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Thermal and flame resistant properties of poly (lactic acid)/poly (methyl methacrylate) blends containing halogen-free flame retardant

E.L. Teoh^a, M. Mariatti^{a,b}, W.S. Chow^{a,b*}

^a*School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, 14300 Penang, Malaysia.*

^b*Cluster for Polymer Composites, Science and Engineering Research Centre, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, 14300 Penang, Malaysia.*

Abstract

Flame retarded poly(lactic acid)/poly(methyl methacrylate) (PLA/PMMA) blend was prepared using melt compounding technique in the presence of isopropylated triaryl phosphate ester flame retardant [FR; 20 parts per hundred resins (phr)]. The effect of FR on the thermal and flame resistant properties of PLA/PMMA blend was studied. The flammability of PLA/PMMA blends was evaluated by UL-94 vertical burning test while the morphology of the residues was analyzed using field emission scanning electron microscope (FESEM). Thermogravimetric analyzer (TGA) was utilized to characterize the thermal decomposition behaviors of PLA/PMMA blends. The UL-94 result revealed that the inclusion of FR has shortened the after-flame time and improved dripping behavior of PLA/PMMA blend, achieving V-0 ranking in the test. An extensive and continuous carbonaceous char-like layer was found on the surface of the PLA/PMMA/FR residue, indicating the existence of condensed phase mechanism by FR. The incorporation of FR has accelerated the thermal degradation of PLA/PMMA blend at low temperature, but enhanced thermal stability of the blend at elevated temperature.

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* Corresponding author. Tel.: +604-599 6160; fax: +604-594 1011.
E-mail address: shyang@usm.my

Nomenclature

FESEM	Field Emission Scanning Electron Microscope
FR	Flame Retardant
IFR	Intumescent Flame Retardant
PLA	Poly(lactic acid)
PDLA	Poly(D-lactic acid)
PLLA	Poly(L-lactic acid)
PMMA	Poly(methyl methacrylate)
TGA	Thermogravimetric Analyzer
TPP	Triphenyl Phosphate

1. Introduction

As increasing awareness in developing eco-friendly polymer, poly(lactic acid) (PLA) has emerged as one of the most promising candidate in replacing conventional petroleum based commodity resins. PLA possesses several environmental advantageous such as biodegradability, low emission of greenhouse gas, and low production energy.^{1,2} Since it exhibits high degree of transparency, good mechanical properties, low toxicity and ability to be process under conventional processing equipments, it holds tremendous potential in packaging industries, household and biomedical applications. However, its low heat resistant, slow crystallization rate, and inherent brittleness limit its usefulness in electronic and automotive industries.^{3, 4}

One way to overcome these limitations is by modification of PLA through blending. Polymer blending is a convenient industrial process that able to improve the properties of existing materials by combining the unique properties of available materials. Through synergistically interacting polymers, great amount of high performance blend could be generated in a most cost-effective approach. In terms of environment sustainability, polymer blends also served as a useful and economic method by upgrading recycled and off-specification polymers. A vast number of literatures reported on the optimization properties of PLA via blending. For example, Anderson *et al.*⁵ have toughened PLA with linear low-density polyethylene. Sarasua *et al.*⁶ have melt mixing optically pure enantiomeric PLA: poly(L-lactide) (PLLA) and poly (D-lactide) (PDLA) and increment in overall crystallinity degree of the PLLA/PDLA blends was reported. Natural rubber was blended with PLA to enhance the toughness, processing properties, and crystallization ability of PLA⁷.

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic well known for its excellent optical properties (allow transmission of visible light up to 92%), outstanding weatherability, high scratch resistant, and low moisture and water absorbing capacity (0.2%). It is amorphous in nature and exhibits low shrinkage during solidification. PMMA could be produced via bulk polymerization, emulsion polymerization, and solution polymerization, depends strongly on the application of the end products.⁸ Its valuable physical and chemical properties, biological stability, wide processing ability, and ease of modification have favored its use in durable external application and medical field. Hence, melt mixing PMMA with PLA could be a successful approach to amend the limitations of PLA.

In order for a thermoplastic to serve as external housing materials for medium-size electronic products, it should exhibit high flame retardancy. Since PLA is highly flammable and severe melt dripping when expose to fire, improvement of flame resistance has remaining as an upmost and important task. While the use of halogenated flame retardant (e.g., polybrominated diphenyl ethers) in daily products are banned in Europe and North America due to their toxicological effects to the environment, wildlife and humans, halogen-free flame retardant formulations are developed as phase out plan for halogen based flame retarded materials. These environmental friendly flame retardant systems are composed of intumescent flame retardants (IFR)^{9, 10}, phosphorus-¹¹ and nitrogen-containing, micro-¹²and nanoparticles¹³, inorganic substances and silica derivatives¹⁴. They could be used either alone or by combination to achieve optimum flame retardancy effect.

Zhang *et al.*¹⁵ had prepared PLA/PMMA blends by solution-precipitation method. The thermal properties of PLA were increased by the addition of PMMA. Canetti *et al.*¹⁶ had reported an improvement in the elastic modulus and tensile properties of the PLA by adding PMMA. In this research work, PMMA with moderate high glass transition temperature (T_g approximately 105°C) was physical blended with PLA in order to maintain its mechanical integrity. Although the incorporation of PMMA into PLA able to improve the mechanical and thermal properties, but it is still unable to develop flame retarded PLA. Therefore, phosphorus-based flame retardant, isopropylated triaryl phosphate ester (FR) was incorporated to obtain PLA/PMMA blends with UL-94 V-0 rating. UL-94 vertical burning test was

performed to characterize the flammability of the blends, while field emission scanning electron microscope (FESEM) was utilized to study the char morphology of the residue. The thermal decomposition of the PLA/PMMA blends was evaluated by thermogravimetric analyzer (TGA).

2. Experimental

2.1. Materials

PLA (Ingeo™ 3051D) with specific gravity of 1.25 g/cm³ and melt flow index of 25 g/10min (2.16 kg load, 210°C) was provided by NatureWorks LLC, USA. PMMA (Acrylex® CM-207) was supplied by Chi Mei Corporation (Taiwan), with specific gravity of 1.19 g/cm³ and melt flow index of 8 g/10min (3.80 kg load, 230°C). The phosphorus-based flame retardant (Reofos® 50) (FR) with 8.3% phosphorus content, was purchased from Chemtura Corporation, USA. This liquid flame retardant has specific gravity of 1.17-1.18 g/cm³ at 20°C and viscosity at 53-64 cps at 25°C, respectively. This clear liquid contain 25-50% triphenyl phosphate (R=H) and more than 50% of isopropylated triphenyl phosphate (R=isopropyl).

2.2. Preparation of PLA/PMMA/FR blends

Eguiburu *et al.*¹⁷ reported that a miscible PLA/PMMA blend could be achieved at low PMMA content (i.e., 10-30 wt%). Therefore, in this study, 20 wt% of PMMA was blended with PLA. According to our previous study¹⁸, 20 phr of FR are required to impart PLA/organo-montmorillonite nanocomposites with self-extinguishing properties. Thus, in this research, we prepared the flame-retarded PLA/PMMA blends composed of 80 wt% PLA, 20 wt% PMMA, and 20 phr of FR. The PLA and PMMA pellets were dried in an oven at 55°C for 24 h before melt compounding to remove any moisture. After that, a predetermined amount of PLA and PMMA pellets were compounded with an internal mixer (Haake Rheomic Polydrive R600/610) for 10 min at mixing speed of 50 rpm and temperature of 170°C. In order to produce flame retarded PLA/PMMA blend, the PLA and PMMA pellets were charged into the internal mixer, followed by FR after 5 min of mixing time. After melt compounding, the compounded materials were dehumidified at 55°C for 24 h before compression molding. The compounded materials were compress molded with a hydraulic press (Gotech, Taiwan) at 170°C and compression pressure of 14 MPa. The specimens with 3.2 mm thickness were produced for further material characterization. Table 1 shows the material compositions and designations for the PLA/PMMA blends.

Table 1. Material compositions and designations for PLA/PMMA blends.

Material Designation	Composition		
	PLA (wt %)	PMMA (wt %)	Reofos® 50 (phr)
PLA	100	-	-
PMMA	-	100	-
PLA/PMMA	80	20	-
PLA/PMMA/FR	80	20	20

1.2. Materials Characterization

Underwriters Laboratories (UL) 94 vertical burning test was performed according to ASTM D3801 using HVUL Horizontal Vertical Flame Chamber (ATLAS Fire Science Product, Chicago USA). A total of two sets of specimens, with five specimens in each set, were prepared for each the composition. Flame was applied twice on the bottom of the specimens. The times which the flame persisted after first (t_1) and second (t_2) applications were recorded and the dripping behavior were observed. The dimensions of the specimens are 120mm x 12.7mm x 3.2mm.

The char morphology of the residues was studied using field emission scanning electron microscope (FESEM, Supra 35VP, Carl Zeiss, Germany). The surface of the tested specimens was sputter-coated with gold prior to FESEM examination. An energy dispersive X-ray microanalysis (EDX 32, Genesis) was used to analyze the occurrence of elements in the char residue of the blends.

The thermal decomposition properties of PLA/PMMA blends were characterized using thermogravimetric analyzer (TGA, Perkin Elmer Pyris 6, USA). An approximately of 10–15 mg samples were heated from 30–600°C, with heating

rate of $10^{\circ}\text{C min}^{-1}$, according to the previous study by Leu *et al.*¹⁹ All the TGA measurement was performed in nitrogen atmosphere.

3. Results and Discussion

3.1. UL-94 vertical burning test

UL-94 test is the most common procedure to evaluate the regulatory compliance of a plastic materials use in devices and appliances, in term of flammability. Table 2 elucidates the burning behavior of PLA/PMMA/FR blends during UL-94 vertical burning test. Severe flaming drips and bubbling were observed when the flame was applied on pure PLA. It was characterized as V-2 since it able to self-extinguish within 30 seconds after first and second flame applications. Kiliaris and Papaspyrides²⁰ reported that melt viscosity and dripping characteristics have played an important role in determining the material's behavior against fire. Through flowing and dripping of PLA, the heat accumulated in the drips was removed from the burning specimen when melting precedes ignition. Furthermore, the vertically mounted specimen in the burning test had caused the breakdown polymer that acted as fuel being withdrawn from the fire source. As a consequent, the fire growth was suppressed and the combustion cycle was terminated.

When burning was performed on PMMA, large busting bubbles and vigorous bubbling were found on the PMMA sample, accompanied by softening and swelling. Due to high viscosity of PMMA, less melting drips occurred but the cotton indicator was still being ignited by flaming drips. The burning of the PMMA proceeded until whole of the specimen was burned out. Thus, PMMA failed to be ranked in UL-94 vertical burning test. This suggested that PMMA is a highly flammable material owing to its intrinsic chemical composition.

From Table 2, it can be seen that the PLA/PMMA blends recorded UL94 V-2 ranking. Although PLA/PMMA specimen was burned with bubbling and dripping, the mean total after-flame time upon two cycles of flame exposure has slightly reduced in comparison to neat PLA. The falling drips have ignited the cotton indicator, leading to a V-2 rating in the test.

The efficiency of FR on enhancing the flame resistance of PLA/PMMA blend was obviously seen when 20 phr of FR was incorporated. In the presence of FR, the melt dripping of PLA/PMMA/FR was accelerated but no flaming drips were observed. Hence, a fire accident caused by the falling drips could be avoided. The burning of PLA/PMMA/FR has ceased within 5 seconds after the removal of two times flame applications, fulfilling the minimum requirement of UL-94 V-0 classification. It was believed that FR has accelerated the breakdown of the polymer, subsequently promoted the melt flow of PLA/PMMA blend, and favored the melt-flow drip mode of extinguishment. Boscoletto *et al.*²¹ studied the mode of action of triphenyl phosphate (TPP) in Noryl® type blend (a blend constituted of poly(phenylene ether)/high impact poly(styrene) blend). They concluded that TPP has decreased the average combustion time of burning polymer by reducing its surface temperature during ignition in UL-94 test.

Table 2. The after-flame time and burning behavior of PLA, PMMA and PLA/PMMA blends under UL-94 vertical burning test.

Material Designation	After-flame time (s)		Flame Dripping	Cotton Ignited	Rating
	1 st Flame	2 nd Flame			
	Application, t_1	Application, t_2			
PLA	6±3	7±2	Yes	Yes	V-2
PMMA	230±6	-	Yes	Yes	NR*
PLA/PMMA	5±1	2±1	Yes	Yes	V-2
PLA/PMMA/FR	2±1	1±1	No	No	V-0

Remarks:

NR = No rating in UL-94 vertical burning test

* = Sample burning up to holding clamp

- = No second flame application

3.2. Morphological Analysis

The morphology of the char residues of PLA/PMMA and PLA/PMMA/FR blends after UL-94 vertical burning test was studied using FESEM. The char morphologies of PLA/PMMA and PLA/PMMA/FR blends at 1500x magnification are presented in Figure 1. For PLA/PMMA blend, smooth surface with no char formation was observed on the surface of specimen after burning (c.f. Figure 1(a)). This can be deduced that both PLA and PMMA are non self-charring polymers. These polymers undergo chain scission and volatile upon ignition, leaving negligible amount

char formation after burning.

After the addition of 20 phr FR, the morphology of PLA/PMMA blend has changed significantly. An extensive, cohesive homogeneous char-like layer was formed on both of the polymer matrix (c.f. Figure 1(b)), indicating the affinity of FR on PLA and PMMA. This type of char morphology able to provide flame resistance to polymer matrix by reducing the penetration of heat flux, oxygen and volatile fuel, subsequently starves the flame propagation. According to Weil and Levchik²², the char formation could be induced by appropriate additives, such as acid-generating additives. The phosphorus containing flame retardant decomposes upon heating, producing polyphosphoric and phosphoric acid that dehydrate and transesterify the oxygen-containing polymers. As a result, double bonds were generated within the polymer and a significant amount of char was formed via cyclization and cross-linking.²³

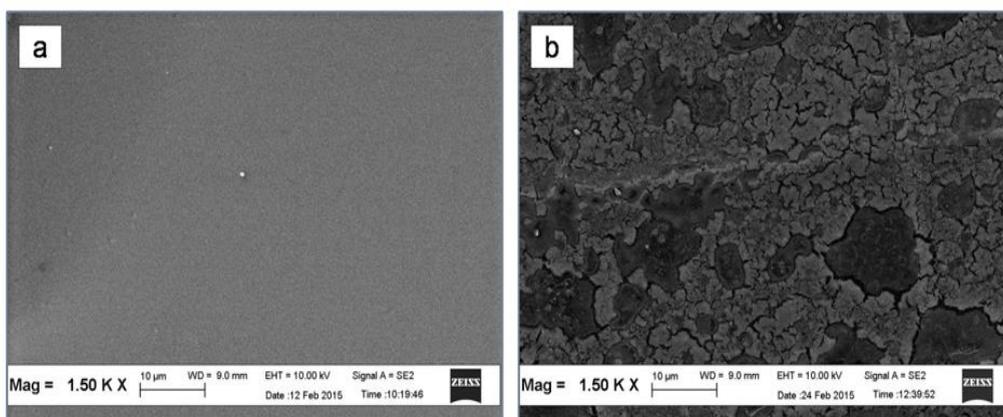


Fig. 1. Char morphology of residues obtained by FESEM after UL-94 vertical burning test. (a) PLA/PMMA; (b) PLA/PMMA/FR.

EDX was utilized to understand the occurrence of elements in the char residue of PLA/PMMA blends after UL-94 vertical burning test and the results are displayed in Figure 2. The EDX result of PLA/PMMA blend shows that only carbon and oxygen elements were found on the polymer blend surface. For PLA/PMMA/FR blend, phosphorus trace was detected on the surface of PLA and PMMA phase (c.f. Figure 2(b) and Figure 2(c)). This further confirm the existence of condense phase mechanism by FR in inducing carbonaceous char formation, further lead to flame extinguishment.

3.3. Thermogravimetric analysis (TGA)

The thermal stability of PLA and its blends were evaluated via TGA under nitrogen atmosphere. Figure 3(a) shows the TGA curves and the extracted data was summarized in Table 3. T_{o1} and T_{o2} indicate the onset degradation temperature at first stage and second stage, T_{10} refers to the temperature at 10% weight loss, and T_d defines as end of decomposition temperature. Maximum weight loss occurred at temperature T_{max} and was determined from the DTG curves.

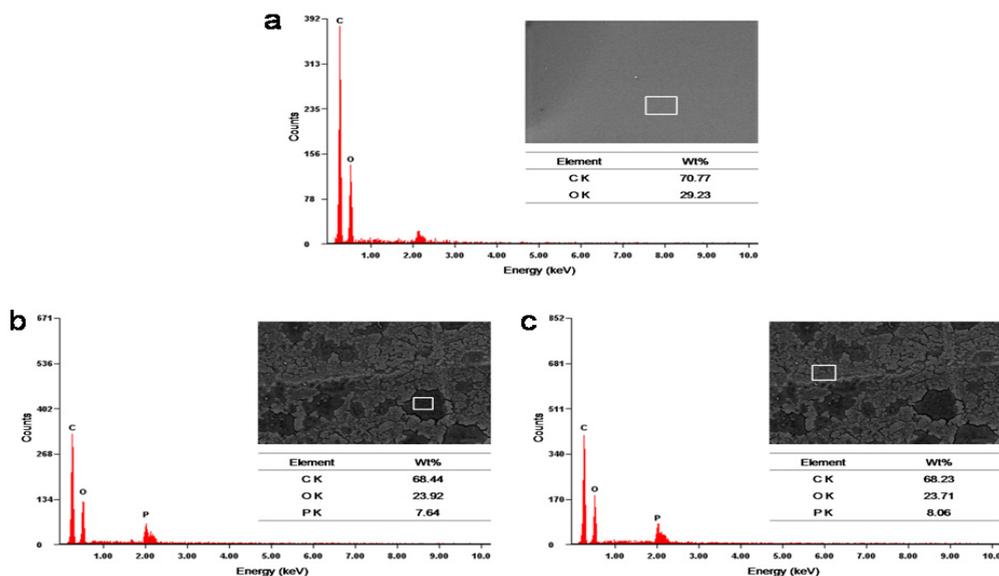


Fig. 2. EDX spectrum of char residues after the UL-94 vertical burning test. (a) PLA/PMMA; (b) PMMA phase, PLA/PMMA/FR; (c) PLA phase, PLA/PMMA/FR.

Figure 3(a) reveals that both of the pristine PLA and PMMA exhibited single-stage decomposition while PLA/PMMA and PLA/PMMA/FR blends under two-stage decompositions. The decomposition stages of all specimens were taken place within the temperature range of 295°C to 430°C. Pure PLA started to decompose at 326°C and experiences maximum mass loss at temperature of 364°C. The thermal decomposition of PLA involves loss of ester group from the main chain and inter- or intra-molecular transesterification, forming oligomers or cyclic oligomers¹⁰. A significant amount of volatilized products such as aldehyde containing compounds, carbon monoxide, aliphatic esters and carbon dioxide was yielded during decomposition process.²⁴ The thermal degradation of PLA ended at 380°C, leaving no residue at the end of the experiment.

The incorporation of 20 wt% of PMMA has caused drastically change on the thermal degradation pathway of PLA. The thermal degradation of PLA/PMMA occurs in two-stage where the first decomposition stage was assigned to the degradation of PLA and the second decomposition stage was attributed to the degradation of PMMA. It is interesting to note that although PLA/PMMA blend exhibited lower T_{o1} and T_{10} than pristine PLA, but the blend showed higher T_d than PMMA. This indicates that the presence of PMMA did not improve thermal stability of PLA at low temperature, but has delayed the thermal degradation at elevated temperature. In other words, PMMA has broadened the thermal decomposition temperature range of PLA.

An interesting phenomenon has been observed when 20 phr of FR was added into PLA/PMMA blend. The existence of FR shifted the T_{o1} of PLA/PMMA/FR to lower temperature by 22°C in comparison with PLA/PMMA blend. This can be explained by low decomposition temperature of FR, due to its low molecular weight and plasticizing effect. The phosphorus containing flame retardant started to decompose at 216°C and lost almost all its mass at temperature 340°C²⁵. Although PLA/PMMA/FR blend having the lowest T_{10} , the temperature difference between T_o and T_{10} of the PLA/PMMA/FR system (i.e., 22°C) was the highest among the temperature difference between PLA (i.e., 10°C), PMMA (i.e., 14°C), and PLA/PMMA (i.e., 12°C). It is worth to mention that the T_{o2} and T_d of PLA/PMMA/FR was the highest compare to all of the systems. These findings proved that thermal degradation process of PLA/PMMA blend has been stabilized and delayed by FR at high temperature.

As a good flame retardant, the agent should decompose at temperature slightly below the decomposition temperature of the polymer matrix. FR has decomposed earlier in the thermal degradation, generating non-volatile polyphosphoric and phosphoric acid in the condensed phase. These acids esterify and dehydrate the oxygen-containing polymer, causing the polymer to form char that acts as a physical barrier to protect the underlying polymer from heat transfer and transportation of oxygen and pyrolysis product. Besides, the phosphoric related acids also form a molten

viscous surface layer, insulating the polymer substrate from heat and oxygen.²⁶ Therefore, the thermal stability of PLA/PMMA/FR blend showed significant improvement at the middle and the end of the thermal decomposition.

Figure 3(b) demonstrates the derivative thermogravimetric (DTG) curves for PLA and its blends. It can be found that both pure PLA and PMMA having only single peak while PLA/PMMA and PLA/PMMA/FR blends exhibited two peaks along the thermal decomposition. This implies that the pristine PLA and PMMA were fully decomposed within one-stage but PLA/PMMA/FR blends underwent two separate decomposition events. The maximum weight loss of PLA and PMMA took place at temperature range of 320–400°C and 330–430°C, respectively. Compare to PMMA, PLA suffered higher weight change and weight loss rate, indicated by the larger area under DTG curve and higher peak height of PLA. This is mainly due to the higher thermal stability of PMMA, retarding the weight loss during decomposition.

With the introduction of 20 wt% PMMA, notably change in the thermal degradation event of PLA/PMMA and PLA/PMMA/FR blends was observed. Major weight loss of PLA/PMMA blend took place at temperature within 285–395°C, corresponding to the degradation of major phase PLA. The thermal decomposition of PMMA occurred at temperature range of 395–445°C, where a small DTG shoulder appeared after the main DTG peak. The presence of PMMA did not cause any change in the T_{max} , although PMMA had higher T_{max} value.

Similar thermal decomposition trend was observed when 20 phr FR incorporated into PLA/PMMA blend. FR has initiated the thermal degradation of PLA/PMMA at low temperature, resulted in earlier weight loss detected at the DTG curve during decomposition. It should be noted that both of the DTG peaks of the PLA/PMMA/FR were relatively lower compared to the PLA/PMMA blend. At the same time, the T_{max} of PLA/PMMA/FR was increased by 4°C in comparison to PLA/PMMA blend. These phenomena were attributed to the condense phase mechanism by FR in reducing the weight loss and enhancing the thermal stability of PLA/PMMA blend, as discussed earlier.

Table 3. TGA thermal properties of PLA, PMMA and PLA/PMMA blends at nitrogen atmosphere.

Material Designation	Decomposition Temperature (°C)				
	T_{o1} (°C)	T_{o2} (°C)	T_{10} (°C)	T_d (°C)	T_{max} (°C)
PLA	326	-	336	380	364
PMMA	332	-	346	422	379
PLA/PMMA	320	378	332	427	362
PLA/PMMA/FR	298	381	320	430	366

Remarks:

T_{max} = Peak temperature at maximum decomposition rate. The data was obtained from DTG curves.

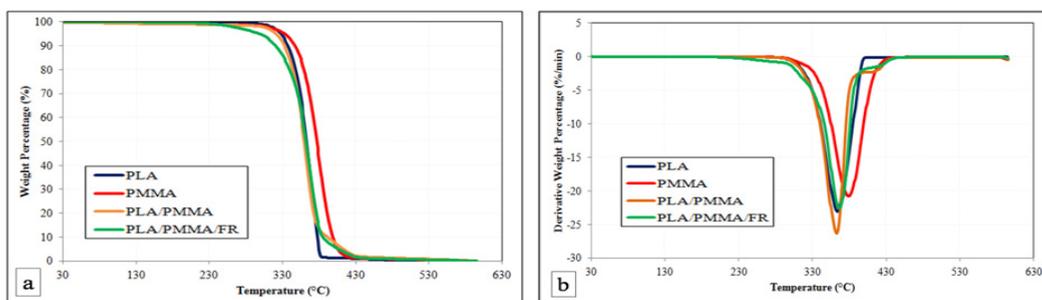


Fig. 3. (a) TGA curves; (b) DTG curves of PLA/PMMA blends.

4. Conclusions

Phosphorus-based flame retardant PLA/PMMA blend was successfully prepared by using a melt compounding technique. The UL-94 vertical burning test revealed that both neat PLA and PLA/PMMA blend burned with flaming drips and bubbling after the flame was applied. The flame resistance of PLA/PMMA was significantly enhanced by the inclusion of FR and the rating of PLA/PMMA was improved from V-2 to V-0. From the FESEM analysis, it was found that an extensive protective char was formed on the PLA/PMMA/FR blend. Adding FR to the PLA/PMMA has affected the thermal stability of the blend. FR readily decomposed at the beginning of combustion to yield phosphoric and polyphosphoric acids that induce char formation in the condense phase, insulating the underlying polymer from heat, flame and oxygen. Thus, the thermal degradation of PLA/PMMA blend was stabilized in the presence of FR.

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