Determination of Kinetics and Thermodynamics of Thermal Decomposition for Polymers Containing Reactive Flame Retardants: Application to Poly(lactic acid) Blended with Melamine and Ammonium Polyphosphate

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Abstract

A methodology for parameterization of kinetics and thermodynamics of decomposition of polymeric materials has been extended to blends of a polymer with condensed-phase active flame retardants. This methodology is based on Thermogravimetric Analysis, Differential Scanning Calorimetry, Microscale Combustion Calorimetry and inverse numerical modeling of these experiments. Material systems consisting of poly(lactic acid), melamine and ammonium polyphosphate were used to demonstrate this parameterization process. The resulting model consists of a set of first and second order (two component) reactions that define the rate of gaseous pyrolyzate production, heats of these reactions, heat capacities of the condensed-phase reactants and products and heats of combustion of the components of the gaseous pyrolyzate. This model is shown to reproduce results of all aforementioned experiments with a high degree of detail and predict relation between the outcome of these experiments and material composition. It is expected that a combination of this model with thermal transport parameters, which determination will be a subject of separate study, will yield a complete pyrolysis model capable of predicting the dynamics of burning and flame spread on these materials and dependence of this dynamics on the flame retardant content.

Keywords: material flammability; pyrolysis; intumescence; thermal analysis; inverse modeling; PLA; APP; ThermaKin

Nomenclature and Abbreviations

A	Arrhenius pre-exponential factor (s^{-1} or $m^3 kg^{-1} s^{-1}$)
APP	Ammonium polyphosphate
a1-4	Coefficients in the heating rate function
c	Heat capacity ($J kg^{-1} K^{-1}$)
DSC	Differential Scanning Calorimetry
E	Activation energy ($J mol^{-1}$)
HRR	Heat release rate (W)
h	Heat of reaction ($J kg^{-1}$)
h_c	Heat of combustion ($J kg^{-1}$)
MCC	Microscale Combustion Calorimetry
MEL	Melamine
MLR	Mass loss rate ($kg s^{-1}$)
m	Sample mass (kg)
m_0	Initial sample mass (kg)
PLA	Poly(lactic acid)
R	Molar gas constant ($J K^{-1} mol^{-1}$)
r	Reaction rate ($kg m^{-3} s^{-1}$)
STA	Simultaneous Thermal Analysis
T	Temperature (K)
TGA	Thermogravimetric Analysis
t	Time (s)
ξ_k	Concentration of reactant k ($kg m^{-3}$)
θ	Condensed-phase product stoichiometric coefficient (or yield)
γ	Stoichiometric coefficient for a reactant in second order reaction

1. Introduction

Pyrolysis plays an important role in the overall combustion of polymeric materials [1,2] and frequently defines their propensity to sustain and spread flames. A number of comprehensive pyrolysis models, including the NIST Fire Dynamics Simulator solid phase model [3], Pyropolis [4], Gpyro [5] and ThermaKin [6], have been developed to gain insight into the details of the mechanism of this process and to enable prediction of material flammability performance in a wide range of scenarios. One factor that has limited widespread use of these models is a lack of knowledge of physical and chemical properties that define material pyrolytic behavior, especially in the case of complex, multi-component solids.

To address this limitation, a methodology has been developed to obtain a core subset of these properties, including decomposition reaction kinetics and energetics, energetics of phase transitions, and heat capacities of condensed-phase species, using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and inverse numerical modeling of these experiments. This methodology has been successfully applied to neat non-charring [7] as well as charring polymers [8]. It was further demonstrated that combining these property values with thermal transport parameters, including thermal conductivities, radiation absorption coefficients and emissivities, measured in separate experiments produces fully parameterized pyrolysis models that predict the rate of gaseous pyrolyzate production from coupon-sized material samples in bench-scale gasification tests [9,10].

In the current study, this methodology is further advanced by adding the Microscale Combustion Calorimetry (MCC) [11] to enable determination of the heats of combustion of gaseous pyrolyzates evolved during various stages of material decomposition and to further verify the decomposition kinetics determined through the analysis of TGA and DSC data. More importantly, an attempt is made to extend this methodology to blends of polymers with additives that react with the matrix polymer and/or each other upon heating. This extension goes beyond pyrolysis model parameterization for a multi-component material of given composition. Feasibility of such parameterization has already been demonstrated [12]. Here, it is shown that it is possible to create a model that provides a quantitative relationship between material composition and key properties defining material flammability. A capability to develop such models is expected to enable researchers to precisely tune material composition to achieve optimum flame resistance.

Poly(lactic acid) (PLA) was chosen in this study as a matrix material. PLA is a biodegradable thermoplastic polyester produced from renewable natural sources. This polymer represents a sustainable alternative to traditional petroleum-based synthetic materials [13]. It is being employed in a widening range of applications including packaging [14] and electronics [15,16].

One of the main limiting attributes of neat PLA is its inability to meet many standard flame resistance requirements. Several studies have been conducted to examine ways to overcome this limitation through additives [16–21]. A PLA-based material blended with halogen-free flame retardants (FRs) was developed by Kimura and Horikoshi [16] to meet the V-2 classification in the UL-94 test, which is

required for the materials used in personal computers. The developed material was found to be comparable to a fiber-reinforced polycarbonate in terms of heat resistance, moldability, and rigidity. Réti et al. [17] reported that intumescence-inducing ingredients incorporated into PLA improved its flame retardancy. These ingredients included ammonium polyphosphate (APP), lignin and starch. Adding APP and starch to PLA produced 88 wt.-% bio-based system with the Limiting Oxygen Index of 32 vol.-%, which is higher than the requirement for commercial application (30 vol.-%). A thermally-insulating coating formed at the surface of the material upon heating was credited for the improved performance.

Fontaine and Bourbigot [18] reported that a low flammability system was formulated by combining PLA with another group of intumescence-inducing ingredients, melamine (MEL) and APP. A range of compositions was tested and it was found that the system's performance, evaluated through measurement of the heat release rate in a fire calorimeter (ASTM E906), is a strong function of the composition. Among examined compositions, 5 wt.-% of MEL and 25 wt.-% of APP loading exhibited the most significant reduction in the total heat release (82% reduction with respect to neat PLA). Based on these observations, APP and MEL were selected as additives to be evaluated in the current study. TGA, DSC and MCC tests were employed to characterize the thermal decomposition behavior of PLA/MEL/APP systems and their constituents. The results of this characterization were analyzed to derive a generalized thermo-kinetic model for these systems. For the first time in our practice, second order reactions between two distinct components were found to be necessary to represent condensed-phase pyrolytic behavior.

2. Materials and Methods

2.1. Materials

In selection of materials for analysis, an attempt was made to minimize the number of compositions and, therefore, the number of tests, necessary to develop the generalized model. Neat PLA, MEL and APP as well as 2 three-component blends were tested to obtain model parameters. The information on neat materials, including room temperature (298 K) mass density, is summarized in Table 1. The blends contained 30 wt.-% of FRs with either MEL or APP in a dominant concentration. Emphasizing one of the additives in each blend helped reveal the impact of the corresponding additive on measured parameters and, therefore, simplify the model building process, as further explained in Section 3. An additional blend, containing equal amounts of FRs, was used to examine extrapolation capability of the developed model. The blend compositions are listed in Table 2.

The blends were produced using a Brabender laboratory E350 mixer (roller blades, constant shear rate of 50 rpm). The mixer was maintained at 458 K. PLA was introduced into the mixer and melted for 5 minutes. Subsequently, the FRs were introduced and mixed for 5 additional minutes. The blends were formed into 10×10×0.3 cm³ plaques. For consistency, neat PLA was processed in exactly the same manner.

Thermal analysis and MCC samples of PLA, PLA(70)MEL(25)APP(5), PLA(70)MEL(5)APP(25) and PLA(70)MEL(15)APP(15) were prepared by cutting thin (≈ 0.5 mm) flat squares from the plaques. Neat MEL and APP were tested in the form of powder, which was compacted flat against the bottom of the crucible to maximize the thermal contact. The initial mass of the samples was between 4 and 7 mg. All samples were conditioned in a desiccator in the presence of Drierite for a minimum of 48 hours prior to testing to obtain measurements with negligible contribution from moisture.

Table 1. Neat materials tested in this study.

Material	Density (kg m^{-3})	Color	Form	Supplier	Trade name
PLA	1240 [22]	Translucent	Pellet/Plaque	Nature Works LLC	Ingeo™ 4032D
MEL	1570 [23]	White	Powder	Sigma-Aldrich	M2659
APP	1900 [24]	White	Powder	Clariant	EXOLIT AP 422

Table 2. PLA/FRs blends tested in this study.

Formulation Name	Form	PLA (wt.-%)	MEL (wt.-%)	APP (wt.-%)
PLA(70)MEL(25)APP(5)	Plaque	70	25	5
PLA(70)MEL(5)APP(25)	Plaque	70	5	25
PLA(70)MEL(15)APP(15)	Plaque	70	15	15

2.2. Experiments

2.2.1. Simultaneous Thermal Analysis (STA)

TGA and DSC tests were conducted simultaneously using a Netzsch 449 F3 Jupiter thermal analyzer. The temperature and heat flow sensors of this instrument were calibrated every 3 months using a set of 8 organic and inorganic compounds with known melting points and heats of melting. The calibration tests were performed under the same conditions (same temperature program, purge flow rate, and crucibles) as those utilized in the majority of experiments on the materials under study. More information concerning the calibration procedure is provided in an earlier publication [7].

Most of the STA tests utilized temperature program that consisted of a conditioning period, when the sample was maintained at 303 K for 25 min, followed by linear heating at a nominal rate of 10 K min^{-1} (0.167 K s^{-1}). This heating rate was chosen to be sufficiently slow to ensure that the sample did

not experience significant temperature or composition gradients. The samples were heated through decomposition up to the temperature where no significant mass loss could be detected. PLA, MEL and PLA(70)MEL(25)APP(5) were heated to the final temperature of 873 K, while APP, PLA(70)MEL(5)APP(25) and PLA(70)MEL(15)APP(15) were heated to 1073 K. The tests were performed in an anaerobic environment established by continuously purging the analyzer's furnace with nitrogen at a rate of 50 mL min⁻¹. Platinum-Rhodium crucibles with lids were utilized in all tests to maximize temperature uniformity and heat flow sensitivity. The lids had a small opening for ventilation to allow gaseous pyrolyzate to escape the crucible.

For PLA, PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25), the STA tests were repeated 10 times to accumulate necessary statistics for the model development. For MEL and APP, the tests were repeated 5 times as they were minor ingredients. The mass (TGA) and heat flow (DSC) data obtained from repeated tests were averaged to minimize random errors. Three tests were performed on the post-decomposition residue of each of the blends to better resolve their heat capacities. The residue samples were prepared by collecting and adding together residue generated in 3-4 tests of a given blend.

Additional TGA-only tests (no heat flow signal was collected) were performed to assess extrapolation capabilities of the developed model. These tests were performed at 5 and 20 K min⁻¹ nominal heating rates on PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) blends and at 10 K min⁻¹ on PLA(70)MEL(15)APP(15) blend. Each of these tests was repeated 3 times and recorded mass signals were averaged prior to further analysis.

2.2.2. Microscale Combustion Calorimetry (MCC)

In MCC, a material sample is heated linearly in a manner similar to the thermal analysis experiments. The gaseous pyrolyzate formed by the sample is carried by a purge gas (nitrogen was used in this study) and mixed with oxygen downstream from the pyrolysis zone. The pyrolyzate-nitrogen-oxygen mixture enters the combustor, a chamber preheated to 1173 K, where the pyrolyzate is completely oxidized. The heat released during oxidation is measured using the oxygen consumption principle. The heat release rate (HRR) is recorded as a function of time and solid sample temperature. A detailed description of the MCC method can be found elsewhere [25].

In the current study, the MCC tests were carried out in an apparatus built in accordance with the standard [11]. The calibration of the apparatus was performed on monthly basis. The oxygen sensor, the outflow flow meter and solid sample temperature sensor were calibrated using the procedures described in detail in an earlier publication [25]. The apparatus was operated using all standard settings with the exception of the prescribed heating rate. The heating rate was set at a value identical to that utilized in the majority of the STA experiments (10 K min⁻¹) to facilitate comparison between the TGA and MCC data sets. The initial sample temperature was 348 K. The final sample temperature was set to be the same as that used in the corresponding STA tests.

Ceramic crucibles without lids were used to contain the samples. The MCC tests of each material were repeated only 3 times due to their high reproducibility. The HRR data obtained for each material were averaged prior to further analysis.

2.3. Modeling

A numerical pyrolysis model, ThermaKin [6,26], was used to analyze the TGA, DSC and MCC data and to determine the reaction kinetics and thermodynamic parameters that describe thermal decomposition of the materials under study. ThermaKin solves non-steady mass and energy conservation equations accounting for the physical and chemical processes that occur in the condensed phase during pyrolysis. Chemical reactions are defined within the ThermaKin using the reaction rate, r , expressed as follows

$$r = A \exp\left(-\frac{E}{RT}\right) \xi_k \xi_l \quad (1)$$

In this equation, A is the Arrhenius pre-exponential factor, E is the activation energy, R is the molar gas constant, T is temperature, and ξ_k is the concentration of reactant k in kg m^{-3} . For first order reactions (with only one reactant), the concentration of the second reactant (l) is set to unity. To compute the rate of consumption or production of a reactant or product in unit volume, the reaction rate is multiplied by the corresponding (mass-based) stoichiometric coefficient. To compute the heat flow in unit volume associated with a given reaction, the reaction rate is multiplied by the heat of reaction, h , which assumes positive value when the reaction is endothermic.

ThermaKin can be used to solve thermally thin (zero-dimensional), one-dimensional or two-dimensional pyrolysis problems. Only zero-dimensional mode was utilized in this study. In this mode, a pyrolyzing object was assigned a spatially uniform temperature history, while both heat and mass transport inside the object were treated as infinitely fast. Details of the setup of zero-dimensional calculations can be found in an earlier publication [7].

To account for the fact that the heating rates prescribed in the experiments were not achieved instantaneously, an exponentially-decaying sinusoid function

$$\frac{dT}{dt}(t) = a_1(1 - (\exp(-a_2 t))(\cos(a_3 t) + a_4 \sin(a_3 t))) \quad (2)$$

was added to the ThermaKin formulation. This function was used to define the temperature of simulated sample as a function of time (t). The parameters of this function were adjusted to reproduce heating rate profiles observed in the STA and MCC experiments. These parameters were determined to have the following values: $a_1 = 0.167 \text{ K s}^{-1}$, $a_2 = 0.0030 \text{ s}^{-1}$, $a_3 = 0.0034 \text{ s}^{-1}$, $a_4 = -1.07$ for 10 K min^{-1} STA tests and $a_1 = 0.167 \text{ K s}^{-1}$, $a_2 = 0.0039 \text{ s}^{-1}$, $a_3 = 0.0065 \text{ s}^{-1}$, $a_4 = 0.256$ for MCC tests. A comparison of the fitted and experimental heating rate profiles is shown in Figure 1. Only one representative experimental heating rate profile is shown for each type of test because these data were found to be highly reproducible. Equation 2 captures the experiments with the coefficient of determination of 0.98 and 0.95 for the STA and MCC tests, respectively. The heating rate function was also parametrized for the 5 and 20 K min^{-1} TGA-only experiments.

Figure 1. Comparison of experimental and fitted heating rate histories for (a) STA and (b) MCC tests conducted at the prescribed heating rate of 10 K min^{-1} or 0.167 K s^{-1} .

3. Results and Analysis

3.1. Overall Approach to Model Development

The generalized thermo-kinetic model development process consisted of 4 steps. In the first step, a reaction scheme (also referred to here as mechanism or MECH) and corresponding parameter set was derived from TGA and DSC data for each of the neat materials (PLA, MEL and APP). In the second step, these reaction schemes, combined together, were used to model TGA and DSC tests of PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) blends, which were initially assumed to be non-reactive mixtures. The differences between the model predictions and experimental data were attributed to chemical interactions between the FR in dominant concentration and PLA. These interactions were parameterized, while contributions of the low-concentration (minor) additives were ignored. In the third step, all reactions were combined into a single mechanism that was used to re-model the TGA and DSC of the blends. This step was used to re-examine the parameters describing PLA and FR interactions by including interactions between PLA and minor additives into consideration. This step was also used to identify and parameterize a potential interaction between the FRs. In the fourth and final step, the reaction model obtained on the basis of the TGA and DSC data was employed to simulate MCC experiments performed on the neat materials and the blends. Heats of combustion of the reaction products representing gaseous pyrolyzate were derived from these simulations.

3.2. TGA and DSC of Neat Materials

The mean experimental results of the TGA and DSC tests of PLA are shown in Figure 2 (as open circles). Figure 2 (a) and (b) contain the dependences of samples mass, m , and mass loss rate, MLR, normalized by the initial sample mass, m_0 , on temperature. Figure 2 (c) and (d) contain initial-sample-mass-normalized heat flow and heat flow integral plotted as a function of temperature and time,

respectively. All error bars correspond to 2 standard deviations of the mean. Figure 2 also displays several additional data sets that are discussed later in this section.

The experimental PLA MLR profile contains a single peak with the maximum at 645 K corresponding to the thermal decomposition process. The decomposition produces about 2 wt.-% of condensed-phase residue. The heat flow curve contains 2 distinct peaks. The lower temperature peak (maximum at 443 K) is attributed to melting, which is consistent with a semi-crystalline nature of this material [27]. The other heat flow peak matches the temperature at which the MLR peak occurs and therefore is attributed to the decomposition.

Inverse modeling of the PLA data was performed using the approach described in detail in earlier publications [7,8,12]. One first order reaction with one condensed-phase and one gaseous product was initially employed to capture the TGA data. The Arrhenius parameters of this reaction were estimated through analytical expressions [28] relating these parameters to the temperature and height of the corresponding MLR peak. Subsequent refinement of the Arrhenius parameters was performed through a manual iterative optimization process using ThermaKin. An increase in the activation energy shifted the MLR curve to a higher temperature, while the height of the peak tended to decrease. An increase in the pre-exponential factor shifted the MLR curve to a lower temperature, while increasing the peak height. The Arrhenius parameters and the condensed-phase product stoichiometric coefficient (or yield), θ , were adjusted until a satisfactory agreement with the experimental TGA data was achieved. If it was impossible to achieve such agreement, an additional first order reaction was added to the reaction scheme. The reactions were arranged in sequence. For each neat material, the satisfactory agreement was defined as differences of less than 5% between the average experimental and modeled maximum MLR, less than 3 K between the positions of the maxima and less than 1% between the values of the total (or final) mass loss.

Figure 2. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA at a set heating rate of 10 K min^{-1} .

The regions of the mean heat flow curve not associated with melting or decomposition were normalized by instantaneous heating rate and fitted with linear temperature functions representing heat capacities, c , of the corresponding condensed-phase components. The heat capacity of the PLA decomposition residue could not be resolved due to an extremely low yield and therefore was assumed to be equal to the average c of chars, $1700 \text{ J kg}^{-1} \text{ K}^{-1}$, formed by several common polymers [8]. An additional first order reaction with one condensed-phase product was added to capture the melting process. Condensed-phase component mass fractions (with respect to the initial sample mass), which temporal evolution was computed by ThermaKin, were multiplied by the corresponding heat capacities to obtain sensible heat flow baseline. Subtraction of this baseline from the total heat flow and subsequent integration of the difference produced the values of the heat of melting and heat of decomposition. These heats were assigned to the corresponding reactions. The thermodynamic parameters were refined until the ThermaKin-predicted heat flow maxima were within 10%, temperatures of the maxima were within 5 K and final integral heat flow was within 5% of the average experimental results.

The resulting neat PLA decomposition mechanism, PLA MECH, is given in Table 3. The component names used in this mechanism are self-explanatory. The reaction parameters and condensed-phase component heat capacities are listed in Table 4 and 5, respectively. As shown in Figure 2 (solid line), this mechanism and parameters capture both TGA and DSC data very well. The modeled sensible heat flow baseline is shown in Figure 2 (c) (dotted line) to illustrate its contribution to the overall heat flow.

Figure 2 also displays modeling predictions obtained using a model of PLA developed in an earlier study [7]. Both TGA and DSC predictions appear to be notably different from the current data, with the most significant difference in the heat of decomposition. A difference in the grade of PLA (Rejueven8Plus was used in [7]) may explain these discrepancies. However, it is somewhat unexpected that a relatively small difference in the material composition (both materials are at least 95 wt.-% neat

PLA resin, according to the manufacturer) has such dramatic impact on the decomposition thermodynamics.

Table 3. Reaction mechanisms derived for neat materials.

Mechanism	Reaction
PLA MECH	(1) $\text{PLA} \rightarrow \text{PLA_Melt}$
	(2) $\text{PLA_Melt} \rightarrow \theta \text{PLA_Res} + (1 - \theta) \text{PLA_Gas}$
MEL MECH	(3) $\text{MEL} \rightarrow \theta \text{MEL_Res1} + (1 - \theta) \text{MEL_Gas1}$
	(4) $\text{MEL_Res1} \rightarrow \text{MEL_Gas2}$
APP MECH	(5) $\text{APP} \rightarrow \theta \text{APP_Res1} + (1 - \theta) \text{APP_Gas1}$
	(6) $\text{APP_Res1} \rightarrow \theta \text{APP_Res2} + (1 - \theta) \text{APP_Gas2}$
	(7) $\text{APP_Res2} \rightarrow \theta \text{APP_Res3} + (1 - \theta) \text{APP_Gas3}$

Table 4. Kinetic and thermodynamic parameters of melting and decomposition for neat materials.

Reaction	A (s^{-1})	E (J mol^{-1})	θ	h (J kg^{-1})
(1)	6.0×10^{40}	3.57×10^5	—	5.20×10^4
(2)	2.1×10^{21}	2.85×10^5	0.02	1.02×10^6
(3)	1.0×10^{16}	1.98×10^5	0.82	1.90×10^5
(4)	5.0×10^{18}	2.40×10^5	—	9.94×10^5
(5)	6.0×10^9	1.40×10^5	0.90	8.80×10^5
(6)	1.0×10^2	6.30×10^4	0.90	5.80×10^5
(7)	6.0×10^{10}	2.23×10^5	0.28	6.80×10^5

Table 5. Heat capacities of condensed-phase components representing neat materials.

Component	c ($\text{J kg}^{-1} \text{K}^{-1}$)
PLA	$100 + 3.70 * T$
PLA_Melt	$1450 + 1.20 * T$
PLA_Res	1700
MEL	$80 + 2.80 * T$
MEL_Res1	$890 + 1.40 * T$

APP	$740 + 1.76 * T$
APP_Res1	$740 + 1.76 * T$
APP_Res2	$2370 + 0.88 * T$
APP_Res3	4000

The thermal decomposition models of MEL and APP were developed following the same approach. These models are summarized in Tables 3-5. The heat capacity of MEL_Res1 intermediate was impossible to determine from the experimental data; therefore, this heat capacity was assigned the mean of the heat capacity of MEL and that of polymer-derived chars, $1700 \text{ J kg}^{-1} \text{ K}^{-1}$ [8]. The heat capacities of APP_Res1, APP_Res2 and APP_Res3 also could not be resolved. APP_Res3, representing the final residue formed during the decomposition of APP, was assigned the heat capacity of phosphoric acid averaged over 950 - 1073 K temperature range [29]. The assumption that this final residue is similar in structure to phosphoric acid was based on the observations reported in the literature [30]. The heat capacity of APP_Res1 was defined to be equal to that of APP. The heat capacity of APP_Res2 was defined as the average of the heat capacities of APP_Res1 and APP_Res3.

A comparison of the MEL and APP model predictions to the experimental TGA and DSC data is provided in Figure 3 and 4. MEL data are predicted very well. The APP model deviates from experiments somewhat when the temperature reaches above 950 K. A decision was made not to include small continuous mass loss observed in this temperature range into the model as it was deemed of little relevance to the flame retardant action of APP. This high temperature mass loss was previously attributed to a continuous fragmentation of poly(phosphoric acid) [31]. It should be noted that TGA of MEL and APP were carried out in several previous studies [30–34]. However, none of these studies yielded a complete thermo-kinetic model of decomposition of these materials similar to that presented here.

Figure 3. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for MEL at a set heating rate of 10 K min^{-1} .

Figure 4. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for APP at a set heating rate of 10 K min^{-1} .

3.3. TGA and DSC of Three-component Blends

3.3.1. Decomposition Models Including Interaction between PLA and Dominant FR

To identify potential interactions between PLA and FRs in the PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) systems, their decomposition was first simulated using reaction mechanisms obtained for neat materials (listed in Table 3) and known blend composition. Comparisons of the results of these simulations with the experimental results are provided in Figure 5 and 6. These comparisons indicate that interactions between PLA and FRs contribute significantly to the kinetics and thermodynamics of the decomposition of the blends. The impact is especially evident in the case of PLA(70)MEL(25)APP(5), where the experimental MLR peak corresponding to the decomposition is increased in height by about 35% and shifted to lower temperature by about 80 K with respect to that predicted by the mixture model (including PLA MECH, MEL MECH and APP MECH). Both blends produce about 20 wt.-% of residue, while the model predicts less than 5 wt.-%.

Figure 5. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(25)APP(5) at a set heating rate of 10 K min⁻¹. The simulation was performed using a combination of PLA MECH, MEL MECH and APP MECH.

Figure 6. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(5)APP(25) at a set heating rate of 10 K min⁻¹. The simulation was performed using a combination of PLA MECH, MEL MECH and APP MECH.

To account for the interaction between the matrix polymer and MEL in the PLA(70)MEL(25)APP(5) system, a second order reaction was added to the reaction mechanism. The stoichiometric coefficient, γ , for the second reactant, MEL, was determined using a consideration that all first reactant, PLA_Melt, must be consumed in this reaction because no peak associated with the decomposition of this component (maximum at 645 K) was detected in the experimental MLR data (shown in Figure 5 (b)). Two additional first order reactions were added in sequence to reproduce slow decay portion of the experimental mass loss (see Figure 5 (a)). Parameters of these reactions were determined by fitting the TGA and DSC experimental data obtained for PLA(70)MEL(25)APP(5) blend. The TGA data fitting criteria were relaxed somewhat for the blends: MLR maxima had to be predicted within 10%, positions of the maxima within 5 K and the final mass loss within 2% of the corresponding average experimental values. The resulting reaction mechanism, PLA_MEL MECH, is given in Table 6. The reaction

parameters are listed in Table 7. The heat capacities of the additional condensed-phase components are given in Table 8. As indicated in Section 2.2.1, the heat capacity of the post-decomposition residue of PLA(70)MEL(25)APP(5) was measured in separate tests, over 400-750 K temperature range. This heat capacity was assigned to PLA_MEL_Res1, PLA_MEL_Res2 and PLA_MEL_Res3.

Table 6. Reaction mechanisms representing decomposition of three-component blends (as well as neat materials).

Mechanism	Reaction
PLA_MEL MECH	(1-7) See Table 3.
	(8) $\text{PLA_Melt} + \gamma \text{ MEL} \rightarrow \theta \text{ PLA_MEL_Res1} + (1 + \gamma - \theta) \text{ PLA_MEL_Gas1}$
	(9) $\text{PLA_MEL_Res1} \rightarrow \theta \text{ PLA_MEL_Res2} + (1 - \theta) \text{ PLA_MEL_Gas2}$
	(10) $\text{PLA_MEL_Res2} \rightarrow \theta \text{ PLA_MEL_Res3} + (1 - \theta) \text{ PLA_MEL_Gas3}$
PLA_APP MECH	(1-7) See Table 3.
	(11) $\text{PLA_Melt} + \gamma \text{ APP} \rightarrow \theta \text{ PLA_APP_Res1} + (1 + \gamma - \theta) \text{ PLA_APP_Gas1}$
	(12) $\text{PLA_APP_Res1} \rightarrow \theta \text{ PLA_APP_Res2} + (1 - \theta) \text{ PLA_APP_Gas2}$

Table 7. Kinetic and thermodynamic parameters of decomposition reactions taking place in three-component blends.

Reaction	A (s^{-1} or $\text{m}^3 \text{ kg}^{-1} \text{ s}^{-1}$)	E (J mol^{-1})	γ	θ	h (J kg^{-1})
(8)	6.0×10^{29}	3.63×10^5	0.28	0.42	5.10×10^5
(9)	3.2×10^{17}	2.05×10^5	—	0.75	1.43×10^5
(10)	3.2×10^{16}	2.06×10^5	—	0.80	5.00×10^4
(11)	7.0×10^{11}	1.71×10^5	0.21	1.10	7.80×10^4
(12)	9.8×10^{10}	1.58×10^5	—	0.22	7.88×10^5

Table 8. Heat capacities of condensed-phase components representing three-component blends.

Component	c ($\text{J kg}^{-1} \text{ K}^{-1}$)
PLA_MEL_Res1	$-100 + 4.70 \text{ T}$
PLA_MEL_Res2	$-100 + 4.70 \text{ T}$

PLA_MEL_Res3	$-100 + 4.70 T$
PLA_APP_Res1	$910 + 2.60 T$
PLA_APP_Res2	$910 + 2.60 T$

The model of decomposition of PLA(70)MEL(5)APP(25) blend was parametrized in a similar manner. A second order reaction was added to the mixture model to account for the interaction between PLA_Melt and APP. The stoichiometric coefficient for APP (γ) was determined using a consideration that APP was not completely consumed in this reaction as suggested by a small MLR peak at around 830 K (see Figure 6 (b)), which closely resembles that produced by neat APP. Only one additional first order reaction was required to represent further decomposition of this blend. The resulting reaction mechanism, PLA_APP MECH, is given in Table 6. The reaction parameters and corresponding component heat capacities are listed in Table 7 and 8, respectively. The heat capacity of PLA_APP_Res1 and PLA_APP_Res2 was assigned that measured for the post-decomposition residue of PLA(70)MEL(5)APP(25) blend over 400-900 K temperature range.

Comparisons of the TGA and DSC predictions generated using PLA_MEL MECH and PLA_APP MECH to the corresponding experimental data are shown in Figure 7 and 8. All PLA(70)MEL(25)APP(5) experimental data are predicted very well. PLA(70)MEL(5)APP(25) data are also predicted well with the exception of a slight mismatch in the position of a small, high temperature MLR peak (see Figure 8 (b)).

Figure 7. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(25)APP(5) at a set heating rate of 10 K min^{-1} . The simulation was performed using PLA_MEL MECH.

Figure 8. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(5)APP(25) at a set heating rate of 10 K min⁻¹. The simulation was performed using PLA_APP MECH.

3.3.2. Decomposition Model Including All Interactions

While the models of the three-component blends described in the previous section accurately capture the experimental TGA and DSC data, these models do not account for a contribution of the low-concentration FR. To examine importance of this contribution, TGA and DSC of both blends were re-modeled using a reaction mechanism consisting of PLA_MEL MECH and PLA_APP MECH combined together. Reactions (1-7) from PLA_APP MECH were not added to the combined mechanism because they were already a part of PLA_MEL MECH. Comparisons of the predictions computed with this mechanism to the experimental data are shown in Figure 9 and 10. The model demonstrates a fair agreement with the experimental data for both blends. However, the simulated curves contain several features, including an MLR peak with the maximum at 625 K in Figure 9 (b) and a relatively large MLR peak with the maximum at 560 K in Figure 10 (b), that are not present in the experimental data. An attempt was made to eliminate or reduce these features by adjusting parameters of the reactions in the combined mechanism. However, this attempt was unsuccessful because each reaction responsible for one of these features in one system was the same reaction that reproduced the main experimentally observed MLR peak of the other system.

Figure 9. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(25)APP(5) at a set heating rate of 10 K min⁻¹. The simulation was performed using a combination of PLA_MEL MECH and PLA_APP MECH.

Figure 10. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(5)APP(25) at a set heating rate of 10 K min⁻¹. The simulation was performed using a combination of PLA_MEL MECH and PLA_APP MECH.

The observed discrepancies between the combined model and experiments indicate the presence of an additional interaction between the constituents of the blends. The only interaction that was not included in the combined model is that between the FRs. Therefore, a second order reaction between APP and MEL was added to the combined model. This reaction was assumed to produce no significant mass loss or heat flow and was postulated to occur in the 440-470 K temperature range, above PLA melting point and below the temperature of any apparent decomposition events in the PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) systems. γ of this reaction was selected to consume a large amount of APP with a small amount of MEL, which is consistent with a high chemical reactivity of APP [35]. Two additional reactions were subsequently added to the mechanism. One of these reactions was employed to represent interaction between PLA_Melt and the product of APP and MEL interaction. This reaction was necessary to capture the main experimental MLR peak associated with

the decomposition of PLA(70)MEL(5)APP(25) blend. The other (first order) reaction was used to represent further (high temperature) decomposition of the product of APP and MEL interaction. Parameters of these reactions were adjusted to simultaneously fit experimental TGA and DSC data for both three-component blends. FINAL MECH constructed as a result of this exercise is given in Table 9. The parameters of the added reactions are listed in Table 10. The heat capacities of the added condensed-phase components are given in Table 11. PLA_APP_MEL_Res1 and APP_MEL_Res2 effectively replace PLA_APP_Res1 and PLA_APP_Res2 in the PLA(70)MEL(5)APP(25) decomposition process and, therefore, are assigned the same heat capacity value.

Table 9. The final reaction mechanism representing decomposition of neat materials and three-component blends.

Mechanism	Reaction
	(1-7) See Table 3.
	(8-12) See Table 6.
FINAL MECH	(13) $\text{APP} + \gamma \text{MEL} \rightarrow (1 + \gamma) \text{APP_MEL_Res1}$
	(14) $\text{PLA_Melt} + \gamma \text{APP_MEL_Res1} \rightarrow \theta \text{PLA_APP_MEL_Res1} + (1 + \gamma - \theta) \text{PLA_APP_MEL_Gas1}$
	(15) $\text{APP_MEL_Res1} \rightarrow \theta \text{APP_MEL_Res2} + (1 - \theta) \text{APP_MEL_Gas2}$

Table 10. Kinetic and thermodynamic parameters of the reactions added to the decomposition mechanism to model interaction between FRs.

Reaction	A (s^{-1} or $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$)	E (J mol^{-1})	γ	θ	h (J kg^{-1})
(13)	6.0×10^{40}	3.90×10^5	0.14	—	0
(14)	2.0×10^5	1.21×10^5	0.06	0.14	1.02×10^6
(15)	5.0×10^3	9.88×10^4	—	0.45	4.50×10^5

Table 11. Heat capacities of condensed-phase components added to the decomposition mechanism to model interaction between FRs.

Component	c ($\text{J kg}^{-1} \text{K}^{-1}$)
APP_MEL_Res1	3000
PLA_APP_MEL_Res1	$910 + 2.60 T$

Comparisons of the TGA and DSC curves computed using FINAL MECH with the experimental results obtained for the blends are shown in Figure 11 and 12. The decomposition of both blends is predicted well using a single reaction mechanism and corresponding set of kinetic and thermodynamic parameters. This mechanism also accurately predicts the decomposition of neat PLA, MEL and APP because the models of decomposition of these constituents are an integral part of this final model. It should be noted that, due to the fact that during decomposition of these blends all APP is consumed in the reaction with MEL, Reaction (11) and (12) (listed in Table 6) remain inactive during the blend decomposition and can be removed from FINAL MECH with no impact on the computed predictions. Nevertheless, these reactions are retained because this mechanism is also believed to adequately represent decomposition of the blends containing only PLA and APP, where Reaction (11) and (12) would be operational.

Figure 11. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(25)APP(5) at a set heating rate of 10 K min^{-1} . The simulation was performed using FINAL MECH.

Figure 12. Experimental and simulated TGA ((a), (b)) and DSC ((c), (d)) data obtained for PLA(70)MEL(5)APP(25) at a set heating rate of 10 K min^{-1} . The simulation was performed using FINAL MECH.

Uncertainties in the parameters defining the final model were estimated by altering the value of each parameter (one at a time) and determining the maximum variation that kept the simulated TGA and DSC curves within the experimental error bars. Based on this procedure, the uncertainties in the pre-exponential factors, activation energies and stoichiometric coefficients were found to be ± 50 , ± 5 , and $\pm 5\%$, respectively. The uncertainties in the thermodynamic parameters, including heats of reaction and heat capacities, were found to be approximately $\pm 15\%$.

3.4. MCC of Neat Materials and Blends

The heats of combustion, h_c , of gaseous components defined in FINAL MECH were determined by fitting the HRR curves obtained from the MCC tests. Initial comparisons between the experimental HRR and modeled MLR profiles generated using the heating rate history specific to the MCC (shown in Figure 1 (b)) revealed some discrepancies. The experimental HRR curves had a tendency to be shifted to a lower temperature by 4-20 K, which was apparent because some portions of the curves indicated heat release in the absence of concurrent mass loss. These shifts were larger for charring and intumescent materials and were attributed to a slightly non-uniform temperature within the MCC crucible, which had no lid and was partially exposed to the radiation from the combustor. The experimental HRR data were shifted to a higher temperature to correct these discrepancies. The magnitude of the shift was determined using the principle that any significant heat release required a concurrent mass loss.

The heats of combustion were first estimated by dividing the mean shifted experimental HRR data by the computed rate of production of gaseous components. A predicted HRR curve was subsequently generated by multiplying the rates of production of each gaseous component, computed using ThermaKin, by the corresponding estimated h_c value and adding these contributions. The h_c values were further refined through incremental adjustments until the predicted and experimental MCC data agreed to within established criteria. These criteria were defined as differences of less than 5% between the average experimental and modeled maximum HRR, less than 5 K between the positions of the maxima and less than 5% between the final integral HRR values.

Comparisons of the experimental and modeled MCC data obtained for neat materials (PLA, MEL, and APP) are shown in Figures 13-15. No error bars are shown for the experimental data because of their high reproducibility. The experimental instantaneous HRR varied from test to test by less than 5%. The non-modified experimental data are shown as open circles; the shifted data are shown as a solid line. In the case of PLA (Figure 13), the non-modified and shifted data are less than 5 K apart and therefore only the shifted experimental data are shown to avoid congestion. The modeled curves obtained using the FINAL MECH and h_c values reported in Table 12 are displayed as dashed lines. The model captures the experimental MCC data of all neat materials well.

Figure 13. Experimental and simulated MCC data obtained for PLA at a set heating rate of 10 K min⁻¹. The non-modified experimental data are not shown to avoid congestion. The simulation was performed using FINAL MECH.

Figure 14. Experimental and simulated MCC data obtained for MEL at a set heating rate of 10 K min⁻¹. The simulation was performed using FINAL MECH.

Figure 15. Experimental and simulated MCC data obtained for APP at a set heating rate of 10 K min⁻¹. The simulation was performed using FINAL MECH.

Table 12. Heats of combustion of components that represent gaseous pyrolyzate. To keep the MCC data presentation in the traditional format [25], these values are listed as positive despite the fact that the combustion processes are exothermic.

Component	h_c (J kg ⁻¹)
PLA_Gas	1.7×10^7
MEL_Gas1	1.3×10^7
MEL_Gas2	9.5×10^6
APP_Gas1	1.4×10^7
APP_Gas2	8.0×10^6
APP_Gas3	4.0×10^5
PLA_MEL_Gas1	9.5×10^6
PLA_MEL_Gas2	5.4×10^7
PLA_MEL_Gas3	6.3×10^7
PLA_APP_MEL_Gas1	2.0×10^7
APP_MEL_Gas2	0
PLA_APP_Gas1	7.0×10^6
PLA_APP_Gas2	2.0×10^7

The h_c values of the gaseous components formed as a result of interactions between the constituents of the blends were obtained by fitting the corresponding experimental data. These values are listed in Table 12 and the results of the fitting are shown in Figure 16 and 17. The experimental data for both blends are captured well by the model with the exception of a slight underestimation of PLA(70)MEL(25)APP(5) HRR in the 600-650 K temperature range.

Due to the fact that Reaction (11) and (12) are inactive during decomposition of the blends, the heats of combustion of the corresponding gaseous components, PLA_APP_Gas1 and PLA_APP_Gas2, cannot be resolved using modeling of these blends with FINAL MECH. Therefore, additional modeling of the MCC of PLA(70)MEL(5)APP(25) system was performed using PLA_APP MECH to determine the h_c values of these components. The resulting heats of combustion are listed in Table 12. The uncertainties in all h_c values were estimated to be approximately $\pm 10\%$. These uncertainties do not account for potential interdependence of these values.

Figure 16. Experimental and simulated MCC data obtained for PLA(70)MEL(25)APP(5) at a set heating rate of $10 K min^{-1}$. The simulation was performed using FINAL MECH.

Figure 17. Experimental and simulated MCC data obtained for PLA(70)MEL(5)APP(25) at a set heating rate of $10\ K\ min^{-1}$. The non-modified experimental data are not shown to avoid congestion. The simulation was performed using FINAL MECH.

3.5. Extrapolation Capabilities of the Final Model

While the decomposition model represented by the FINAL MECH was shown to simultaneously predict the outcome of TGA, DSC and MCC experiments for PLA, MEL, APP and PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) blends, all these experiments were performed under similar heating conditions. To demonstrate that the model is capable of extrapolating beyond these conditions, simulations of TGA experiments conducted at 5 and $20\ K\ min^{-1}$ nominal heating rates on PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) blends were carried out. A comparison of the simulation results with the corresponding mean experimental data are shown in Figure 18. Good predictions are observed for both blends and both heating rates. The largest deviation appears to be a small peak with the maximum at about $610\ K$ in Figure 18 (a), which is notable in the modeled curve and negligible in the experimental data.

Another challenge for the model is to be able to predict decomposition behavior of a blend which composition significantly deviates from those used in the model development process. A comparison of the TGA simulation results obtained for PLA(70)MEL(15)APP(15) blend to the corresponding mean experimental data is shown in Figure 19. The model accurately predicts the main mass loss rate peak and final mass loss. However, the shape of the high temperature portions of the mass and MLR curves are not fully captured. Overall, the model demonstrates a satisfactory capability for composition extrapolation.

Figure 18. Experimental and simulated TGA data obtained for PLA(70)MEL(25)APP(5) and PLA(70)MEL(5)APP(25) blends at a set heating rate of 5 K min⁻¹ ((a), (c)) and 20 K min⁻¹ ((b), (d)). The simulations were performed using FINAL MECH.

Figure 19. Experimental and simulated TGA data obtained for PLA(70)MEL(15)APP(15) blend at a set heating rate of 10 K min^{-1} . The simulation was performed using FINAL MECH.

4. Conclusions

This study demonstrates an approach to development of a model that predicts the kinetics and thermodynamics of decomposition of blends of a thermoplastic and condensed-phase-active flame retardants. This approach is based on TGA, DSC and MCC experiments and their inverse modeling. The final model is shown to simultaneously reproduce results of all these experiments with a good accuracy. The most important aspect of this model is that it provides a quantitative relationship between key aspects of pyrolytic behavior of the blends and their composition, as demonstrated on a range of blends with significantly different flame retardant content.

This approach does not resolve chemical species involved in the decomposition. Instead, it defines this process by a mechanism consisting of virtual chemical reactions, which presence in the mechanism is dictated solely by the necessity to accurately represent available experimental data. It is expected that this mechanism and associated parameters provide sufficient information about decomposition to successfully predict the rate of burning and flame spread on the studied materials. This expectation is supported by a number of recent studies where similar decomposition models were combined with thermal transport measurements to produce complete pyrolysis models that successfully predicted the rates of gasification, burning [9,10,12,36] and flame spread [37] on coupon-sized specimens. Parametrization of intumescence and thermal transport in the PLA/MEL/APP systems will be a subject of future work. In that work, it will be determined whether the presented decomposition model provides the necessary foundation for capturing the impact of MEL and APP on these processes. Determination of this impact will complete a quantitative link between the material composition and flammability and will provide further insight into the mechanism of action of these flame retardants.

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