducing environmental pollution, has been used widely for several applications in agricultural, biomedical, pharmaceutical, packaging, and tissue engineering fields^[3, 4]. It has high mechanical strength, transparency, and renewability, and is easily processed, and non-toxic^[5, 6]. Its major drawbacks are low crystallinity, a slow crystallization rate, brittleness, and poor flame retardation with heavy melt dripping, preventing some potential widespread applications in the electronic and automotive industries^[7, 8]. For example, poor fire resistance and hot molten dripping of plastics may cause injuries and accelerate the progression of fire^[9]. Flame retardant performance is needed to improve PLA's fire retardation and anti-dripping performance during the burning process^[10, 11]. Halogen flame retardants have been widely used for many polymeric materials; however, their toxicity and corrosion during combustion releasing acidic halogen

gases make them limited for wide usages. Thus, eco-friendly additives are used to replace these halogen flame retardants. Studies of improvements to the flame inhibition of PLA have looked at several flame retardants, including compounds containing hydroxides^[12], inorganics^[13], phosphates^[14, 15], and intumescent^[16–18]. These promising halogen-free additives can be effective flame retardants for PLA, especially intumescent materials. During the combustion process, they produce carbon residue or inorganic char acting as a barrier which helps to reduce the heat released and the mass lost^[19]. Intumescent flame retardants have been increasingly investigated because of their low environmental impact and high resistance to ignition^[20]. Generally, the use of a flame retardant alone requires a relatively high content to improve the flame resistance of polymers, which affects other properties. On one hand, the addition of these flame retardants greatly enhances the fire retardation of the materials; on the other hand, the mechanical and processing properties are severely diminished^[21]. Hence, a balance needs to be found between the flame retardation and mechanical characteristics of PLA and this is the main aim of this research.

Blending a plasticizer and a flexible polymer with PLA is an effective way of improving its flexibility and toughness. Tricresyl phosphate (TCP), one of the phosphate-containing compounds, can be used as both plasticizer and flame

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retardant in poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET), and natural rubber^[22, 23]. Montmorillonite (MMT) has received attention due to its intercalation properties, high thermal stability, and submicron size^[24]. Many research works have revealed that the addition of MMT enhanced both flame retardancy and mechanical performance of polymers^[25, 26]. Furthermore, montmorillonite (MMT), which is an inorganic reinforcing filler, can form a compact char barrier during the combustion process and reduce the molten dripping of the polymer^[24]. Thus, blending TCP and MMT with PLA should be a way of improving both the flame retardation and mechanical properties of PLA. Furthermore, poly(butylene succinate) (PBS), a flexible and biodegradable polyester, has been used as film packaging, bottles, and injection-molded products^[27] due to its high toughness, flexibility, and biodegradability in a few weeks^[28]. These advantages of PBS make it a promising candidate for blending with PLA to enhance the flexibility and toughness of the resulting materials while remaining its biodegradability. To the best of our knowledge, no work has yet investigated the synergistic effect of a combination of TCP and MMT on the mechanical characteristics and flame inhibition of PLA/PBS blends. Therefore, the objective of this research is to investigate a new alternative route to the enhancement of these properties through the synergistic combination of TCP and MMT in PLA and PLA/PBS blends determined *via* limiting oxygen index (LOI), vertical combustion testing (UL-94), and tensile and impact testing. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) analysis are used to evaluate the synergistic influence on their thermal transition changes, crystallization behavior, and morphological properties as well.

EXPERIMENTAL

Materials

Poly(lactide (PLA 4043D) was purchased from NatureWorks LLC (Cargill-Dow, Minneapolis, MN) and used as a polymer matrix. The PLA pellets were transparent and exhibited a specific gravity of 1.25 g/cm³. The glass transition temperature (T_g) and melting temperature (T_m) of neat PLA were about 60 and 170 °C, respectively, characterized by DSC. Poly(butylene succinate) (PBS FZ91PD) with a specific gravity of 1.26 g/cm³ was supplied by Mitsubishi Chemical corporation (Chiyoda-ku, Tokyo, Japan). The T_g and T_m of neat PBS, as determined by DSC, were approximately –35 and 110 °C, respectively. Tricresyl phosphate (TCP) and metal cation exchanged montmorillonite K10 (MMT) were purchased from Sigma-Aldrich LLC, St. Louis, MO. TCP with a specific gravimetric of 1.16 g/cm³ is a colorless liquid, whereas MMT with a surface area 20–40 m²/g exists as a fine powder.

Material Preparation

The PLA and PBS pellets were dried in a vented oven at 60 °C overnight to eliminate any moisture before extrusion. The PLA was used as the polymer matrix. TCP and MMT were used as additives to enhance the mechanical performances and flame retardant properties of PLA and PLA/PBS blends. The TCP content was varied from 5 phr to 20 phr, and MMT

from 0.5 phr to 2 phr. PBS was used together with the additives as a flexible filler to enhance the flexibility and toughness of the PLA blend. The PBS content was fixed at 20 wt% for blend compositions. The polymer pellet and its additive were manually pre-mixed before the extrusion process. The mixture was melted in a twin screw extruder (Prism TSE 16TC, Thermo Electron Corporation, Karlsruhe, Germany) having an L/D ratio of 15 and a screw diameter of 15.6 mm. The temperature profiles of the extrusion were controlled in three zones ranging from 110 °C to 170 °C along the extruder barrel. A screw speed of 30–40 r/min was maintained for all experiments. The extruded blend was then allowed to cool in air and pelletized into the compounding pellets, which were dried in a vented oven at 60 °C overnight and then compression molded by a hydraulic press (KT-7014, Kao Tieh Machinery Industrial, Taichung, Taiwan) under the optimum conditions: a holding temperature of 190 °C; a pressure of 13.8 MPa; a cycle time of 22 min. Neat PLA was also prepared by the same method as a reference material. The formulations and their abbreviations are listed in Table 1.

Table 1 Designation and blend composition of the samples

Sample ID	PLA (wt%)	PBS (wt%)	Additives (phr)	
			TCP	MMT
Neat PLA	100	–	–	–
PLT5	100	–	5	–
PLT10	100	–	10	–
PLT20	100	–	20	–
PLM0.5	100	–	–	0.5
PLM1	100	–	–	1
PLM2	100	–	–	2
PLS	80	20	–	–
PLST5	80	20	5	–
PLST10	80	20	10	–
PLST20	80	20	20	–
PLST20M1	80	20	20	1

Characterization and Testing

Thermal behaviors

The crystallization behaviors and thermal transitions of the PLA and the PLA/PBS blends were analyzed and monitored by a differential scanning calorimeter (DSC; DSC 200 F3 Maia, NETZSCH Instruments, Selb, Germany). The sample (approximately 6–8 mg) was encapsulated in a hermetically sealed aluminum pan (30 μ L). A first heating scan was operated from 40 °C to 180 °C at a heating rate of 10 K/min and held at 180 °C for 3 min to completely eliminate the thermal history of the sample. The sample was then cooled to –60 °C with a cooling rate of 10 K/min. Finally, the specimen was reheated to 180 °C (the second heating cycle) at a heating rate of 10 K/min to evaluate non-isothermal crystallization behaviors and thermal transition changes. All experiments were performed under nitrogen atmosphere. The glass transition temperature (T_g), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), melting temperature (T_m), and specific melting enthalpy (ΔH_m) of the samples were also recorded. The degree of crystallinity (χ_c) of the neat PLA and its blends was calculated following Eqs. (1) and (2)

$$\chi_c(\%) = \frac{(\Delta H_{m,PLA})}{(1 - W_f)(\Delta H_{m,PLA}^0)} \times 100 \quad (1)$$

$$\chi_c(\%) = \frac{(\Delta H_{m,blend})}{(1 - W_f)(0.8\Delta H_{m,PLA}^0 + 0.2\Delta H_{m,PBS}^0)} \times 100 \quad (2)$$

where W_f is weight fraction of the additive, $\Delta H_{m,PLA}^0$ is the melting enthalpy of the 100% crystalline PLA (93.0 J/g)^[29], being, $\Delta H_{m,PBS}^0$ is the melting enthalpy of the 100% crystalline PBS (110.3 J/g)^[30].

Tensile properties

The tensile specimens (dumbbell shape type IV) had dimensions of 12.7 mm in length, 2 mm in width and about 3 mm in thickness. After compression molding, the specimens were stored overnight at room temperature before testing. All samples were tested on a universal testing machine (Instron 3365, Illinois Tool Work, IL) using a crosshead speed of 10 mm/min and a gauge length of 7 mm, in accordance with ASTM D638-14. A load cell of 5 kN was employed. At least five specimens of each blend were tested and the results were averaged to obtain a mean value. The tensile strength, elongation at break, and Young's modulus of the samples were reported.

Impact testing

Notched Izod impact testing determined the impact strength or impact toughness of the sample. The impact bar specimens were 63.5 mm long, 12.7 mm wide and about 3 mm thick. The impact tester (Zwick 5102 Pendulum, Zwick/Roell Group, Ulm, Germany) had a deflection angle of 160°, an exchangeable pendulum set to 4 J, an impact velocity of 2.93 m/s, and a pendulum length of 225 mm, in accordance with ASTM D256-10. All specimens were stored overnight at room temperature before testing. The mean values were obtained from at least five repeats. The thickness of the samples was determined by an analog thickness gauge. The impact strength (E_{lm}) was calculated following Eq. (3):

$$E_{lm} = \frac{E_{ab}}{b \times h} \quad (3)$$

where E_{lm} is impact strength or impact toughness (kJ/m²), E_{ab} is impact energy (kJ), b is the thickness of specimen (m), h is the ligament width of specimen (m).

Electron microscopy analysis

The tensile fractured surface of the PLA and PLA/PBS blends was characterized using a scanning electron microscope (SEM; Quanta 400, FEI Company, Hillsboro, OR). The fractured surface after tension of the sample was sputter-coated with a thin layer of gold in order to avoid electrostatic charge and poor resolution during the measurement. The SEM was operated at an accelerating voltage of 20 kV to image the samples at 2000× magnification. The failure behavior and phase separation of the blends were followed by morphological results.

Flammability evaluation

Vertical combustion testing (UL-94) was used to determine the flammability, dripping behavior and extinguishing characteristics of the PLA and the PLA/PBS blends. Bar specimens of 130 mm in length, 13 mm in width and about

3 mm in thickness were tested by the UL-94, following ASTM D3801-10. The specimens were placed above a cotton patch and ignited with a 20 mm blue flame. The time to self-extinguish after the first flame application (t_1), and second flame application (t_2) were recorded. The cotton ignition from melt dripping and total flame time are the important factors in evaluating the flammability rating under UL-94 testing. The total flame time from five specimens can be calculated following Eq. (4):

$$t_f = \sum_{i=1}^5 (t_{1,i} + t_{2,i}) \quad (4)$$

where t_f is the total flame time (s) from five samples, t_1 is the afterflame time (s) in the first flame application for 10 s, t_2 is the afterflame time (s) in the second flame application for 10 s.

Limiting oxygen index (LOI) testing

The LOI value indicates the lowest amount of oxygen in a laboratory controlled mixture of oxygen and nitrogen in which combustion of the specimen is still self-supporting. LOI values of bar specimens with dimensions of 110 mm × 6.5 mm × 3 mm (length × width × thickness) were measured according to the ASTM D2863-13. At least six specimens of each sample were tested and the average values were reported.

RESULTS AND DISCUSSION

Characterization of the PLA Blends

Thermal behaviors

Figure 1 shows the DSC thermograms of neat PLA and the PLA blends with various additive amounts during the cooling and 2nd heating processes. Neat PLA exhibits a glass transition temperature (T_g) at 60.5 °C, an exothermic cold crystallization temperature (T_{cc}) at 115.9 °C, and a double melting temperature (T_{m1} , T_{m2}) at 150.2 and 155.2 °C, respectively. No crystallization peak (T_c) appeared during the cooling cycle, indicating that the neat PLA did not easily crystallize when subjected to a rapid cooling rate (10 K/min). As a result, the recrystallization of the laminated PLA was observed, leading to the appearance of a cold crystallization peak. Furthermore, the double melting phenomenon of neat PLA occurred during the 2nd heating cycle, corresponding to α' and α crystal formation, as reported in previous articles^[31, 32]. The lower melting temperature was related to imperfect crystal (α' -form) and the higher melting temperature was concerned in perfect crystal (α -form) of PLA^[32, 33]. The DSC results indicated brittle behavior, slow crystallization, and low crystallinity of neat PLA with high T_g , no T_c , and low χ_c . This behavior is in agreement with its mechanical properties. The effects of types and contents of the additives (TCP and MMT) on the thermal transition and thermal behavior of PLA are summarized in Table 2.

As shown in Figs. 1(a) and 1(b), there was no appearance of T_c during cooling process of the PLA/TCP (PLT) and PLA/MMT (PLM) blends. These results indicated that the addition of both TCP and MMT did not affect the crystallization of the PLA polymeric chains in the cooling cycle. However, the presence of these additives significantly affected other thermal behaviors of the PLA. With increasing

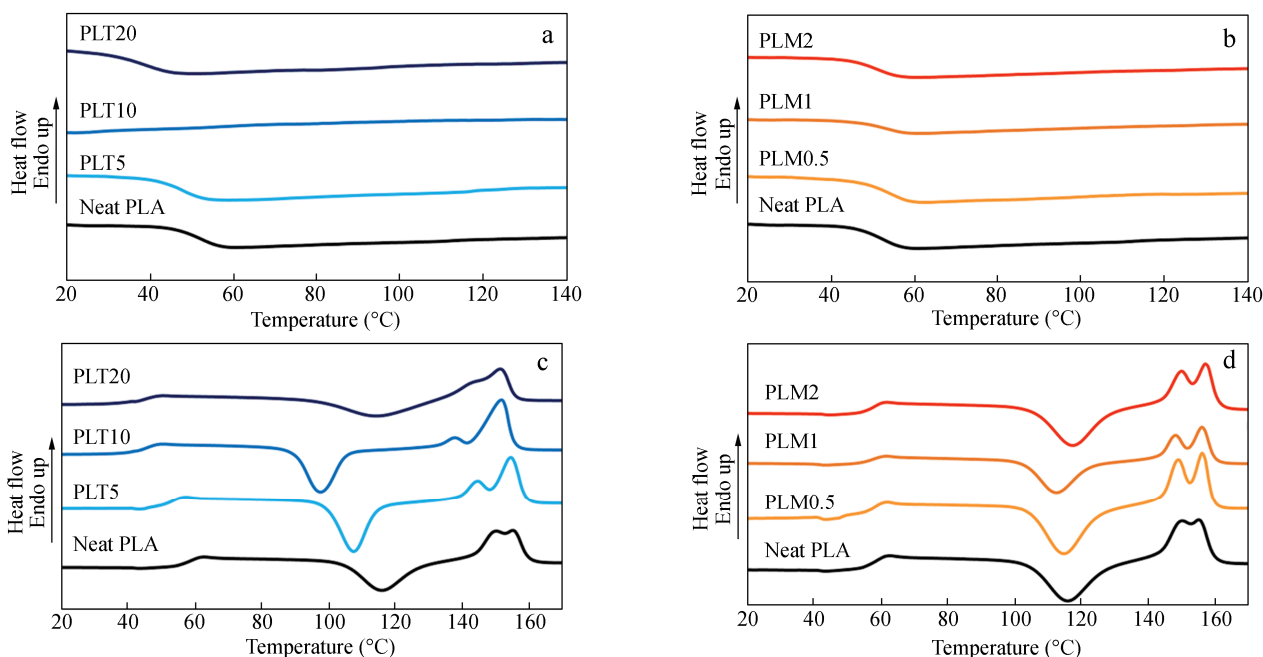


Fig. 1 DSC thermograms of neat PLA and the PLA blends with various TCP and MMT contents: (a, b) cooling and (c, d) 2nd heating cycles

Table 2 DSC data of neat PLA and the PLA blends with different additive contents

Sample ID	Thermal transitions (°C)					ΔH_m^c (J/g)	χ_c^d (%)
	T_g	T_c	T_{cc}	T_{m1}^a	T_{m2}^b		
Neat PLA	60.5	—	115.9	150.2	155.2	29.91	32.16
PLT5	51.0	—	107.4	144.6	154.6	36.56	41.28
PLT10	47.0	—	97.6	137.8	151.7	37.38	44.21
PLT20	41.8	—	114.5	—	151.4	32.84	42.37
PLM0.5	55.0	—	114.6	149.0	156.3	32.13	34.72
PLM1	56.6	—	112.7	148.5	156.9	27.66	30.04
PLM2	57.8	—	116.5	149.0	156.2	33.12	36.34

^a The lower melting temperature of the melting; ^b The higher melting temperature of the melting; ^c Heat of fusion of PLA blends from 1st heating cycle; ^d Degree of crystallinity of PLA blends from 1st heating cycle

levels of TCP (5 phr to 20 phr), the T_g of PLT decreased in the range from 41.8 °C to 51 °C. In other words, the T_g of the PLA blends decreased about 9–20 °C, compared to that of neat PLA (as listed in Table 2). This reduction of T_g occurred because the TCP played an important role as a plasticizer for PLA and the TCP molecules enhanced the chain mobility and free volume by embedding themselves between the PLA polymeric chain. However, the reduction of T_g of PLA might not be enough to change its failure behavior from brittle to ductile, as evidenced by the mechanical results. Besides, the DSC data revealed that the T_{cc} of the PLA blends decreased with the increment of TCP content, compared to that of neat PLA. Hence, the cold crystallization of PLA could be further promoted when TCP was present. The χ_c of the PLA blends significantly increased from 41.3% to 44.2% with the introduction of TCP. Interestingly, the double melting behavior of PLA changed. It seemed that the peak height of lower T_m was reduced but that of higher T_m increased. It is possible that the preponderance of imperfect over perfect crystals of PLA was reduced with the addition of TCP, which was in agreement with the lower T_{cc} . In other words, the TCP might help generate more perfect crystals resulting in an increment of the peak area of higher T_m .

As listed in Table 2, DSC data suggested that the MMT only slightly affected the T_g , T_c , T_{cc} , and T_m of the PLA blends. The T_g and T_{cc} of the blends decreased slightly with increasing MMT contents, by about 3–5 °C and 1–3 °C, respectively, compared to those of neat PLA. These results indicated that the introduction of MMT has a slight effect on the chain mobility and cold crystallization process of the PLA polymeric chains. Generally, the T_g change depends primarily on several factors; *i.e.*, chain flexibility, molecular weight, branching/crosslinking, intermolecular interaction, and steric effect on polymeric chains. It might be possible that the intermolecular interactions (H-bonding between PLA chains) were interrupted by the MMT layers and the expanded distance between the PLA polymeric chains induced additional chain mobility. This led to the slight reduction of the T_g of the PLM. Similar results have been reported by Lee *et al.*^[34]. They reported that the T_g of the pristine PLLA was 63.4 °C but it decreased with the addition of MMT clay. It could also be addressed that the MMT nanoparticles might provide steric hindrances that seemingly enhanced the chain flexibility of PLLA backbones, resulting in the decreased T_g . A clear peak splitting of T_m appeared with increasing amounts of MMT, whereas the χ_c of the PLA

blends was enhanced. It might be possible that MMT particles could act as a nucleating agent for PLA, promoting the χ_c via the heterogeneous nucleation process. The presence of MMT might induce different crystal perfections in the crystal formation of PLA, resulting in a significant peak splitting of the T_m .

Mechanical properties

The tensile strength, Young's modulus, and elongation at break of neat PLA and the PLA blends with different additive contents are illustrated in Fig. 2 and Table 3. The neat PLA displayed a high tensile strength of 52.7 MPa, Young's modulus of 1893.6 MPa, but very low elongation at break of 1.8%, which is characteristic of a brittle polymer. Clearly, it needed to be modified with some additives, so we investigated the effects of TCP and MMT contents on the tensile properties of the PLA blends. Obviously, the tensile properties of the PLA blends depended on the TCP and MMT contents. With increasing amounts of TCP, the tensile strength of the PLA blends tended to decrease; in contrast, the elongation at break slightly increased. These results were not related to the general function of plasticizers for enhancing the flexibility of polymers. This behavior might have occurred from an inadequate level of TCP in the PLA chains,

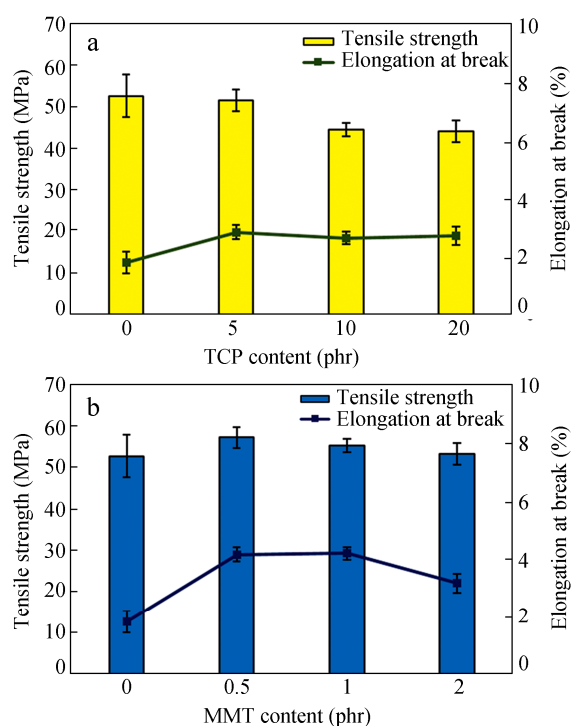


Fig. 2 Tensile properties of neat PLA and the PLA blends with various additive contents: (a) TCP and (b) MMT

Table 3 Mechanical properties of neat PLA and the PLA blends with various additive amounts

Sample ID	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Impact strength (kJ/m ²)
Neat PLA	52.71 ± 5.11	1.80 ± 0.38	1893.64 ± 120.00	1.26 ± 0.18
PLT5	51.68 ± 2.58	2.84 ± 0.25	1822.51 ± 120.00	2.88 ± 0.65
PLT10	44.61 ± 1.56	2.64 ± 0.22	1754.74 ± 125.25	3.34 ± 0.08
PLT20	44.11 ± 2.60	2.71 ± 0.32	1777.62 ± 128.32	3.14 ± 0.50
PLM0.5	57.17 ± 1.25	4.13 ± 0.16	2109.01 ± 70.68	2.82 ± 0.72
PLM1	55.28 ± 1.23	4.17 ± 0.40	2116.38 ± 68.65	2.69 ± 0.23
PLM2	53.28 ± 2.05	3.13 ± 0.26	1994.32 ± 58.88	2.85 ± 0.41

a position supported by the DSC results. With 20 phr of TCP, the T_g of the PLA blend was still higher than room occurred from an inadequate level of TCP in the PLA chains, temperature (41.8 °C, as shown in Table 2). The slight increment in elongation at break showed that the PLA blends were still brittle. However, in our previous work, excess TCP contents (> 20 phr) brought about a blooming effect on the PLA blends caused by the plasticizer migration to the polymer surface, leading to poor physical and mechanical properties. To solve this problem, this work used a combination of TCP and flexible polymer (PBS). TCP showed great benefits, acting as plasticizer, impact modifier, and flame retardant for PLA blends as evidenced by thermal, mechanical, and UL-94 testing.

The addition of MMT to the PLA blends tended to increase tensile strength, Young's modulus, and elongation at break, compared to neat PLA. The tensile strength, Young's modulus and elongation at break of the PLM were in a range of 53.3–57.2 MPa, 1994.3–2116.4 MPa, and 3.1%–4.2%, respectively. This behavior may be caused by the action of MMT as a reinforcing filler and nucleating agent, improving the tensile properties of PLA blends through the cracking mechanism. The DSC results also revealed that the presence of MMT led to the increment of χ_c affecting the mechanical properties of the PLA blends^[35].

Impact resistance testing gave us a better understanding of the effects of TCP and MMT contents on the mechanical performance of the PLA blends. The normalized impact toughness of neat PLA and the various PLA blends is presented in Fig. 3. Neat PLA has quite a low impact strength (1.26 kJ/m²), reflecting its brittle behavior but these results revealed that the inclusion of TCP and MMT significantly affected the impact toughness of the PLA blends. As shown in Table 3, the impact strength of the PLA blends greatly increased with increasing contents of TCP. For example, the impact toughness of PLT20 was 3.14 kJ/m², which was an increase of about 250% compared to that of neat PLA. These results indicated that TCP could act structurally as an impact modifier for PLA, improving the impact energy absorption in the PLA polymeric chains because of the presence of the phenylene groups and oxygen atom in the TCP molecules. Another crucial factor in the increased impact toughness of the blends is the crystallinity induced by the cold crystallization process, and the addition of TCP could help to accelerate the rate of cold crystallization and to enhance the χ_c , which is in agreement with the DSC results.

The impact resistance of the PLA blends with MMT (PLM) ranged from 2.69 kJ/m² to 2.85 kJ/m² or about 210% to 230%

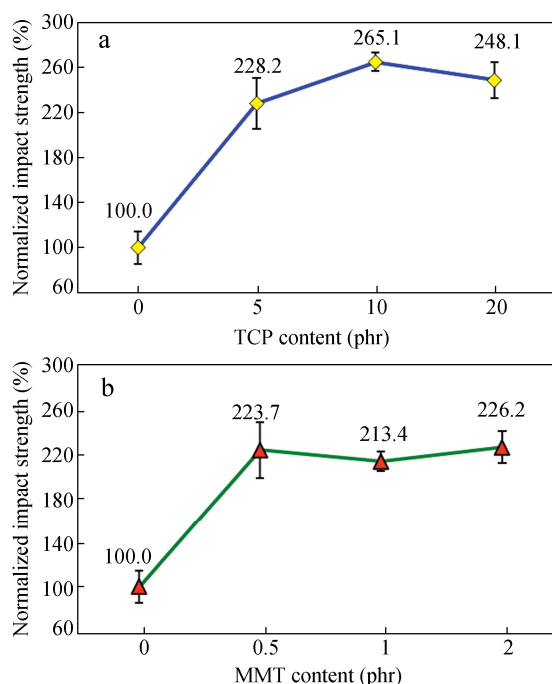


Fig. 3 Normalized izod impact strength of neat PLA and the PLA blends with various additive contents: (a) TCP and (b) MMT

greater than that of neat PLA. It might be because MMT particles acted as an impact modifier and reinforcing filler for PLA by producing physical crosslink spots that constrained the molecular chains, increasing certain mechanical properties^[36]. Besides, it might be a result of the increased χ_c from the addition of MMT. Also, the DSC results revealed significantly increased peak areas of higher T_m and increased χ_c with the introduction of MMT into the blends. It is possible that the crystal size of PLA expanded due to the nucleating action of MMT and the bigger crystals induced an increment of the impact energy absorption and impact toughness of PLM. Thus, comparatively, TCP displayed greater efficiency as an impact modifier for PLA blends than MMT.

Flame retardant properties

Dripping behavior and flammability of materials are widely evaluated by LOI and UL-94 tests. Table 4 summarizes the effect of TCP and MMT contents on the dripping behavior, relative flammability, and LOI value of the PLA blends. The results indicated that neat PLA is a flammable polymer with a low LOI value (18.0%), heavy dripping of plastic melt, and no rating in UL-94 testing, suggesting that neat PLA should be modified with an appropriate additive to expand its

applications. The introduction of TCP markedly increased the LOI values. For instance, the LOI value of PLT10 improved from 18.0% to 30.2%. In other words, the normalized LOI value of PLT10 was about 68% greater than that of neat PLA, as displayed in Fig. 4. In addition, UL-94 results indicated that the addition of TCP effectively decreased the observed dripping of plastic melt. Interestingly, the cotton did not ignite in the UL-94 test. In other words, the heat from dripping plastic melt of PLT was not enough to ignite the cotton. All the PLA/TCP blends (PLT) could self-extinguish with very short total flame time (< 14 s) and achieved V-0 rating in UL-94. In contrast, neat PLA had a long total flame time over 250 s with no rating. Therefore TCP significantly retarded the melt dripping and flammability of PLA. The phosphorous atoms in the molecular structure of TCP played an important role in reducing the heat and continuity of combustion by the formation of a char layer^[1]. Proposed mechanisms for the flame retardant action of TCP with the PLA blends are displayed in Fig. 5. The phosphorous-based TCP thermally decomposed releasing a lot of phosphoric acid and *o*-cresol molecules. After that, these molecules of phosphoric acid reacted with the hydroxyl groups in PLA and

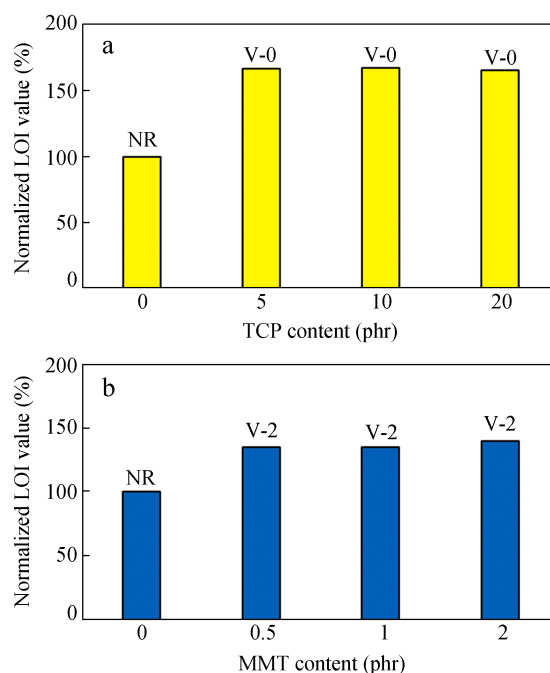


Fig. 4 Normalized LOI values of neat PLA and the PLA blends with different additive contents: (a) TCP and (b) MMT

Table 4 UL-94 data, dripping behavior, and LOI results of neat PLA and the PLA blends with different additive contents

Sample ID	UL-94 data						LOI (%)
	t_1^a (s)	t_2^b (s)	$\sum_{i=1}^s (t_1 + t_2)^c$ (s)	Ignition of cotton	Observed dripping	Grade	
Neat PLA	20.00 ± 14.00	36.00 ± 24.54	281.00	Yes	Heavy	NR ^d	18.0
PLT5	1.74 ± 0.17	1.00 ± 0.00	13.70	No	Drip	V-0	30.1
PLT10	1.64 ± 0.16	1.00 ± 0.00	13.20	No	Drip	V-0	30.2
PLT20	1.51 ± 0.29	1.00 ± 0.00	12.55	No	Drip	V-0	29.8
PLM0.5	6.59 ± 0.61	2.66 ± 0.08	46.25	Yes	Drip	V-2	24.3
PLM1	6.00 ± 1.30	1.20 ± 0.50	36.00	Yes	Drip	V-2	24.3
PLM2	4.23 ± 1.28	1.00 ± 0.00	26.15	Yes	Drip	V-2	25.2

^a After flame time in the 1st flame application for 10 s; ^b After flame time in the 2nd flame application for 10 s; ^c Total flame time; ^d NR represents no rating

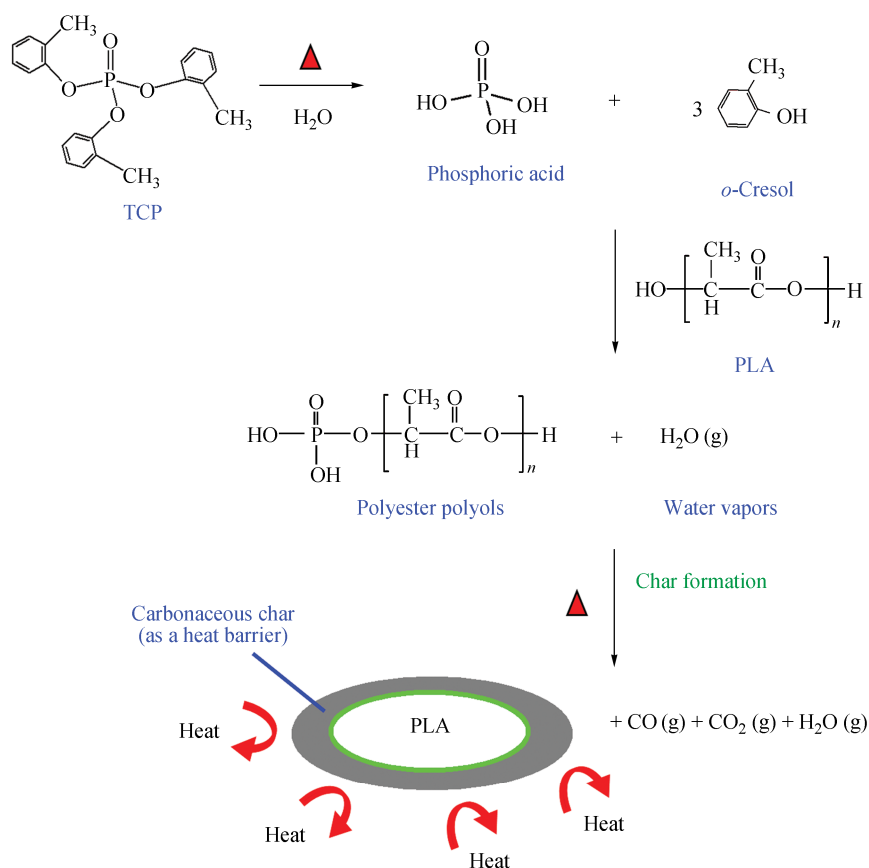


Fig. 5 The proposed mechanisms for flame retardant reaction of TCP with the PLA blends

created polyester polyols and water vapor. These polyols with multiple hydroxyl functional groups would decompose and form a carbonaceous char layer acting as a heat barrier^[37] and a large number of water vapor molecules released during the reaction between phosphoric acid and PLA helped to reduce the total heat in the system, inhibiting the burning process^[38].

The addition of MMT to the PLA blends (PLM) led to a reduction of observed melt dripping and an increment of LOI value. The normalized LOI value, compared to that of neat PLA, increased about 35% to 40% with the presence of MMT (as shown in Fig. 4b). Moreover, the PLA/MMT blends (PLM) self-extinguished with the total flame time less than 30 s to 50 s. This behavior occurred because the low surface energy of MMT enables it to form lamellae that migrate to the surface of PLA, forming heat and oxygen barriers and inhibiting dripping^[2]. Although the addition of MMT improved the melt dripping and LOI results of the blends, the cotton was ignited by molten drips during the UL-94 test for all compositions of PLM. Therefore, the PLM samples were rated V-2 under UL-94 measurement. Comparatively, TCP should be a more effective flame retardant than MMT for PLA.

Characterization of the PLA/PBS Blends (PLS)

Thermal behaviors

Figure 6 shows the DSC thermograms of neat PLA and the PLA/PBS blends. As discussed above, neat PLA indicated a single T_g of 60.5 °C and a T_{cc} of 115.9 °C without T_c . Blending PLA with 20 wt% of PBS (*i.e.* PLS) remarkably

affected its thermal behaviors. The DSC results revealed that the T_g of PLS decreased to 34.4 °C in the presence of 20 wt% PBS, or reduced almost 26 °C compared to that of neat PLA. These results indicated the increased chain mobility of the PLA/PBS blends affecting its flexibility. A significant reduction in T_{cc} of the PLS compared to neat PLA of 22 °C was also observed. It implied that the presence of PBS accelerated the cold crystallization process in the polymeric chains. However, the T_c of the PLS still disappeared under experimental conditions due to the high cooling rate (10 K/min), leading to recrystallization of PLA lamellae. These evidences indicated that the drawbacks of PLA are brittleness and a slow crystallization rate. Furthermore, the melting endotherms of PLS were separated into three positions. A single endothermic peak associated with the melting temperature of PBS (T_{m1}) was noticed at 111.1 °C. The higher melting peaks (T_{m2} and T_{m3}) related to α' and α crystals of PLA appeared at 141.8 and 154.0 °C, respectively. The χ_c of PLS increased to 38.7% from 32.2% for neat PLA. The thermal parameters of neat PLA and the PLA/PBS blends from DSC results are summarized in Table 5.

The influences of TCP levels and combinations of TCP and MMT on the thermal behaviors of the PLA/PBS blends were investigated. At low concentrations of TCP (< 20 phr), the differences in thermal behaviors of the PLA/PBS blends were not clearly observable. The T_g , T_{cc} , T_m , and χ_c values of the PLA/PBS blends with low TCP contents are in the same range, comparable to those of the PLA/PBS blend without

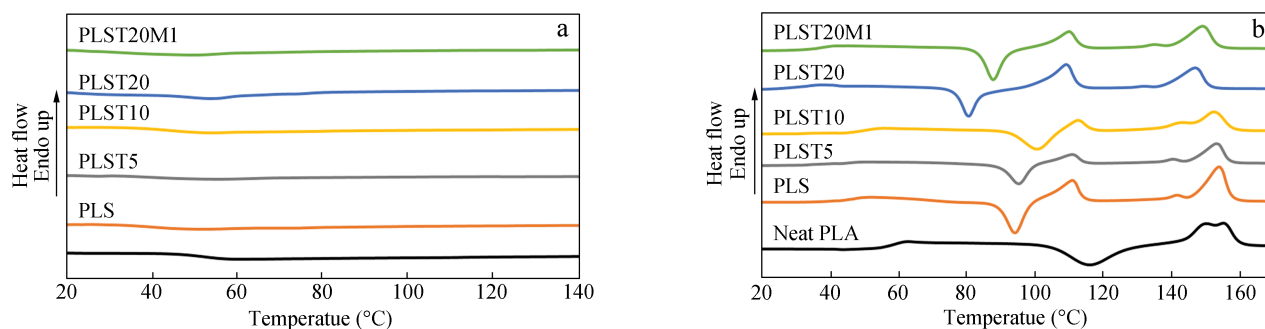


Fig. 6 DSC thermograms of neat PLA and the PLA/PBS blends: (a) cooling and (b) the 2nd heating curves

Table 5 DSC data of neat PLA and the PLA/PBS blends

Sample ID	Thermal transition (°C)						$\Delta H_{m,blends}^d$ (J/g)	χ_c^e (%)
	T_g	T_c	T_{cc}	T_{m1}^a	T_{m2}^b	T_{m3}^c		
Neat PLA	60.5	–	115.9	–	150.2	155.2	29.91	32.16
PLS	34.4	–	94.1	111.1	141.8	154.0	37.31	38.68
PLST5	32.8	–	95.2	110.9	140.6	153.3	24.26	26.40
PLST10	42.6	–	100.7	112.8	143.4	152.6	30.88	35.21
PLST20	29.0	–	80.5	109.2	132.0	147.2	40.24	50.06
PLST20M1	37.3	–	87.8	110.0	135.2	149.2	41.76	52.39

^a The melting temperature of PBS; ^b The lower melting temperature of PLA; ^c The higher melting temperature of PLA; ^d Heat of fusion of the PLA/PBS blends from the 1st heating cycle; ^e Degree of crystallinity of the PLA/PBS blends from the 1st heating cycle

TCP (PLS). These results indicated that the addition of TCP with < 20 phr slightly affected the thermal transitions of the PLA/PBS blends. The lower levels of TCP were possibly not adequate to increase the chain mobility and crystallization of the blends. Interestingly, with the addition of 20 phr TCP, the T_g value of the blends (PLST20) decreased dramatically to 29.0 °C, indicating a significant increase of chain mobility in the PLA polymeric chains. The failure mode of the PLST20 changed from brittle to ductile compared to neat PLA which was evidenced by the mechanical results. These results also revealed that the efficiency of PLA plasticization is enhanced by increasing the concentration of TCP. In other words, the T_g of PLST20 was reduced by approximately 31.5 °C compared to that of neat PLA (60.5 °C). TCP could be an effective plasticizer for both PLA and PLA/PBS blends with the appropriate loading. Besides, the T_{cc} of PLST20 decreased to 80.5 °C, indicating a promoted cold crystallization process. Moreover, the χ_c of the PLST20 sharply increased to 50.1%, as shown in Table 5. It is implied that TCP could increase the free volume in the PLA/PBS blends and accelerate the spherulite growth rate during the recrystallization process. However, the double melting phenomenon was not observed in the PLA/PBS blends with the addition of 20 phr TCP. It might be because the presence of 20 phr TCP reduced the variety of spherulite size and crystal perfection, leading to a single endothermic melting peak. Similar behavior was observed in the PLA/PBS blend with the addition of 20 phr TCP and 1 phr MMT (PLST20M1). The DSC parameters of the PLST20M1 showed similar tendencies to those of PLST20. Its T_g and T_{cc} values decreased compared to that of PLS, whereas the double melting peak of PLA disappeared. Moreover, the χ_c greatly increased to 52.4%, greatly affecting its impact toughness. As discussed above, the presence of MMT effectively induced the heterogeneous

nucleation process, leading to the increment of χ_c . A similar result has been reported by Ray *et al.*^[35]. They reported that the thermal and mechanical properties of the PLA composites were improved with the addition of MMT. Furthermore, MMT acted as a nucleating agent for PLA and its crystallinity greatly increased. These results indicated that the combination of PBS, and TCP and MMT acted in synergy on the thermal behavior of the PLA/PBS blend.

Mechanical properties

Figure 7(a) presents the tensile strength and elongation at break of neat PLA and the PLA/PBS blends. Neat PLA showed a high tensile strength but very low elongation at break which is the characteristic of brittle materials. The tensile strength and Young's modulus of the blends slightly decreased with the addition of 20 wt% PBS; however, the elongation at break increased to 14.85%, as displayed in Table 6. As expected, the addition of PBS caused a significant improvement in the flexibility of the PLA blends. The tensile properties of the PLA/PBS blends were clearly affected by the presence of TCP.

At lower TCP levels (5 and 10 phr), both the tensile strength and elongation at break of the PLA/PBS blends decreased compared to those without TCP. These changes might result from an anti-plasticization effect due to too little plasticizer content in the polymer chains, producing a reduction in tensile properties. With further increasing TCP content (*i.e.* > 10 phr), the elongation at break of the PLA/PBS blends (PLST20 and PLST20M1) magnificently increased to 94% and 141%, respectively. With an appropriate concentration of plasticizer, TCP molecules helped to increase the free volume and improve the chain mobility of the polymeric chains *via* the plasticization process, leading to a significant reduction of T_g and the dominant increase in flexibility, as evidenced by thermal and mechanical properties. These results revealed the synergistic

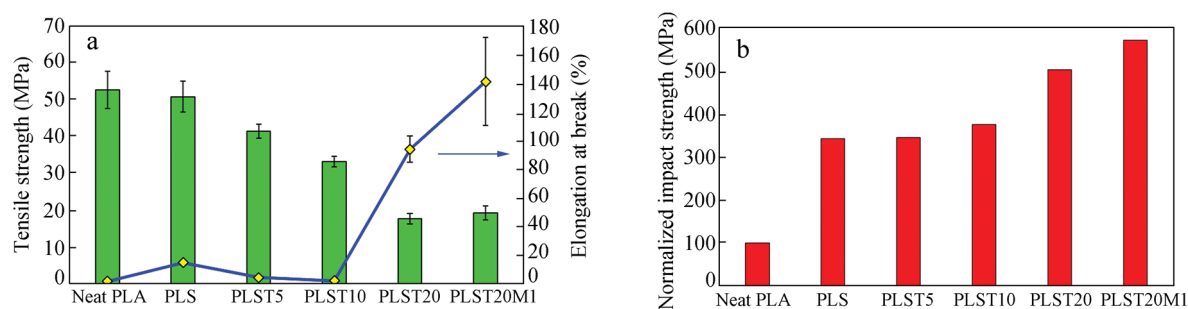


Fig. 7 Mechanical properties of neat PLA and the PLA/PBS blends: (a) tensile strength and (b) normalized impact strength

Table 6 Mechanical characteristics of neat PLA and the PLA/PBS blends

Sample ID	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Impact strength (kJ/m ²)
Neat PLA	52.71 ± 5.11	1.80 ± 0.38	1893.64 ± 120.00	1.26 ± 0.18
PLS	50.87 ± 4.23	14.85 ± 1.21	1795.96 ± 95.52	4.34 ± 0.18
PLST5	41.47 ± 1.84	4.36 ± 1.06	1589.30 ± 160.00	4.38 ± 0.20
PLST10	33.23 ± 1.46	2.16 ± 0.24	2262.96 ± 132.04	4.76 ± 0.44
PLST20	17.63 ± 1.45	94.04 ± 9.24	1044.73 ± 26.33	6.37 ± 0.23
PLST20M1	19.25 ± 1.94	141.44 ± 30.86	1016.98 ± 13.03	7.25 ± 0.67

combination of PBS and TCP on the flexibility of the PLA/PBS blends. Conversely, the tensile strength and Young's modulus decreased which are typical characteristics of softer materials. Similar results were observed in the PLA/PBS/TCP blends in the presence of MMT (PLST20M1). However, both tensile strength and elongation at break of the blends were higher than those without MMT (PLST20). This behavior occurred because the MMT acted as a reinforcing filler to increase the tensile properties of the PLA/PBS blends via the cracking mechanism.

To understand the synergistic combination of PBS, TCP, and MMT on the mechanical performance, the impact toughness of the PLA/PBS blends was investigated. Table 6 illustrates the impact toughness of neat PLA and the PLA/PBS blends. Neat PLA shows a brittle failure with low impact strength (1.26 kJ/m²). The impact energy of the PLA blends increased with the addition of PBS (PLS), leading to an impressive increment of impact strength. For example, the impact resistance of PLS increased to 4.34 kJ/m² when the PBS content increased to 20 wt%. That means the impact strength of PLS increased by about 244%, as shown in Fig. 7(b). The important factor in the increased toughness of the PLA/PBS blends is the structure of PBS, which contained oxygen atoms in polymeric main chains. This structure improved the impact energy absorption and flexibility of PLS polymer chains. The combination of PBS and TCP led to increased impact resistance of the blends. The impact strength of the PLA/PBS blends increased to 4.38, 4.76, and 6.37 kJ/m² when TCP was added in 5, 10, and 20 phr, respectively; in other words, the impact toughness of the blends increased by about 350% to 500%. The synergistic combination of PBS and TCP accelerated the rate of cold crystallization and increased the χ_c , compared to that of neat PLA. Both the phenylene groups and the oxygen atoms in the chemical structure of TCP molecules could be crucial factors in the increased capability of the PLST20 to absorb the impact energy. The DSC measurement further confirmed the promoted cold crystallization and the improved

crystallinity. Surprisingly, the synergistic influence of PBS, TCP, and MMT greatly increased the impact resistance of the PLS from 4.34 kJ/m² to 7.25 kJ/m² for PLST20M1. Ultimately, the normalized impact strength of PLST20M1 was 450% higher than that of neat PLA. Investigation of the PLA/PBS blends' mechanical properties revealed that both flexibility and impact toughness were considerably increased by the addition of TCP and MMT due to the synergistic effect via the plasticization and heterogeneous nucleation process discussed in the sections on thermal behaviors and mechanical performances.

Morphological study

The SEM micrographs in Fig. 8 show the tensile fractured surfaces of neat PLA and the PLA/PBS blends with and without additives. The tensile fractured surface of neat PLA is smooth, which is typical of a brittle structure (Fig. 8a). After blending with 20 wt% PBS (Fig. 8b), the fractured surface is rougher and some elongated fibrils appear after tension, indicating the change in failure behavior from brittle to ductile. This is in agreement with the reduction of T_g and increment of elongation at break of PLS. However, a large number of PBS particles and numerous holes are visible on the tensile fractured surface. These are evidence of poor interfacial adhesion between the two phases, which allowed PBS particles to be pulled out of the matrix during fracturing. Therefore, the tensile strength and Young's modulus of the blends decreased when PLA was blended with PBS. The anti-plasticization phenomenon was clearly noticed on the surface after tension of the PLST5 (Fig. 8c), as discussed in the section on tensile properties. The phase separation of PLA, PBS, and TCP appeared clearly with the addition of 5 phr TCP. The PBS fillers were seemingly detached from the PLA matrix and large defects were noticeable in the PLST5 as the fracture mechanism led to severe deterioration of the tensile properties. Normally, to reduce the influence of the anti-plasticization process, the concentration of the plasticizer in the blends should increase. The appropriate TCP level (20 phr) led to an improvement of the tensile

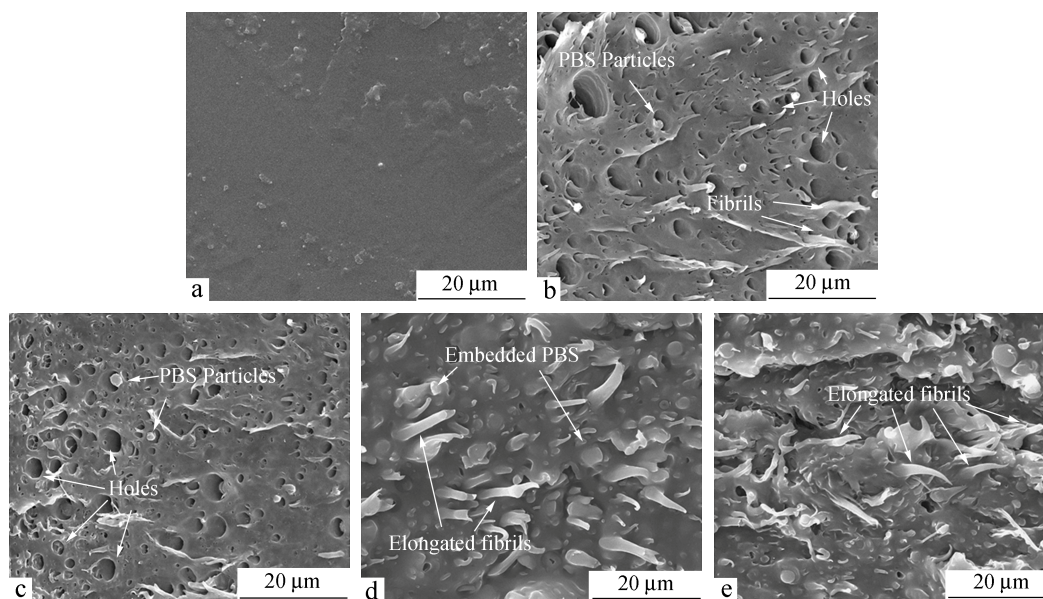


Fig. 8 SEM images at 2000 $\times$ magnification of the tensile fracture surface of (a) neat PLA, (b) PLS, (c) PLST5, (d) PLST20, and (e) PLST20M1

fractured surface and better mechanical performance of the blends, as displayed in Figs. 8(d) and 8(e), and a lot of the holes and isolated PBS particles resulting from tensile cracking disappeared. In the presence of 20 phr TCP, more uniform and less isolated PBS was clearly seen on the fracture surface of PLST20 and PLST20M1. Furthermore, a large number of elongated fibrils after tension were observed in the PLA matrix, suggesting that the embedded PBS was well wetted by the PLA matrix and some fractures occurred at some of interfaces between PLA and PBS.

The well wetting and interfacial bonding significantly influenced the mechanical and morphological properties of the polymer blend, leading to an increment of fracture energy^[36]. The elongated fibrils were a result of the significant improvement in flexibility of the blends from the addition of MMT and 20 phr TCP consequent to the increased chain mobility and free volume in the polymeric chains. These results confirmed the synergistic effect of this combination of PBS and additives on the mechanical performance of the PLA/PBS blends. The elongation at break of PLST20 and PLST20M1 increased over 90% and 140%, respectively, compared to that of PLA (1.8%). Nevertheless, their tensile strength and Young's modulus decreased, which is a typical behavior of a softer material. Last but not least, it must be kept in mind that each blend of PLA and PBS may

have its own optimum additive contents.

Flame retardant properties

Neat PLA is a flammable polymer with low LOI value, heavy melt dripping, and no rating in UL-94 testing. We evaluated the influences of PBS, TCP, and MMT on the flammability, dripping behavior and extinguishing characteristics of PLA and the data are summarized and presented in Table 7. Figure 9 shows that 20 wt% PBS improved the LOI value of the PLA/PBS blend to 24.0%. This effect might have occurred because PBS has a higher LOI value than neat PLA and affected the flame retardant properties when blended. Similar behavior has been reported by Wang *et al.*^[2]. At 43.55 s, the total flame time of the PLS was significantly shorter than that of neat PLA (281 s). However, the observed dripping of plastic melt was also heavy and burned the cotton during the UL-94 testing. Hence, the PLS achieved only a V-2 rating. With increments of TCP contents (5, 10, and 20 phr), the plastic melt dripping and total flame time of the PLA/PBS blends significantly reduced while the LOI value obviously increased. The normalized LOI values of the PLA/PBS blends with TCP increased to within a range of approximately 140% to 170% (as shown in Fig. 9). PLST20 produced no plastic dripping and the cotton did not ignite during the flammability test, indicating that an adequate level of TCP could improve the flammability, dripping behavior, and

Table 7 UL-94 data, dripping behavior, and LOI values of neat PLA and the PLA/PBS blends

Sample ID	UL-94 data						LOI (%)
	t_1^a (s)	t_2^b (s)	$\sum_{i=1}^5 (t_1 + t_2)^c$ (s)	Ignition of cotton	Observed dripping	Grade	
Neat PLA	20.00 $\pm$ 14.00	36.00 $\pm$ 24.54	281.00	Yes	Heavy	NR ^d	18.0
PLS	7.00 $\pm$ 1.4	1.70 $\pm$ 0.60	43.55	Yes	Heavy	V-2	24.0
PLST5	1.40 $\pm$ 0.30	1.00 $\pm$ 0.00	12.00	Yes	Drip	V-2	30.2
PLST10	4.42 $\pm$ 0.72	0.67 $\pm$ 0.58	25.45	Yes ^e	— ^f	V-2	26.4
PLST20	5.56 $\pm$ 1.11	0.00 $\pm$ 0.00	27.80	No	—	V-0	26.0
PLST20M1	6.64 $\pm$ 1.33	0.67 $\pm$ 0.58	36.55	No	—	V-0	25.5

^a After flame time in the 1st flame application for 10 s; ^b After flame time in the 2nd flame application for 10 s; ^c Total flame time; ^d NR represents no rating;

^e Ignition of cotton from plastic melt during 10 s flame application; ^f No dripping UL-94 test

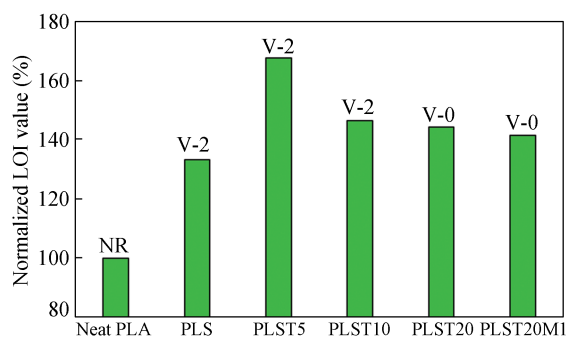


Fig. 9 Normalized LOI values of neat PLA and the PLA/PBS blends

extinguishing characteristics of the blends to the point that they could achieve V-0 rating in UL-94 testing.

At lower TCP concentrations (< 20 phr), the PLA/PBS blends self-extinguished with very short total flame time (< 50 s) and high LOI values (> 26%), suggesting that TCP could be an effective flame retardant for PLA and PBS. The polyester polyols and water in the proposed mechanism in Fig. 5 release water vapor and form carbonaceous char as a heat barrier, which are the important keys to reducing the heat of combustion and retarding the flammability of the PLA/PBS blends. Nonetheless, some melt dripping did occur at these lower loadings of TCP, and it led to the ignition of the cotton, resulting in a downgrading of the rating from V-0 to V-2. The addition of both TCP and MMT on the PLA/PBS blend (PLST20M1) displayed similar results to PLST20 in terms of LOI value, dripping behavior, and UL-94 data. The tendency of observed dripping and UL-94 results was excellent with V-0 rating. The flame retardant properties of the blend were not worse for the presence of MMT. In contrast, the tensile strength, elongation at break, and impact toughness of the PLST20M1 increased remarkably, revealing a balance of flame retardant properties and mechanical performances from the synergistic influence of PBS, TCP, and MMT in the PLA matrix. Conclusively, these results indicated that TCP acted as a plasticizer, an impact modifier, and a flame retardant, enhanced the chain mobility, and improved the impact energy absorption and flame retardation of PLA. PBS and MMT played a crucial role as flexible fillers, impact modifiers, and flame retardants, improving the flexibility, impact resistance, and flame retardation synergistically.

CONCLUSIONS

This work set out to search for a balance between flame retardancy and toughness in PLA and PLA/PBS blends through the synergistic effect of TCP and MMT. TCP was successfully used as a plasticizer, an impact modifier, and a flame retardant for PLA blends. The plasticization mechanism, derived from the introduction of TCP, improved the chain mobility and accelerated the cold crystallization of the PLA blends. T_g and T_{cc} of the PLA blends were lower than those of neat PLA. The addition of TCP increased the degree of crystallinity of the PLA blends and their impact resistance significantly increased in agreement with the increment of χ_c .

However, too much TCP content reduced the tensile strength and Young's modulus of the PLA blends. Introducing MMT into the PLA blends increased the mechanical strength and Young's modulus. Both TCP and MMT could be effectively blended with PLA to improve its dripping behavior, LOI value, and flammability. Nevertheless, comparatively, TCP was a more efficient flame retardant for PLA blends than MMT.

In the case of PLA/PBS blends with and without TCP, the DSC data revealed significant changes in thermal behaviors. The thermal transitions (T_g , T_{cc} , and T_m) of the PLA blends decreased with the addition of PBS and TCP, affecting flexibility, cold crystallization, and double melting phenomena. These changes in thermal behaviors were directly related to the changed mechanical properties of the PLA/PBS blends, indicating that the appropriate level of TCP (20 phr) is a crucial factor in balancing the mechanical performance and flammability. The synergistic effects of PBS, TCP, and MMT afforded the PLA/PBS blends increased elongation at break, impact toughness, and flame retardancy, indicated by the improved χ_c , LOI value, and UL-94 results. The PLST20 and PLST20M1 blends self-extinguished without dripping of plastic melt or ignition of the cotton, and achieved V-0 rating. These results went some way towards achieving the aims of our work and the evidence of the morphological studies showed that the failure behavior of the PLA/PBS blends with TCP and TCP/MMT changed from brittle to ductile.

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