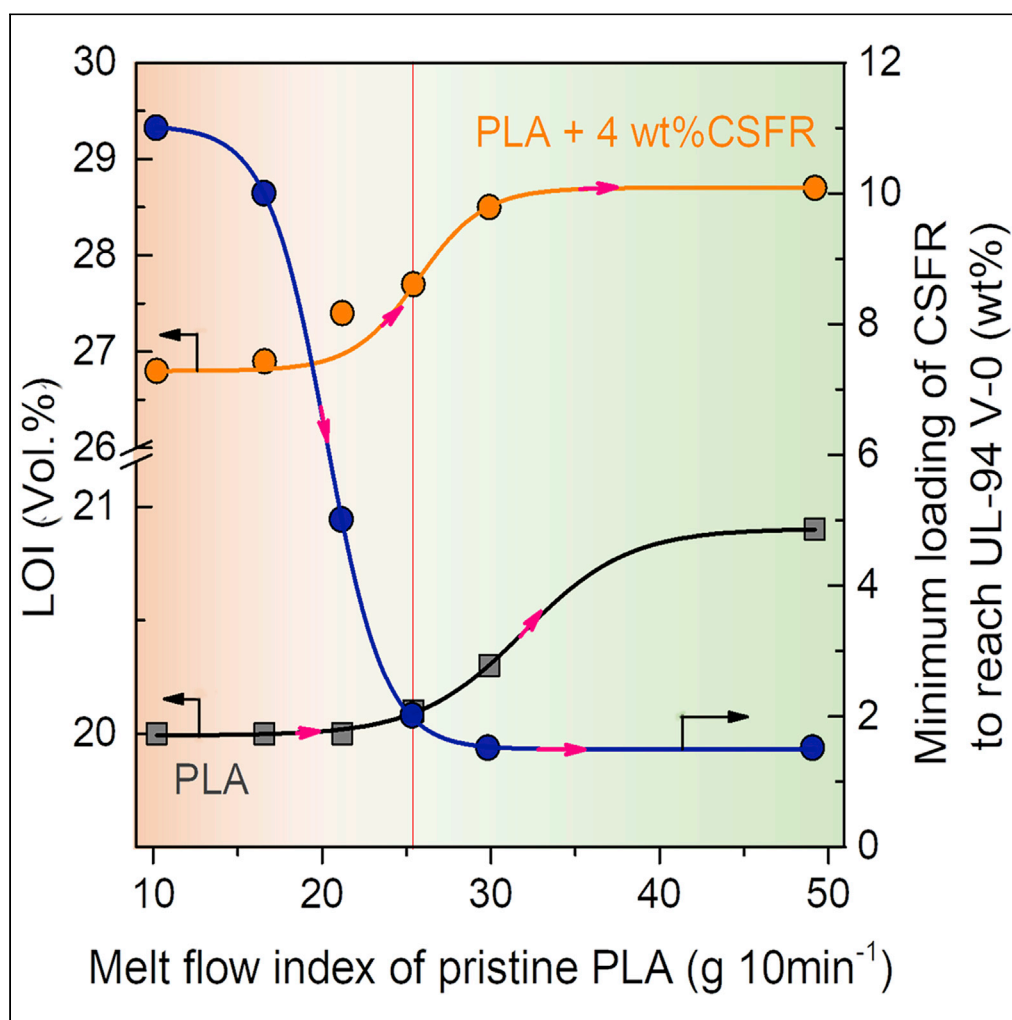


Article

Governing effects of melt viscosity on fire performances of polylactide and its fire-retardant systems



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Highlights

The polymer melt viscosity plays a governing role in fire performances of PLA

PLA with higher MFI shows higher LOI and needs less FR to get the UL-94 V-0

A critical MFI range of 16.5–29.9 g/10min is found to affect the fire performance

Melt viscosity does not affect fire performances when PLA was tested horizontally

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Article

Governing effects of melt viscosity on fire performances of polylactide and its fire-retardant systems

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SUMMARY

Extreme flammability of polylactide (PLA) has restricted its real-world applications. Traditional research only focuses on developing new effective fire retardants for PLA without considering the effect of melt viscosity on its fire performances. To fill the knowledge gap, a series of PLA matrices of varied melt flow index (MFI) with and without fire retardants are chosen to examine how melt viscosity affects its fire performances. Our results show that the MFI has a governing impact on fire performances of pure PLA and its fire-retardant systems if the samples are placed vertically during fire testing. PLA with higher MFI values achieves higher limiting oxygen index (LOI) values, and a lower loading level of fire retardants is required for PLA to pass a UL-94 V-0 rating. This work unveils the correlation between melt viscosity and their fire performance and offers a practical guidance for creating flame retardant PLA to extend its applications.

INTRODUCTION

Bioderived polylactic acid (PLA) features good biodegradability (Xie et al., 2020; Zhang et al., 2020), high transparency, high mechanical strength, low shrinkage, and ease of processability, making it one of the most commercially valuable bio-sourced polymers (Vahabi et al., 2018; Wen, 2019). As a result, PLA has been extensively used in packaging, electric and electronic, transport fields, and so forth. However, inherent high flammability significantly impedes its widespread applications in industries (Kong et al., 2000). Therefore, great attempts have been made to develop fire-retardant PLA materials (Jing et al., 2018a; Liu et al., 2018; Jing et al., 2018b; Zhang et al., 2021; Chen et al., 2017a; Wen et al., 2020; Gao et al., 2020).

Heretofore, intumescent flame retardants (IFRs) represent one halogen-free highly efficient fire-retardant system for PLA (Zhang et al., 2018; Jing et al., 2017) and often endow PLA with significantly increased limiting oxygen index (LOI) values and a desirable fire-retardancy rating during vertical burning tests. Take the widely used ammonium polyphosphate (APP)-based IFRs for example. Surprisingly, the required loading levels of APP-based IFRs for reaching a UL-94 V-0 rating vary from 5 to 40 wt% (Réti et al., 2008; Zhang et al., 2012; Chen et al., 2017b; Xu et al., 2020; Song et al., 2011; Ye et al., 2016). For instance, the combination of 12 wt% APP and 28 wt% starch leads to a UL-94 V-0 classification and a LOI of 32% (Réti et al., 2008), whereas the addition of only 5.0 wt% APP and 2.0 wt% chitosan (CS) gives rise to the same UL-94 V-0 rating but a higher LOI value of 33.1 % (Chen et al., 2017b). The results seem to imply that the fire performance (LOI values and UL-94 ratings) of resultant PLA and the required loading of flame retardants is dependent on the fire retardant structures (e.g., chemical compositions).

Upon exposure to heat fluxes, semi-crystalline PLA first melts to rapidly develop many melt droplets and drips by the gravity, which is significantly affected by polymer melt viscosity. During the fire testing, melt dripping may lead to possible flame propagation, whereas it may also contribute to helping extinguish the flame by taking away the combustion heat from flame zones and cooling the sample surface below the flashpoint (Kempel et al., 2015; Wang et al., 2012, 2018; Zhang et al., 1997; Denecker et al., 2006). Even for cone calorimeter testing where samples sealed in a foil box are placed horizontally, the developed polymer molten droplets tend to flow to the edges of samples. Hence, from a perspective of fire testing instruments and protocols, the polymer melt viscosity or melt flow rates (MFI) flow should play a major role in the fire behavior of polymer (Sag et al., 2020). However, to date it has remained unclear how polymer

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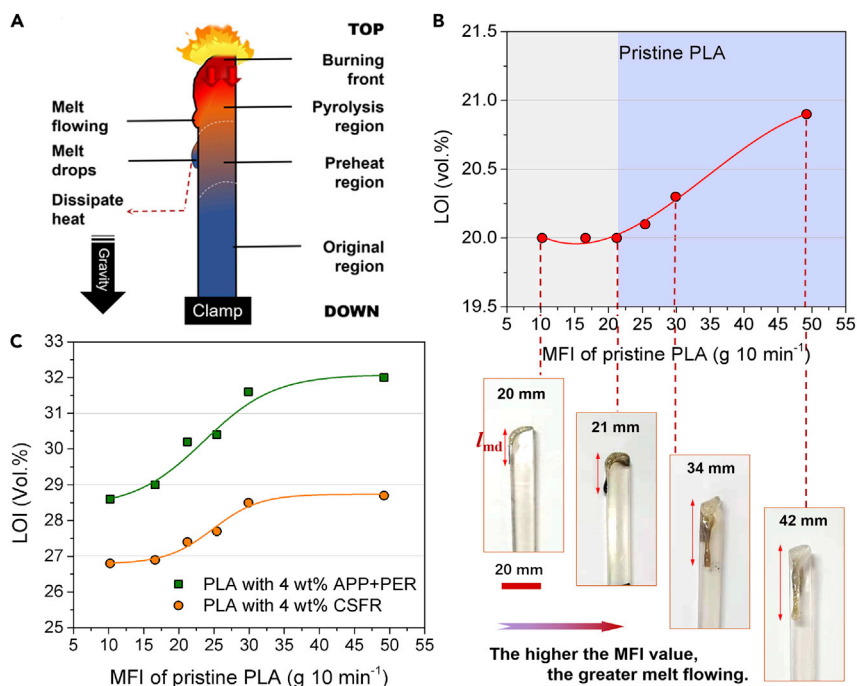


Figure 1. Relationships between LOI and MFI

(A) Combustion process of PLA during LOI tests,

(B) LOI of PLA as a function of MFI,

(C) LOI of flame-retardant PLA with 4 wt% APP+PER or CSFR as a function of MFI of the pristine PLA compared with the corresponding PLA matrix.

melt viscosity affects fire performances of PLA and the relationship between MFI and fire performance parameters (e.g., LOI, UL-94 ratings and heat release rate).

To date, many nonhalogenated flame retardants (FRs) systems have been developed for polymeric materials in recent years. Among them, ammonia polyphosphate (APP) has been regarded as one of the most common flame retardants (Jasinski et al., 2021; Samiee et al., 2022; Yin et al., 2018). For this reason, we, herein, focus on two kinds of flame retardants containing APP in this work. One system is the typical intumescent flame retardants (IFR) such as APP and pentaerythritol (PER), and the other one is a biobased IFR system containing APP, CS, and sodium phytate (PA-Na). In these systems, APP serves as an acid source and a gas source; PER, CS, and PA-Na act as carbon sources, and both flame retardants can play a dominant role in the condense phase. They are used as representative fire retardants to understand how polymer melt viscosity affects the fire behavior of PLA. Our results reveal that the MFI values of PLA closely correlate with their LOI values and UL-94 ratings of pristine PLA, and a similar trend is also found in its both flame retardant systems. This work provides an in-depth insight into the relationship between polymer melt viscosity and fire performances of PLA and significantly contributes to the design of high-performance fire-retardant PLA materials.

RESULTS AND DISCUSSION

LOI data analysis

During LOI testing, a common tool for assessing flammability of polymers in industry, PLA specimens are fixed vertically on the clamp and ignited from their top (see Figure 1A). After ignition, the combustion heat from the burning front induces the generation of melt dripping in the pyrolysis region, which removes part of heat from the burning top. As a result, the heat dissipation occurs in succession with a continuous stream of falling droplets, leading to insufficient heat or temperature for keeping combustion. To maintain the burning of the sample, the relative O₂ concentration needs to be raised, bringing about a higher LOI value.

Such presumed mechanism is confirmed by our following experimental data. As seen from Figure 1B, pure PLA with different MFI values behave differently. For instance, the LOI values of different pure PLA increase from

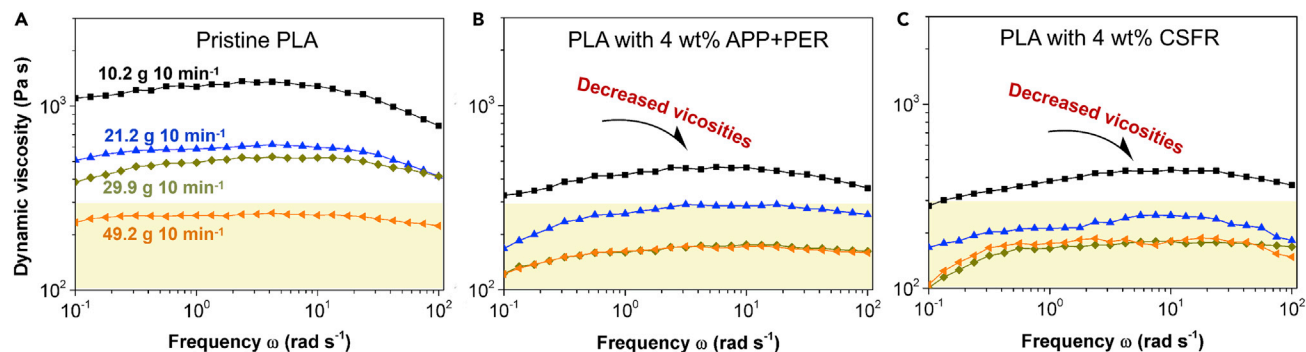


Figure 2. Rheological curves of PLAs

(A) Pristine PLA,
(B) the corresponding PLA with 4 wt% APP + PER, and
(C) the corresponding PLA with 4 wt% CSFR.

20.0% to 20.9% when the MFI rises from 10.2 to 49.2 g/10min. Although a 0.9% increase in LOI values of pure PLAs is not very significant, Figure 1B presents a more obvious change in the melt dripping length (l_{md}) from 20 to 34 mm when the MFI value increases from 10.2 to 29.9 g/10min. This means that the more heat is taken away from the burning forefront by melt drippings, and thus the PLA achieves higher LOI values.

Likewise, the increased dripping and MFI values affect the LOI value of PLA with fire retardants more obviously. Upon the addition of 4.0 wt % APP + PER or CSFR (see Figure 1C), it is impressive to find that the magnitudes of increment in the LOI values of both fire-retardant systems growingly increase with the MFI values of parent PLAs. Interestingly, there is a fast uphill in the LOI values in the MFI range of 16.6–29.9 g/10min of pristine PLA. When the MFI is greater than 29.9 g/10min, a platform appears in the LOI values, indicating that the LOI value does not further increase with a further increase in MFI values.

To further understand the relationship between LOI and MFI, viscoelastic behaviors of all PLAs with and without FR are investigated (see Figure 2). As expected, the viscosities of pure PLAs have a negative correlation to their MFI values (see Figure 2A). The PLA with a lower viscosity normally generates polymer fluid more easily and more melt drippings upon exposure to a flame or heat. This is in good accordance with previous work (Xie et al., 2014; Matzen et al., 2015), indicating that the viscosity of a polymer melt is a critical factor that determines the fire retardancy of a polymer.

Upon the addition of 4 wt% of APP + PER or CSFR, the viscosity values of the flame retardant PLA decrease in a similar but smaller manner than those of pristine PLAs due to their plasticization or degradation effects on PLA. Dynamic viscosities of all fire-retardant PLAs except the PLA with the highest MFI (refer to the pristine PLA with MFI = 10.2 g/10min) decrease to a value less than 2×10^2 Pa s (see Figure 2B). The improved melt flowability of the PLA matrix corresponds to a fast uphill of LOI values in the MFI range of 16.6–29.9 g/10min of the pristine PLA (also see Figure 1C), which indicates that such a dynamic viscosity range (below 2×10^2 Pa s) is more sensitive to the effect of polymer melt viscosity on the LOI values of flame retardant PLA. This is another factor for improving flame retardancy of PLA, apart from the condensed-phase mechanism of both APP + PER and CSFR via forming a char layer.

More interestingly, the loading level of 4 wt % APP + PER or CSFR results in similar dynamic viscosities of the flame retardant PLA systems when the MFI values of the parent PLAs are 29.9 and 49.2 g/10min, respectively. This leads to close LOI values, namely, 31.6% and 32.0%; 28.5% and 28.7% are related to the LOI values of PLA with 4 wt % APP + PER and CSFR, respectively. The results illustrate that the polymer melt viscosity or MFI does have a close relationship with the LOI values of flame retardant PLAs.

PLAs with 4 wt% APP + PER and 4 wt % CSFR exhibit similar dynamic viscosities (see Figure 2B and 2C). However, the LOI values for PLAs with 4 wt% APP + PER are 1.8%–3.3% higher than those of PLAs with 4 wt% CSFR (also see Figure 1C), indicating a superior flame retardancy efficiency for APP + PER systems in PLA at a similar melt viscosity. Based on the similar polymer melt viscosity, the flame retardancy efficiency of different fire retardants in PLA can be evaluated more accurately.

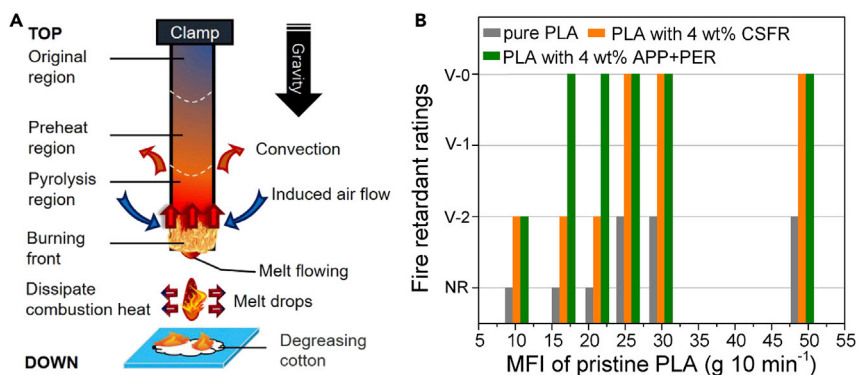


Figure 3. UL-94 tests

(A) Burning process and the corresponding mechanism during UL-94 tests, (B) correlations between UL-94 rating and MFI of PLA.

UL-94 rating discussion

UL-94 vertical burning testing is another widely used tool for evaluating fire safety of polymeric materials and products in industries (Kandola et al., 2013). Different from LOI tests, each specimen is fixed vertically ca. 300 mm above the underlying cotton and ignited from its bottom by a Bunsen flame in tests. The UL-94 fire-retardant classifications of specimens are judged according to whether the dripping occurs, cotton is ignited, and recorded flaming time (Wu et al., 2014). During UL-94 testing, the combustion heat transfers between the burning forefront and the pyrolysis zone of PLA samples (see Figure 3A), and once the temperature increases above the melting point or viscous flow temperatures of PLA, PLA becomes soft and then begins to flow like a fluid (Turski Silva Diniz et al., 2020). Meanwhile, the pyrolysis region growingly develops due to polymer thermal degradation, and degraded small products (e.g., small molecules) of low viscosity can, in turn, promote the melt dripping with the aid of gravity.

For pristine PLA, the MFI values or melt viscosities control their dripping rates and final fire-retardant ratings (see Figure 3B). When the MFI value of pure PLA is smaller than 24.4 g/10min, it takes more time for melt drops to leave from the PLA bulk because of their poor fluidity, thereby resulting in the heat retention at the forefront of the sample during testing. With the continuous heat and sufficient oxygen supplies, the flame eventually reaches the sample clamp, resulting in no UL-94 ratings. When the MFI is greater than 24.4 g/10min, the melt droplets are much easier to form and separate from the bulk polymer, which is conducive to heat dissipation and helps cool down the burning forefront (Wang et al., 2010). Consequently, the combustion duration time is significantly shortened, thus bringing about a UL-94 V-2 rating (see Video S1 and S2).

The governing effect of MFI on the UL-94 ratings is further evidenced in fire-retardant PLA systems. After the addition of 4 wt % CSFR, the UL-94 ratings of all fire-retardant PLA systems improve to different extents because CSFR can promote the char formation, which is conducive to suppressing the combustion and melt dropping of the PLA matrix. Likewise, the PLAs with MFI values greater than 24.4 g/10min achieve a UL-94 V-0 rating, whereas only a V-2 classification is obtained for PLAs with an MFI value smaller than 24.4 g/10min (see Video S3 and S4). This further highlights the governing effect of the polymer melt viscosity on the fire performance during UL-94 testing. In contrast to CSFR, the APP + PER system shows better flame retardancy in PLA (also see Figure 3B). Except the sample with the MFI value of the pristine PLA at 10.2 g/10min, all PLAs with 4 wt % APP + PER achieve UL-94 V-0 rating, which is in good accordance with its higher LOI values.

To reveal the relationship between MFI, thermographic images and temperatures (T_f) of the burning front during tests and UL-94 grades of the PLAs are investigated, which are analyzed comparatively in Figure 4. Here, it is noted that images labeled with "2 s", "10 s", and "20 s" were captured at 2, 10, and 20 s after 10-s ignition. As for pristine PLAs (see Figure 4A), there is no significant differences in T_f of all PLA at 2 s after ignition. The T_f values of all samples are above 410°C. Even though the sample continues cooling for 10 s, T_f s of PLA samples with MFI values of 10.2 g/10min still show great values close to those of PLAs at 2 s. Only a small number of drippings from the burning forefront of the UL-94 samples are found, which

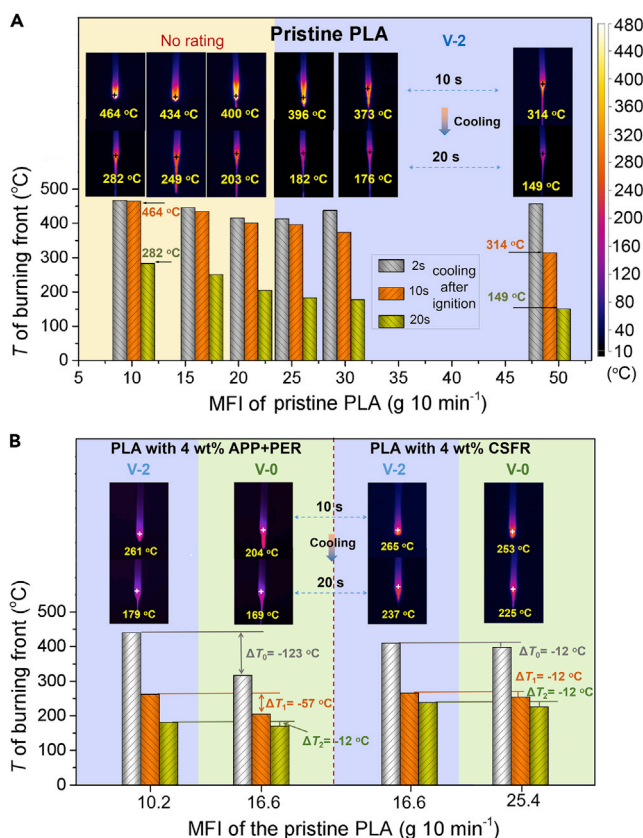


Figure 4. Thermographic images and burning front temperatures (T_f) of different PLA matrices as a function of time

(A) Pristine PLAs,
(B) flame retardant PLA blends.

is consistent to the small l_{md} values of the LOI samples (see Figure 1B). As the MFI increases to 21.2 g/10min, the elongation of the sample bottom occurs because a higher MFI means a lower viscosity and an increased dripping rate. When the MFI exceeds 25.4 g/10min, the sample bottoms become sharper because of fast molten droplets. Correspondingly, T_f of PLA with MFI of 49.2 g/10min go down to the lowest value of 314°C. A similar trend is also observed after 20 s. From the MFIs of pure PLA varying from 10.2 g/10min to 49.2 g/10min, the T_f s at 20-s cooling after ignition decrease from 282 to 149°C. These results show that the increased dripping and decreased T_f s can help improve the UL-94 rating of pure PLAs from no rating to V-2.

Aforementioned MFI impact on fire retardancy is further evidenced by fire-retardant PLA systems (see Figure 4B). We choose PLA with 4 wt% APP + PER or CSFR samples based on UL-94 ratings. For instance, the addition of 4 wt% of APP + PER endows the parent PLA (MFI = 10.2 g/10min) with a V-2 rating, whereas it leads to a V-0 rating for the parent PLA (MFI = 16.6 g/10min). Their T_f values and thermographic images are analyzed comparatively. As shown in Figure 4B, the retention of melt drops of the sample with an MFI = 10.2 g/10min of its parent PLA results in the heat accumulation, and the melt droplets have flame or high temperatures that is sufficient for igniting the underlying cotton, thus T_f values after 2-, 10-, or 20-s cooling are higher than those of the sample with an MFI = 16.6 g/10min of its parent PLA. As for the latter, the prolonged specimen images and dripping are found earlier, which causes a significant decrease in the T_f to a lower value. This facilitates a rapid dissipation of burning heat, afterwards the heat removal from melt droplets, leading to cooled droplets before reaching the underlying cotton. The same is for PLA with 4 wt % CSFR. The PLA/CSFR samples with different viscosity (MFIs of corresponding parent PLAs are 16.6 and 25.4 g/10min) are compared, and the results show that their trends of T_f values and thermographic images are similar to those of PLA with 4 wt % APP + PER, leading to V-2 and V-0 ratings, respectively.

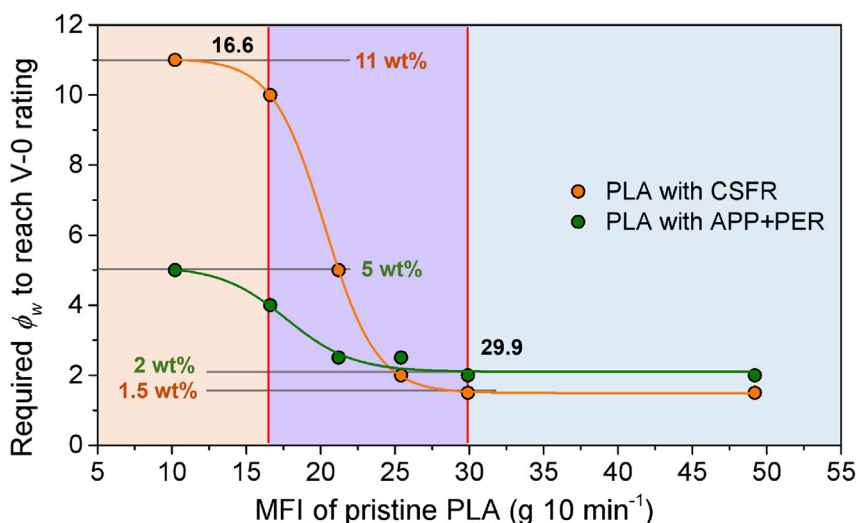


Figure 5. Required flame retardant concentration (ϕ_w) to reach V-0 rating of PLA as a function of MFI of the pristine PLA

The chemical compositions of melt dripping, melt droplets from two PLAs (MFIs of the pristine PLAs: 16.6 and 25.4 g/10min) with or without 4 wt % CSFR during UL-94 tests are also collected for further investigation. There are no significant differences in their chemical structures/compositions in infrared spectra (see Figure S1), indicating that UL-94 ratings of PLAs are independent with the chemical structure of droplets and PLA themselves.

To further assess how MFI controls the fire-retardant ratings during UL-94 tests, the required minimum FR loading level (ϕ_w) for PLA to reach a desirable UL-94 V-0 rating is also determined and presented as a function of MFI. Interestingly, the fire retardant APP + PER and CSFR show similar trends of the varied ϕ_w , as shown in Figure 5. As for PLA and APP + PER systems, the values of ϕ_w decrease from 5 to 2 wt % with an increased MFI values of pristine PLA from 10.2 to 49.2 g/10min. That means that the higher the MFI values of PLA, the less flame retardant is required for PLA to pass a UL-94 V-0 rating. This trend is more obvious for PLA and CSFR systems. The ϕ_w varies from 1.5 to 11 wt % with the increased MFI values of pristine PLA in the same range.

Impressively, there is a fast downhill in the MFI range of 16.5–29.9 g/10min of the pristine PLA, clearly demonstrating the enormous governing effect of MFI on fire-retardant ratings of PLA during UL-94 testing. Such an MFI range is in good accordance with the LOI results (see Figure 1).

Cone calorimetry tests

In comparison with LOI and UL-94 tests, cone calorimetry tests can provide a more precise fire evaluation of a material in a real fire scenario. Therefore, it is more important to use cone tests to further assess the polymer melt viscosity on fire behaviors of PLA. Unlike both LOI and UL-94 tests, the specimen is placed horizontally (see Figure 6A) in a tin foil box and exposed to a certain heat flux (here in 35 kW/m²). For this reason, even if the temperature of bulk PLA reaches up to the melting point, polymer melts only flow horizontally and are still confined in the box. This means that any molten part cannot be separated from the parent PLA, and the radiation heat applied externally is then accumulated to induce the vigorous thermal decomposition and combustion of PLA. As a result, the impact of MFI on the fire performances is expected to be not as significant as LOI and UL-94 tests.

Completely different from both LOI and UL-94 results, three key fire performance parameters, e.g., time to ignition (t_{ign}), peak heat release rate (PHRR), and fire growth index (FGI), extracted from cone tests do not show clear dependence on the MFI of PLA (Figures 6B–6D). For example, the t_{ign} of PLAs only fluctuates up and down around an average value of 75 s. The PLA with the greatest MFI (49.2 g/10min) gives the longest t_{ign} of ~89 s, whereas the PLA with the second highest MFI (29.9 g/10min) shows the lowest TTI, indicating that there is no correlation between t_{ign} and MFI of PLA. Likewise, there is no close relationships between

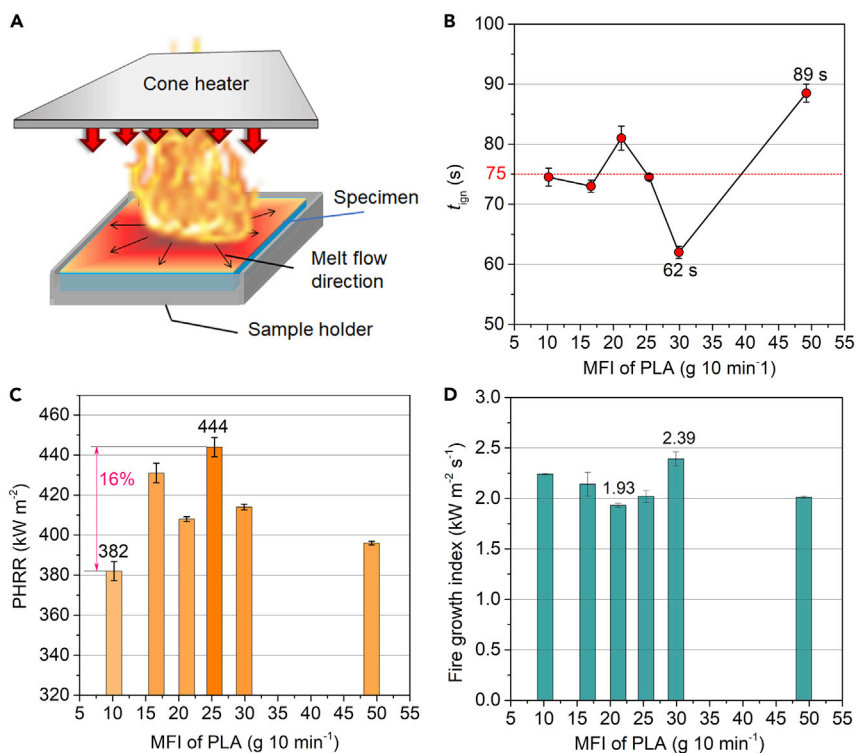


Figure 6. Combustion behaviors of PLA matrices with different MFIs

(A) Schematic illustration of cone calorimeter tests,
(B) time to ignition (t_{ign}),
(C) peak heat release rate (PHRR),
(D) fire growth index as a function of MFI.

PHRR and MFI. The difference between the maximum and minimum PHRR values is only around 16%. Both values are associated with PLAs with the lowest and medium MFI, respectively, which is quite inconsistent with the t_{ign} trend. In addition, the FGI of PLAs does not correlate with their MFI values either. In brief, the melt viscosity has a limited impact on fire performances of PLAs during cone tests where no molten droplets can take away heat effectively.

Other property and MFI of PLA

The molecular weight and polydispersity index and thermal properties (e.g., melting enthalpy and degree of crystallinity) of PLAs are also investigated (see Table 1). These parameters of PLAs also do not show certain dependence on or relationships with fire performances, indicating that the melt viscosity governs fire performances of PLAs during LOI and UL-94 tests but has an insignificant impact during cone tests.

CONCLUSIONS

In brief, melt viscosity of PLA is as important as fire retardants affecting the flame retardancy, which plays a governing role in the fire performances of PLA when samples tested vertically. The data show the higher the MFI value of PLA, the higher the LOI value and the higher the UL-94 rating regardless of the presence of FR. Interestingly, the MFI of 16.5–29.9 g/10min of pristine PLA is a critical range for fire retardant PLA. In this range, the LOI values increase, whereas a lower loading level of fire retardants is required for the PLA with higher MFI values to achieve a UL-94 V-0 rating. In addition, the MFI value has an insignificant impact on fire performances during cone tests where samples are placed horizontally for the inseparable melt dripping. This work for the first time provides an insightful yet practical guidance for creating fire-retardant PLA on a basis of melt viscosity.

Limitations of the study

In this work, we put emphasis on two kinds of flame retardants containing APP in this work. One is the typical IFR system such as APP and pentaerythritol (PER) and the other is the bio-based IFR

Table 1. Characterization data of PLAs

Sample	MFI (g/10min)	GPC		DSC			$\Delta H_m/\Delta H_{cc}$	χ_c (%)
		M_n/M_w	PDI	T_{mc}^a (°C)	T_{cc}^b (°C)	T_m (°C)		
L175	10.2	79846/148846	1.86	97.5	92.6	175.1	42.8/39.0	17.4
4032D	16.6	89212/156860	1.76	/	97.6	171.0	36.4/32.7	3.9
3052D	21.2	78478/128352	1.64	/	107.6	148.6 153.6	27.4/25.0	2.5
4043D	25.4	78874/142973	1.81	/	106.6	147.6 154.1	21.1/20.7	0.5
3001D	29.9	70798/102906	1.45	/	101.5	170.1	33.4/24.2	9.8
L105	49.2	48287/86250	1.79	101.9	90.6	176.0	54.1/38.4	25.1

^a T_{mc} : molten crystallization temperature.

^b T_{cc} : cold crystallization temperature.

system containing APP, chitosan (CS), and sodium phytate (PA-Na). In these systems, APP performs as the acid source and gas source; PER, CS, and PA-Na perform as the carbon source, so both of the flame retardants mentioned earlier can play their roles by condense-phase mechanism. We applied them as the representatives of IFR to study how polymer melt viscosity affects the fire behavior of PLA. However, the flame retardants performed in gas-phase mechanism can also endow PLA with good flame retardancy. How these gas-phase flame retardant PLAs have relationship with the melt viscosity of matrix is still not investigated until now, which may be a good supplementary study for this work.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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 - Materials availability
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- METHOD DETAILS
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SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2022.103950>

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AUTHOR CONTRIBUTIONS

Y.Z. and P.S. designed and supervised this work. Y.Y., H.S., and Z.F. wrote and revised the whole manuscript. Y.Y. and L.X. carried out the synthesis of the flame retardant, the processing, and the characterization of the pure and the flame retardant PLA. M.Y. and L.L. did the rheology experiments and analyzed the corresponding data. All the authors took participation in the discussion, analysis, and revision.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Polylactic Acids (PLA) 4032D, 3052D, 4043D and 3001D	Nature works (USA)	CAS: 26100-51-6
Polylactic Acids (PLA) Luminy PLA L175 and Luminy PLA L105	Total Corbion PLA (Thailand)	CAS: 26100-51-6
Ammonium polyphosphate (APP, P%=31.0-32.0 wt%, degree of polymerization (DP) > 1000)	Hangzhou JLS Flame Retardants Chemical Co., Ltd (China)	CAS: 68333-79-9
Chitosan (CS, deacetylation degree \geq 95%, viscosity = 100-200 mpa·s)	Shanghai Macklin Biochemical Co., Ltd (China)	CAS: 9012-76-4
Phytic acid (PA, 70 wt% solution in H ₂ O)	Shanghai Macklin Biochemical Co., Ltd (China)	CAS: 83-86-3
Sodium hydroxide (NaOH)	Sinopharm Chemical Reagent Co., Ltd (China)	CAS: 1310-73-2
Acetic acid	Sinopharm Chemical Reagent Co., Ltd (China)	CAS: 64-19-7
Pentaerythritol (PER)	Sinopharm Chemical Reagent Co., Ltd (China)	CAS: 115-77-5

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Yan Zhang (zhangyan@nbt.edu.cn).

Materials availability

This study did not generate new materials.

Data and code availability

No new code is generated and all original data are available from the authors upon request.

METHOD DETAILS

Materials

Polylactic acids (PLA) (4032D, 3052D, 4043D and 3001D) were obtained from Nature Works (USA) and other PLAs (Luminy PLA L175 and Luminy PLA L105) were provided by Total Corbion PLA (Thailand). These PLAs possess different melt flow indexes (MFI) shown in [Table 1](#). Ammonium polyphosphate (APP, P% = 31.0-32.0 wt%, degree of polymerization (DP) > 1000) was purchased from Hangzhou JLS Flame Retardants Chemical Co., Ltd (China). Chitosan (CS, deacetylation degree \geq 95%, viscosity = 100-200 mPa s) and phytic acid (PA, 70 wt% solution in H₂O) were supplied by Shanghai Macklin Biochemical Co., Ltd (China). Sodium hydroxide (NaOH), acetic acid and PER were provided by Sinopharm Chemical Reagent Co., Ltd (China). All reagents are used as received.

Preparation of flame retardant PLA blends

APP@CS@PA-Na (CSFR) was synthesized according to our previous study, which endowed PLA with improved flame retardancy by condensed-phase mechanism ([Xiong et al., 2019](#)). In a typical procedure, 10 g of APP were evenly dispersed in 200 g of deionized water to form a suspension. The CS acetic acid solution (1 wt%) was slowly dropped into the APP suspension, and then stirred for 2 min to make the APP and CS fully adsorbed. The solid particles were then separated by centrifugation, and 300 mL of deionized water was added to the solid particles for stirring and washing. Before assembling the next layer, the washed particles were dispersed evenly with 200 g of deionized water. Meanwhile, the prepared phytic acid solution (1 wt%) was adjusted to neutral with sodium hydroxide to obtain PA-Na solution. The third layer was self-assembled by dropping the PA-Na solution into the suspension in the same way. The obtained particles were dried at 80°C for 12 h in a vacuum drying oven finally. After grinding, the particles were dried at 60°C for 6 h to get CSFR. Prior to mixing, PLA and CSFR were dried at 60°C for 12 h in vacuum oven. All pure PLAs and its blends with different amounts of FR were processed using a Thermo Haake

rheomixer (Polylab, Germany) at 170°C for 8 min with a rotor speed of 60 rpm. The processing of PLA, APP and PERz are similar to that of PLA and CSFR. Here, the mass ratio of APP and PER is set to the typical ratio 3 : 1.

Characterization

MFI of all PLA samples were measured by a melt flow indexer (MTS\SANS ZRZ1452, China) with a load of 2.16 kg at 210°C. The MFI values were calculated according to the average of 5 parallel measurements. Since PLA is easy to thermally decompose during the melt mixing resulting in the reduced MFI, the melt processing were employed to all PLA samples including pure PLA prior to the tests. The MFI values of PLAs are listed in [Table 1](#).

Dynamic rheological tests were performed using a stress-controlled rotational rheometer (Thermo HAAKE MARS 60, Germany) at 180°C under air atmosphere with the parallel plates geometry (plate diameter 35 mm, gap 0.5 mm). The frequency range of 0.1-100 rad/s was measured in the dynamic frequency sweep tests.

LOI values were measured on HC-2 Oxygen Index Instrument (Jiangning Analysis Instrument Company, China) according to ASTM D2863.

UL-94 vertical burning tests were performed on a CZF-III Vertical Burning Tester (Jiangning Analysis Instrument Company, China) according to ASTM D3801 standard, with the sheet dimension of 127 × 12.7 × 3 mm³. In order to measure the temperature distribution of specimen during UL-94 tests, a thermographic camera (Ti400, Fluke Corporation, USA) was placed at about 80 cm far from the specimen with the calibrated focus on the burning front of the samples. The average values of the temperatures measured at 2 s, 10 s, and 20 s were calculated according to those of five specimens measured in parallel.

Cone calorimetry tests (Cone) were carried out on a cone calorimeter (Fire Testing Technology, UK) with the sample dimension of 100 × 100 × 3 mm³ at a heat flux of 35 kW/m² according to ISO 5660 standard.

The weight-average molecular weights (M_w), number-average molecular weight (M_n) and polydispersity index (PDI) were determined using a Gel permeation chromatograph (GPC, waters1525 & Agilent PL-GPC220, USA) with chloroform as the solvent and mobile phase. Polymethyl methacrylate standards with different molecular weights were applied to generate the calibration curve. The relative GPC data are shown in [Table 1](#).

Differential scanning calorimetry (DSC) analysis were carried out under N₂ on a DSC instrument (NETZSCH 200 F3, Germany). Conventional DSC heating and cooling runs were performed from 0°C to 200°C at a heating rate of 5°C/min. ΔH_m and ΔH_{cc} are the melting enthalpy and cold crystallization enthalpy of PLA composites were calculated from DSC curves. Crystallinity (χ_c) was determined to Ref ([Fischer et al., 1973](#); [Zhang et al., 2020](#)). The thermal data are also shown in [Table 1](#).

QUANTIFICATION AND STATISTICAL ANALYSIS

The data in [Figures 6B–6D](#) are the average results of three parallel tests.