



Thermal stability of binary and ternary biodegradable polymer blends assessed by isoconversional kinetic analysis

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ABSTRACT

Here we report on kinetic analysis of thermal degradation of polymer blends based on incremental isoconversional method coupled with mathematical deconvolution of thermogravimetric curves based on Fraser–Suzuki peak function. The measured kinetic envelope was decomposed into contributions approximately corresponding to degradation of each constituent of a polymer blend. Kinetic parameters from isoconversional analysis were further used for estimating the effect of blending on thermal stability of the constituents. Compared to routinely used parameters such as degradation onset temperature or DTG-peak temperature, the deconvolution analysis allows to determine stability of all components in a mixture regardless of their relative content. Here we also show that deconvolution analysis can be carried out directly on integral $\alpha(T)$ curves, thus bypassing the work with differential data da/dt . Isoconversional analysis of deconvoluted $\alpha(T)$ curves allows to calculate various parameters for assessing the potentially accelerating or inhibiting effect on thermal degradation, for example, by means of decomposition half-time $t_{0.5}$. The results can be made more robust by utilizing relative criteria for stability such as $t_{0.5}(\text{blend})/t_{0.5}(\text{neat polymer})$. Using this approach, detrimental effect of PHBV and PBAT on thermal stability of PLA above 300 °C was confirmed. On the other hand, stability of PHBV in both binary and ternary mixtures was improved compared to neat polymer.

1. Introduction

The environmental concerns stemming from the increasing accumulation of plastic wastes and high carbon footprint of fossil-derived polymers have prompted an unprecedented interest in the development of sustainable plastics, which are meant to be either biobased, biodegradable, or optimally both [1,2]. According to the European Bioplastics report [3], these polymers currently represent only around 0.5 percent of the over 400 million tonnes of plastic produced annually; however, the global bioplastics production capacity is forecast to increase significantly from around 2.18 million tonnes in 2023 to approximately 7.43 million tonnes in 2028. One of the most used and investigated biopolymers is poly(lactic acid) (PLA), due to its several good mechanical properties (tensile strength and flexural modulus), biodegradability and lower associated carbon dioxide emissions and lower energy costs compared to conventional plastics [4,5]. PLA, like any other material, is not devoid of drawbacks, especially due to its brittle nature (poor toughness and impact strength) and also has

relatively low thermal stability. Melt blending of polymers is likely the easiest, effective, and economical way of developing new plastic materials with tailored properties. This approach has been widely investigated with other biopolymers, such as polyhydroxyalkanoates, poly(butylene succinate) (PBS), poly(butylene-adipate-co-terephthalate) (PBAT) [5–9]. In particular, PBAT is a biodegradable copolymer with high flexibility, which allows its use only in specific applications while PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) has properties similar to polypropylene (PP), but it is stiff, brittle, and expensive. None of these three polymers can fulfill the requirement for almost all semi-structural or functional materials in commercial application when used alone. However, PLA, PHBV and PBAT show very interesting complementary properties, so that one can tailor the mechanical properties, processing properties and thermal performance by a simple melt blending method. A limited number of studies have explored these ternary blends [10], especially without the use of compatibilizers to improve the interfacial adhesion between PLA and the other components [11,12].

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Table 1
Compositions and codes of the polymer formulations.

Sample ID	PLA (wt.%)	PHBV (wt.%)	PBAT (wt.%)
PLA	100	0	0
PHBV	0	100	0
PLA:PHBV 60:40	60	40	0
PLA:PHBV 40:60	40	60	0
PLA:PHBV:PBAT 60:30:10	60	30	10
PLA:PHBV:PBAT 60:20:20	60	20	20

Another issue that deserves attention is the fact that much information is available on thermal and mechanical properties of the resulting bio-based blends, but parameters such as thermal degradation kinetics have not been extensively studied [13–15]. In fact, for many industrial processes, it is important to avoid degradation of raw materials and approaching the materials' processing temperature limits, therefore calling for a detailed characterization of their thermal degradation behavior. From the opposite point of view, kinetics of pyrolysis (or thermal degradation) may provide information for developing processes producing valuable chemicals from plastic waste [16–18].

In this work, binary (PLA/PHBV) and ternary (PLA/PHBV/PBAT) blends were prepared and characterized by dynamical mechanical analysis (DMA) in order to assess the effect of blending on mechanical properties (storage modulus and $\tan \delta$) as well as on the glass transition temperature. Isoconversional kinetic analysis coupled with mathematical deconvolution analysis (MDA) was applied to thermal decomposition of neat polymers (PLA and PHBV) as well as to that of their binary and ternary blends. The results are mainly discussed from the general point of view of interpretation of results obtained by isoconversional kinetic analysis. Criteria for assessing the effect of blending on thermal stability are derived from kinetic parameters.

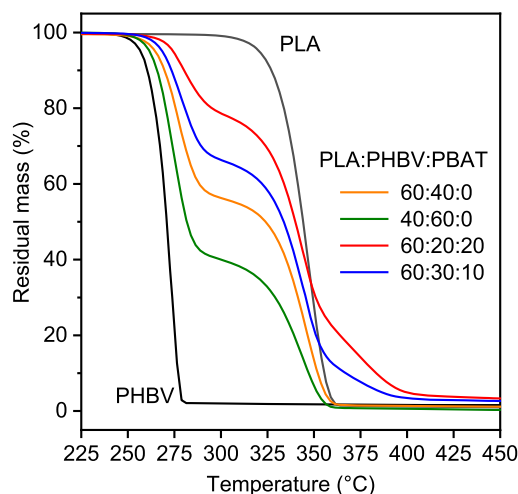


Fig. 2. Comparison of TG records of neat polymers with those of their binary and ternary blends at a heating rate of 3 °C min^{-1} .

2. Materials and methods

2.1. Materials

The polymer blends were prepared from the following constituents: Poly(lactic acid) (PLA, CAS 26100-51-6) Luminy™ LX175 manufactured by TotalEnergies Corbion, density 1.24 g cm^{-3} , melt flow index (MFI) 6 g/10 min (210 °C , 2.16 kg); poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, CAS 80181-31-3) ENMAT™ Y1000P manufactured by TianAn Biopolymer, density 1.25 g cm^{-3} , MFI 12–25 g/10 min (190 °C , 2.16 kg); and poly(butylene-adipate-co-terephthalate) (PBAT, CAS 60961-73-1) BIO-DI™ XF100 manufactured by Enyax Srl, density 1.22 g cm^{-3} , MFI 6–8 g/10 min (190 °C , 2.16 kg). All polymers were used as received.

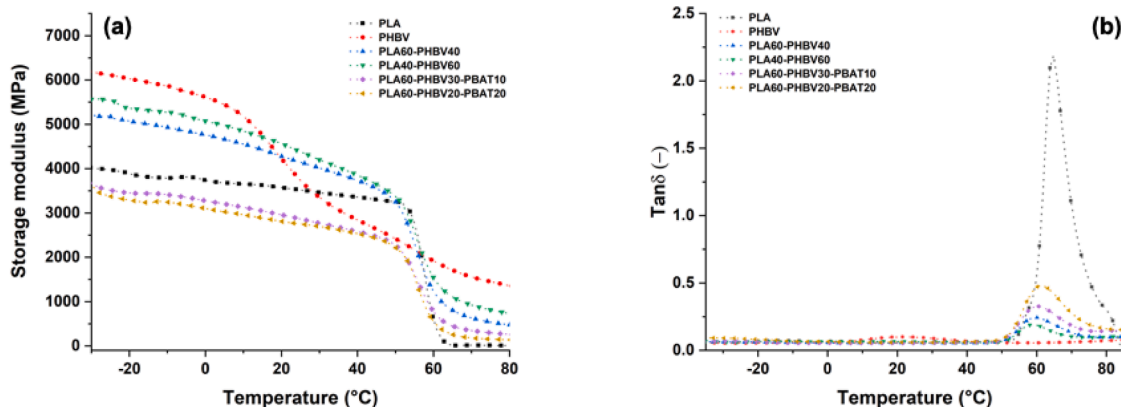


Fig. 1. DMA curves of PLA:PHBV:PBAT binary and ternary blends at various composition: (a) storage modulus versus temperature; (b) $\tan \delta$ versus temperature.

Table 2
Storage modulus (E') at selected temperatures and glass transition temperatures for the polymer formulations.

Sample ID	E' (GPa)				T_g (°C) PLA	T_g (°C) PHBV
	-50 °C	0 °C	25 °C	50 °C		
PLA	4.50 ± 0.03	3.74 ± 0.01	3.52 ± 0.02	3.25 ± 0.02	64.6 ± 0.9	–
PHBV	6.36 ± 0.03	5.62 ± 0.02	3.73 ± 0.02	2.41 ± 0.02	–	21.6 ± 0.7
PLA:PHBV 60:40	5.50 ± 0.02	4.76 ± 0.02	4.15 ± 0.02	3.35 ± 0.02	59.6 ± 0.7	23.3 ± 0.3
PLA:PHBV 40:60	5.71 ± 0.02	5.07 ± 0.02	4.38 ± 0.02	3.36 ± 0.02	58.9 ± 0.6	17.4 ± 0.4
PLA:PHBV:PBAT 60:30:10	4.13 ± 0.02	3.28 ± 0.02	2.86 ± 0.02	2.28 ± 0.02	60.2 ± 0.3	20.9 ± 0.5
PLA:PHBV:PBAT 60:20:20	4.08 ± 0.02	3.10 ± 0.02	2.75 ± 0.02	2.22 ± 0.02	61.3 ± 0.4	21.6 ± 0.3

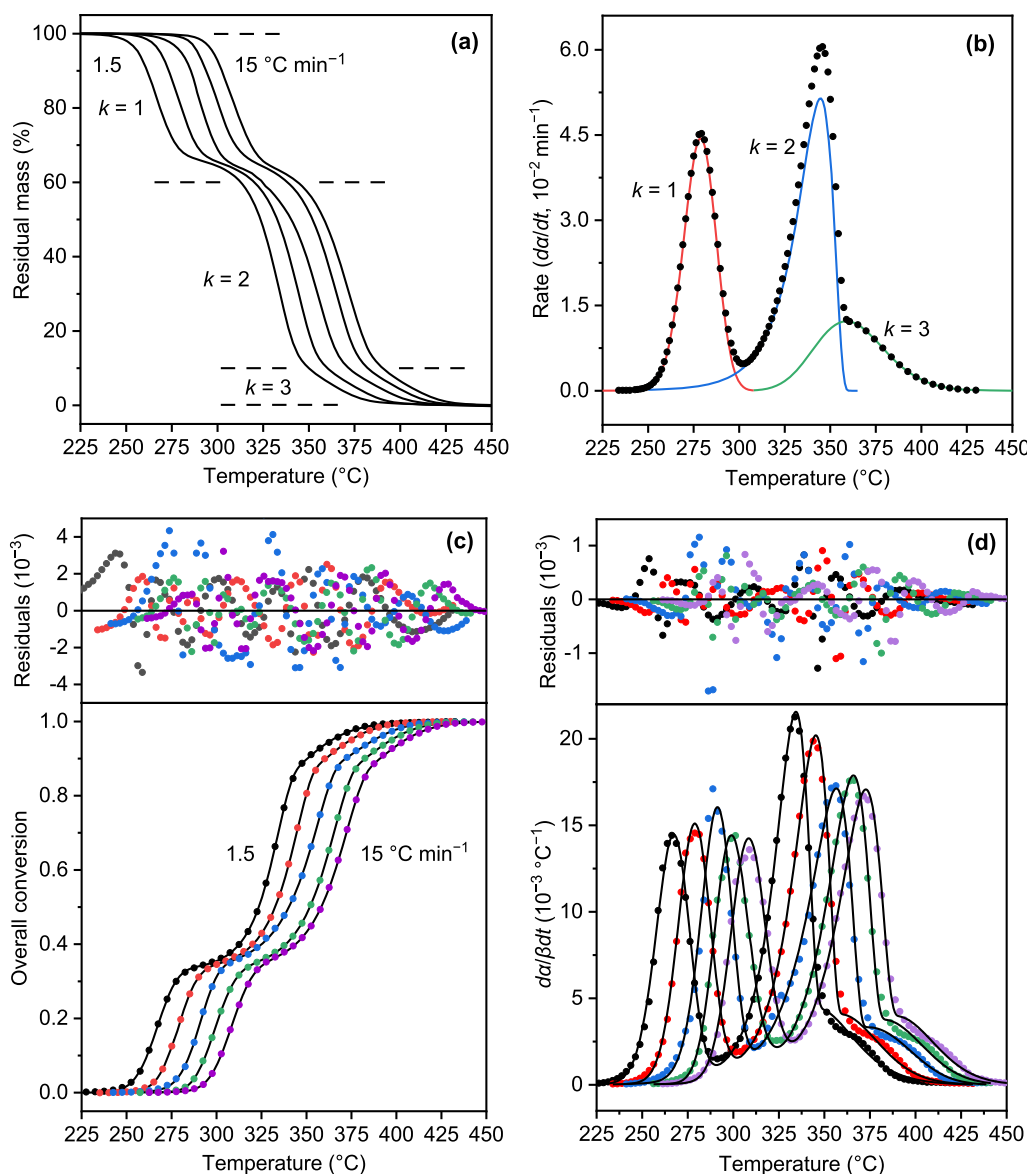


Fig. 3. (a) decomposition of PLA:PHBV:PBAT 60:30:10 blend at various heating rates with theoretical ranges of kinetic contributions to the overall mass loss; (b) deconvolution of a overall rate curve of the same blend (heating rate 3 °C min^{-1}) into three steps: overall rate (points) and partial contributions (lines); (c) least-squares fit of Eq. (5) (lines) to experimental $\alpha(T)$ data (points); (d) comparison of experimental overall decomposition rate (points) and first derivative of Eq. (5) parametrized from fits shown in (c).

Note: The experimental datapoints were decimated in order to improve visual clarity

2.2. Preparation of blends

Neat biopolymers were first dried for 24 h at 80 °C ; the blends were obtained using a laboratory co-rotating twin-screw extruder Process 11 (Thermo Scientific, Karlsruhe, Germany) with the following temperature profile (from feed to extrusion die): $165 \rightarrow 170 \rightarrow 175 \rightarrow 180 \rightarrow 185 \rightarrow 185 \rightarrow 180\text{ °C}$, at a screw rotation rate of 150 rpm. Neat polymers for comparison were processed similarly; compositions of the polymer formulations are listed in Table 1.

2.3. Thermogravimetry (TG)

TG measurements were carried out using a TG 209 F1 Libra thermogravimetric analyzer (NETZSCH, Selb, Germany). The samples (18 ± 1) mg were placed in open 85- μL alumina crucibles; the purge gas was nitrogen at a flow rate of 60 mL min^{-1} . Each sample was heated from room temperature to 800 °C at five different heating rates (1.5, 3, 6, 10

and 15 °C min^{-1}).

2.4. Dynamic mechanical analysis (DMA)

The storage modulus and $\tan \delta$ of the specimens were measured as a function of temperature using a dynamic mechanical analyzer DMA 242 E Artemis (NETZSCH, Selb, Germany). The tests were carried out in a three-point bending mode by heating the samples ($60 \times 10 \times 4\text{ mm}$) from -50 to 90 °C at a rate of 2 °C min^{-1} with a frequency of 1 Hz and amplitude of $30\text{ }\mu\text{m}$. Tests were performed in triplicate.

3. Kinetic analysis

3.1. Incremental isoconversional method

From a mechanistical point of view, pyrolysis of polymers is a complex process involving multiple parallel and consecutive reactions

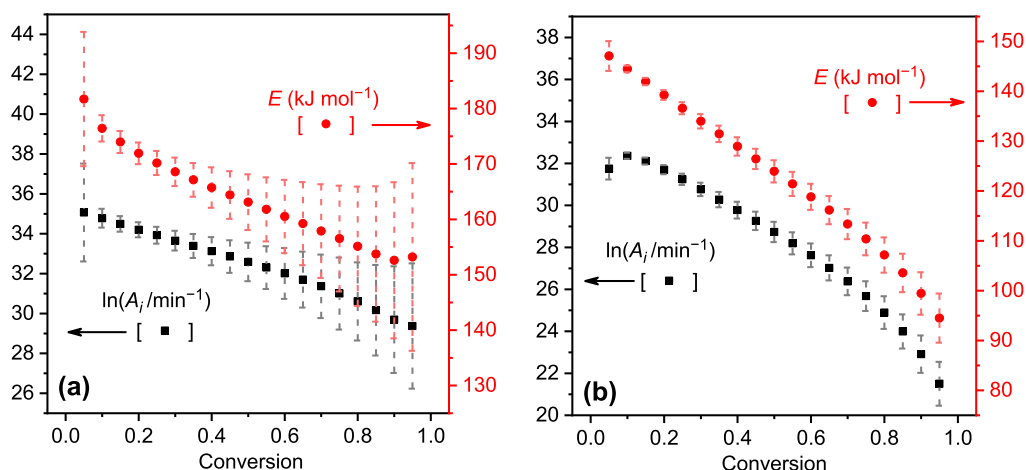


Fig. 4. Isoconversional kinetic parameters for thermal decomposition of neat polymers: (a) PLA; (b) PHBV. The error bars represent ± 1 standard error.

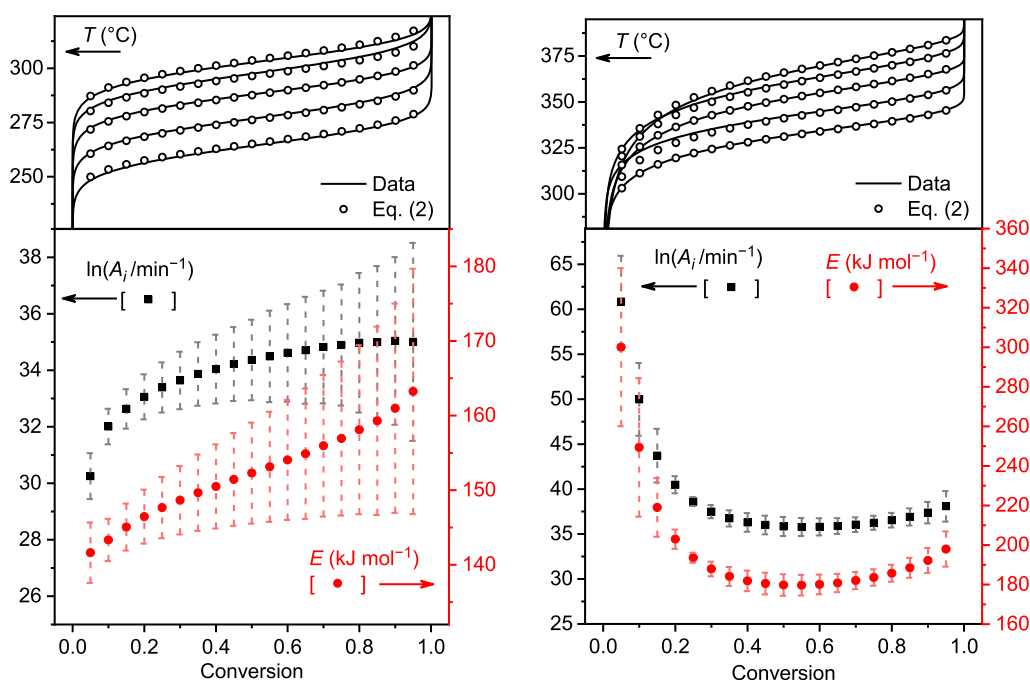


Fig. 5. Isoconversional kinetic parameters for thermal decomposition of PLA:PHBV 60:40 blend (left: $k = 1$, right: $k = 2$).

yielding a large variety of products [19]. Apart from chemical changes, purely physical phenomena such as heat and mass transfer contribute to overall rate of the process. Thermogravimetry alone, as any other “bulk” method, does not provide deeper insight into pyrolysis mechanism since the measured signal (sample mass) inevitably leads to underdetermined system of kinetic equations whenever complex mechanisms are considered. The starting point of essentially all kinetic evaluations of thermoanalytical data is the general rate equation [20,21]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where $k(T)$ and $f(\alpha)$ are the functions depending solely on temperature and conversion, respectively. In contrast to “classical” kinetics, the conversion here is defined in a purely operational way as the observed mass change normalized to the total change associated with given process, $\alpha(t) = [m_i - m(t)]/[m_i - m_f]$, where the indices stand for initial and final value. The temperature function is almost exclusively expressed by the Arrhenius equation, $k(T) = A_k \exp(-E/RT)$. Assuming a series of

measurements performed at linear heating, the following equation can be derived [22]:

$$\beta = \frac{A_k}{g(\alpha_i) - g(\alpha_{i-1})} \int_{T_{i-1}}^{T_i} \exp(-E_i/RT) dT, \quad (2)$$

where $\beta = dT/dt$ is the heating rate, $g(\alpha)$ is the antiderivative of $1/f(\alpha)$ and T_{i-1} and T_i stand for the temperature at which the conversion α_{i-1} and α_i was reached, respectively. Eq. (2) allows to determine the activation energy E_i and composite parameter $A_i = A_k/[g(\alpha_i) - g(\alpha_{i-1})]$ for any considered conversion range (α_{i-1} , α_i); details of the method employed are given in [23]. In brief, the heating rate β is treated as an independent variable with a negligible error; the values of E_i and A_i are optimized so that the total sum of squares is minimized:

$$S = \sum \left[(T_{i-1}^{\text{exp}} - T_{i-1}^{\text{calcd}})^2 + (T_i^{\text{exp}} - T_i^{\text{calcd}})^2 \right]$$

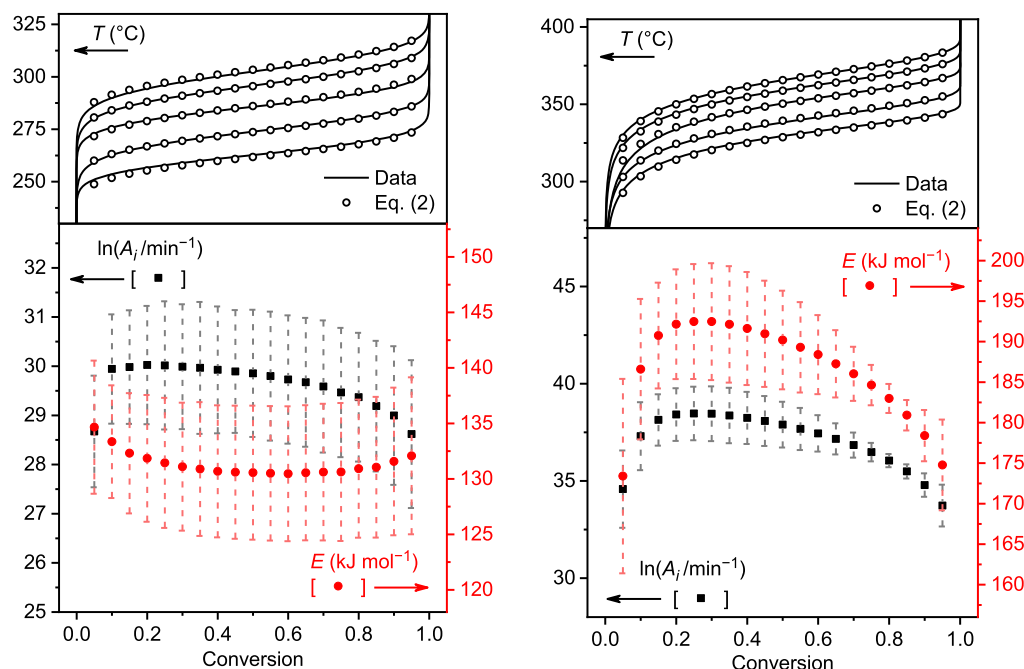


Fig. 6. Isoconversional kinetic parameters for thermal decomposition of PLA:PHBV 40:60 blend (left: $k = 1$, right: $k = 2$).

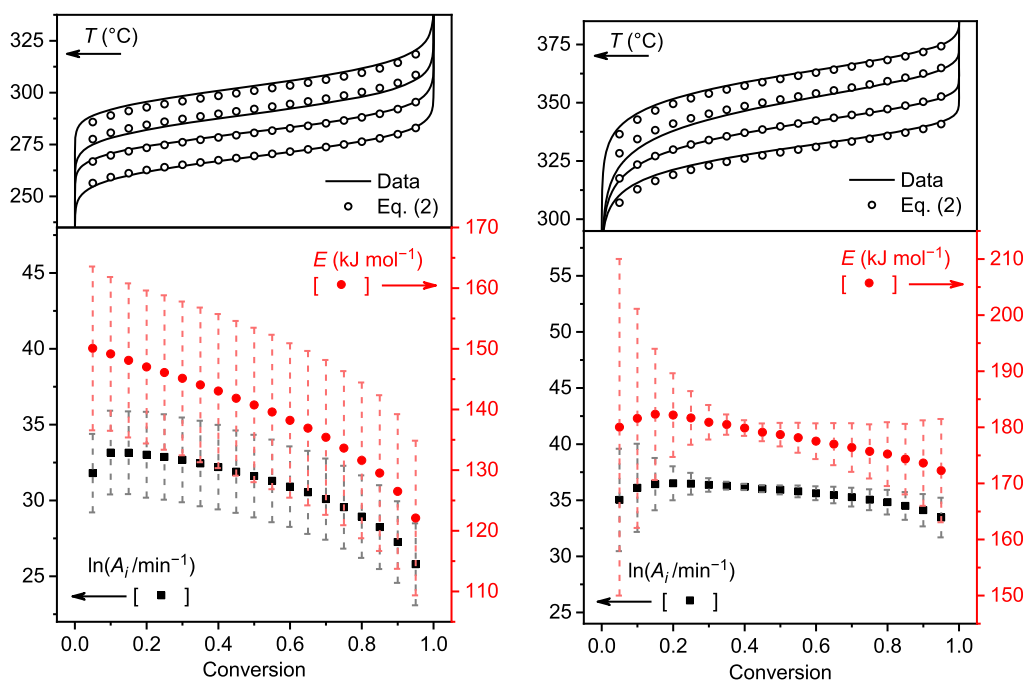


Fig. 7. Isoconversional kinetic parameters for thermal decomposition of PLA:PHBV:PBAT 60:20:20 blend (left: $k = 1$, right: $k = 2$).

where “exp” and “calcd” indicate the experimental and calculated value of isoconversional temperature, respectively. The summation indicated in the objective function S is performed over all heating rates employed.

3.2. Deconvolution procedure

The TG records of pyrolysis of neat polymers (PLA and PHBV) exhibit single mass loss stage proceeding in a relatively narrow temperature range. Thermal behaviour of binary and ternary polymeric blends under study is more complicated as the mass loss occurs in two and three partially overlapping steps, respectively. In such cases the ICTAC rec-

ommendations [24] suggest various procedures; we adopted the mathematical deconvolution analysis (MDA) with certain modifications described here. Considering pyrolysis of a polymer blend as a series of n independent reaction steps, the overall rate can be expressed as

$$\frac{d\alpha}{dt} = \sum_{k=1}^n F(\mathbf{p}_k, t) \quad (3)$$

where $F(\mathbf{p}_k, t)$ is a suitable peak function with a vector of adjustable parameters \mathbf{p}_k . Eq. (3) allows to parametrize the time course of the rate of the process on a purely empirical basis. In this work, Fraser–Suzuki

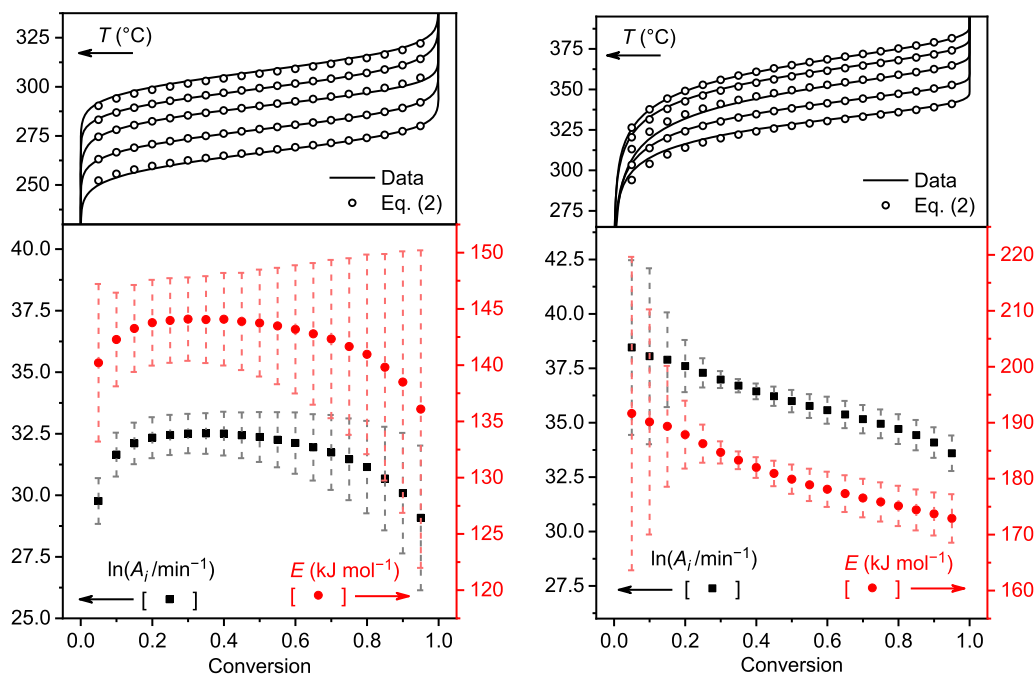


Fig. 8. Isoconversional kinetic parameters for thermal decomposition of PLA:PHBV:PBAT 60:30:10 blend (left: $k = 1$, right: $k = 2$).

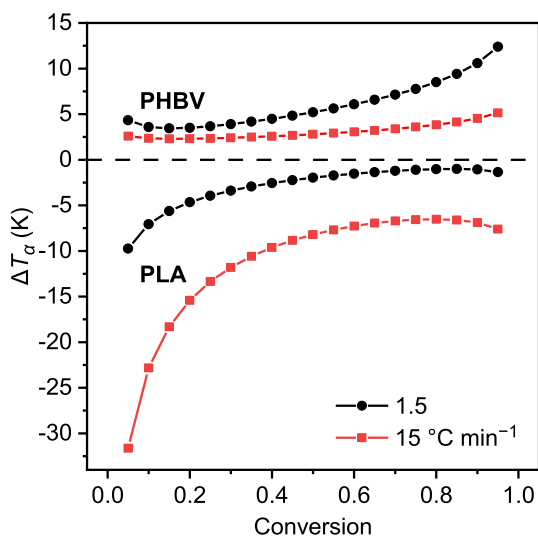


Fig. 9. Effect of blending on pyrolysis rate in PLA:PHBV 60:40 blend assessed by differences in isoconversional temperatures (Eq. (6)).

(FS) function [25,26] was used in the following form:

$$F(\mathbf{p}_k, x) = a_{1k} \exp \left\{ - \frac{\ln 2}{a_{4k}^2} \left[\ln \left(1 + 2a_{4k} \frac{x - a_{2k}}{a_{3k}} \right) \right]^2 \right\} \quad (4)$$

where $\mathbf{p}_k = (a_{1k}, a_{2k}, a_{3k}, a_{4k})$ are the parameters controlling the peak height, position, width, and asymmetry, respectively. This function is usually flexible enough to describe most da/dt curves with 1:1 correspondence of number of experimentally discernible steps and number of terms in form of Eq. (4). It should be noted that each term itself may represent a complex process which cannot be described by a single kinetic triplet $(A, E, f(\alpha))$ [27].

The deconvolution procedures are usually carried out on differential data (da/dt); however, the thermogravimetric signal has integral nature, i.e., it is proportional to α . The advantage of incremental methods,

including the one based on Eq. (2), is that they do not require evaluating da/dt data. In order to preserve this advantage while still performing mathematical deconvolution of a multi-step process, the FS function was fitted directly to the experimental $\alpha(T)$ curves in the following form:

$$\alpha(T) = \sum_{k=1}^n \frac{1}{a_{0k}} \int_{T_0}^T F(\mathbf{p}_k, T) dT \quad (5)$$

where a_{0k} is the area under k -th FS peak (with unit height) which can be calculated as $(a_{3k}/2) \sqrt{\pi/\ln 2} \exp(a_{4k}^2/\ln 16)$. Normalizing the peak area to unity allows to treat the parameter a_{1k} as contribution of a given process to the overall conversion. Fitting of Eq. (5) to experimental $\alpha(T)$ curves was done using OriginPro 2018 software package (OriginLab Northampton, MA, USA); the integral of FS function was calculated numerically with a built-in routine.

Procedure based on Eq. (5) allows bypassing the need for numerical derivatives of TG data; the deconvolution was performed in temperature domain. The resulting parameters can subsequently be used to calculate conversion curve $\alpha_k(T)$ for k -th contributing process. Finally, a series of these $\alpha_k(T)$ dependences obtained at various heating rates can be analyzed isoconversionally by applying Eq. (2).

3. Results and discussion

3.1. Dynamic mechanical analysis

The storage modulus (E') curves of neat PLA and PHBV binary, and ternary blends are shown in Fig. 1(a); numerical values and obtained glass transition temperatures (T_g) are summarized in Table 2. PLA showed the typical values of a glassy polymer below its T_g (around 3.5 GPa at room temperature), but this value decreased sharply when the glass transition was reached (around 65 °C). Neat PHBV displayed a higher storage modulus compared to PLA below its T_g (20 °C) and the decrease was not as sharp as the one observed for PLA, thus delivering a material with better thermomechanical stability over the investigated temperature range. This behavior is maintained also by binary blends, which exhibited higher storage modulus values compared to neat PLA both below and above the PLA's glass transition temperature.

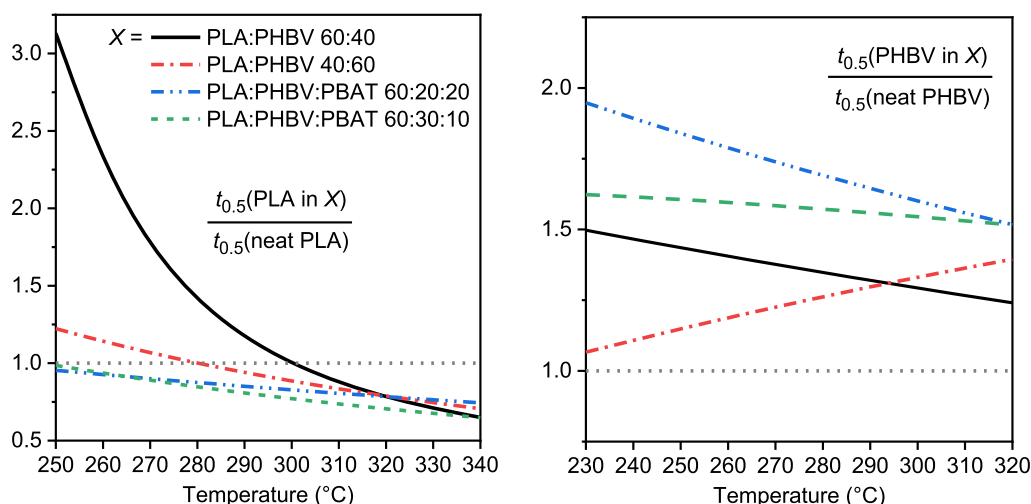


Fig. 10. Effect of blending on pyrolysis rate assessed by Eq. (7). The vertical axis represents ratio of reaction half-times at given temperature. The dotted line divides the regions of increased thermal stability (above 1) and decreased thermal stability (below 1) relative to neat polymers.

Tan δ , defined as the ratio between the loss modulus (E'') and the storage modulus (E') displayed peaks linked to the transition in molecular mobility representing the T_g of the polymer materials. As seen from Fig. 1(b), a sharp peak was found around 65 °C for neat PLA. A transition in the tan δ peak toward the lower end of temperature range was found with increasing amount of PHBV and PBAT in the blends, suggesting limited mutual solubility of PLA with PHBV and presence of PBAT minor phases [28]. Also evident is the toughening caused by the presence of PBAT in the ternary blends, demonstrating the possibility of achieving a good balance of stiffness and toughness by fine-tuning the relative amounts of PHBV and PBAT.

3.2. Isoconversional kinetic analysis

The TG records (heating rate 3 °C min⁻¹) of all polymers and their respective blends under study are shown in Fig. 2. Both studied neat polymers (PLA and PHBV) exhibit thermal decomposition seemingly proceeding in a single step. Comparing the blends with neat polymers, the pyrolysis proceeds in order (with respect to temperature) PHBV → PLA → PBAT; this observation holds within the whole range of heating rates employed as exemplified on PLA:PHBV:PBAT 60:40:10 blend in Fig. 3(a). The kinetic parameters of neat PLA and PHBV can be determined directly from normalized TG records, thus treating the process as a simple one with regard to the general rate equation. On the other hand, the normalized TG records of all blends were fitted by Eq. (5) considering two or three FS terms for binary and ternary systems, respectively. A typical example of this procedure is depicted in Fig. 3(c) on the PLA:PHBV:PBAT 60:40:10 blend; the residuals plotted in the top panel all fall within $\pm 0.5\%$ of the experimental overall conversion. As mentioned in the previous section, the approach traditionally established for MDA is based on fitting of weighed sum of empirical peak functions to overall da/dt curve. Working with differential data has an advantage residing in improved visual separation and identification of overlapping sub-processes. However, once the number of contributing sub-processes has been established, either visually or by a statistical test, the original $\alpha(T)$ curve is equally suitable for determining the parameters of empirical functions. It is matter of course that the resulting MDA parameters will differ between these two approaches since different criteria are optimized. Fig. 3(d) shows (for PLA:PHBV:PBAT 60:40:10 blend) an overlay of experimental $da/\beta dt$ datapoints with curves calculated by differentiating the FS function fitted in its integral form given by Eq. (5). In this particular case, direct fitting of FS peak functions to differential data yields a global sum of squares (all heating rates) equal to $3.8 \times 10^{-5} \text{ K}^{-2}$; the differentiated Eq. (5) with parameters

obtained from integral $\alpha(T)$ curve yields a higher value of $5.1 \times 10^{-5} \text{ K}^{-2}$. However, the situation is reversed when the comparison is performed on a basis of correlation with $\alpha(T)$ curve rather than on its first derivative: optimization of Eq. (5) leads to a global sum of squares between α_{exp} and α_{calcd} of 8.6×10^{-4} while the integral of FS peak functions with parameters obtained by “classical” MDA gives almost twice as high value (1.5×10^{-3}). This comparison shows that no definite answer can be given when comparing the performance of Eq. (5) with da/dt -based MDA. However, since the subsequent isoconversional kinetic analysis is based on evaluation of isoconversional temperatures by Eq. (2), a more logical step would be performing the MDA on $\alpha(T)$ curves as demonstrated here.

Fitting each $\alpha(T)$ curve of a given blend separately led to problematic results with respect to the parameter a_{1k} whose value should reflect the contribution of a partial step to the overall mass loss [24]. Allowing the a_{1k} parameter to vary with heating rate resulted into negligible improvements in goodness-of-fit criteria; however, interpretation of variable a_{1k} is difficult. The phenomenon of variable kinetic contribution of each step into the overall $\alpha(T)$ curve can be attributed to purely empirical nature of the FS function; it is also mentioned in a recent ICTAC recommendations paper on decomposition kinetics [29] as one of the main drawbacks of MDA. In our case, some of the deconvoluted $\alpha_i(T)$ curves exhibited erratic behaviour as they mutually crossed multiple times in the regions of significant overlap with other process. However, Eq. (2) requires monotonous increase of T_i for a given T_{i-1} value with respect to increased heating rate. Therefore, in order to preserve the physical meaning of the scaling parameter a_{1k} , all the records for each blend were fitted simultaneously with the parameter a_{1k} shared among all heating rates; despite imposing such constraint the resulting R^2 values were always higher than 0.99995. The values of FS parameters for all four blends are listed in Table S1 in the Electronic Supplementary Material. Comparing the theoretical values of a_{1k} given by the mass ratios of constituents with those listed in Table S1 shows good agreement for both PLA:PHBV mixtures (60:40 vs. 56:44, and 40:60 vs. 41:59). In case of ternary mixtures, significant differences can be seen, especially for PLA:PHBV:PBAT 60:30:10 for which a_{1k} parameters give contributions 38:19:43. This discrepancy most probably stems from the empirical nature of mathematical deconvolution and significant overlap between the temperature regions of PLA and PBAT decomposition as seen in Fig. 2. For this reason, the deconvoluted $\alpha_k(T)$ curves only approximately correspond to the components of ternary blends.

The experimental $\alpha(T)$ curves for neat polymers and deconvoluted $\alpha_k(T)$ curves for blends were further evaluated by incremental isoconversional method described in Section 3.1 in the conversion range

from 0.05 to 0.95 with a step of 0.05. The kinetic analysis by this method yields two parameters (A_i, E_i) per isoconversional level. For neat PLA and PHBV the determined kinetic parameters are plotted in Figs. 4(a) and (b), respectively. In both cases the apparent activation energy exhibits approximately linear decrease with conversion. In case of PLA the E_i dependence spans similar range as the uncertainty of the parameter itself; for PHBV the uncertainties are significantly lower and the trend in E_i is thus more pronounced. As recently pointed out by Várhegyi [30], the $E(\alpha)$ dependences tend to be rather “fragile” with respect to experimental uncertainties usually encountered in experimental $\alpha(T)$. Combined with unclear physical meaning of apparent activation energy of condensed-phase processes [31–33] even in the case of its constant value when analyzed by general rate equation, we refrain from mechanistical interpretation of any particular $E(\alpha)$ dependence. The same also applies to comparing these dependences obtained for neat polymers and their blends. The kinetic parameters obtained in the same way for the first two sub-processes ($k = 1$ and 2) in binary and ternary blends are shown in Figs. 5–8. As can be seen, the $E(\alpha)$ behaviour differs significantly, including the coefficients of variability. For ternary mixtures (Figs. 7 and 8) the second step ($k = 2$) associated with decomposition of PLA shows that the highest uncertainties correspond to $E(\alpha)$ at low conversions (below 0.20), mainly due to significant overlap with the preceding step. Noticeable discrepancies can be seen between the fitted isoconversional temperatures and deconvoluted $\alpha_2(T)$ curves for the second process at $\alpha_2 < 0.20$ as shown in Figs. 8 and 5 (see the top panel of each plot).

The problems with robustness of $E(\alpha)$ dependences, lack of clear physical meaning also combined with the kinetic compensation effect imply that the kinetic parameters themselves are not a suitable basis for judging the effect of blending on the kinetics of pyrolysis. Even though higher $E(\alpha)$ values are usually associated with higher thermal stability, there are at least two objections against such approach. First, higher $E(\alpha)$ does not necessarily imply lower degradation rate [31], mainly due to the aforementioned kinetic compensation effect. Second, comparison of two $E(\alpha)$ dependences is purely qualitative: this approach is even less meaningful in practical terms than a direct comparison of TG curves which provides differences in isoconversional temperatures without performing any kinetic analysis at all.

As mentioned above, a straightforward approach resides in a direct comparison of the isoconversional temperatures of pyrolysis of a given polymer in its neat and blended state:

$$\Delta T_\alpha = T_\alpha(\text{blend}) - T_\alpha(\text{neat}) \quad (6)$$

where both temperatures correspond to the same heating rate. A clear advantage of this approach is that calculating ΔT_α does not require kinetic analysis and the isoconversional temperatures if the comparison is done within the experimental range of heating rates. For neat and blended polymers both $T_\alpha(\text{neat})$ and $T_\alpha(\text{blend})$ can be determined from experimental and deconvoluted $\alpha_k(T)$ curves, respectively. On the other hand, the resulting ΔT_α values are hard to interpret in a quantitative manner as they are bound to the corresponding heating rate which may not be relevant in practical settings. An example of comparison based on Eq. (6) is shown in Fig. 9 on both components of PLA:PHBV 60:40 blend. In case of PLA, the negative values of ΔT_α imply destabilizing effect of blending with PHBV at given composition while the opposite is true ($\Delta T_\alpha > 0$) for blended and neat PHBV. The same observation in regard to ΔT_α also holds for PLA and PHBV in all blends under study.

The kinetic parameters plotted in Figs. 4–8 allow for calculation of isoconversional times at chosen fixed temperature. Once again assuming Arrhenius form of $k(T)$, separation of variables in Eq. (1) and subsequent integration between (t_{i-1}, t_i) and (α_{i-1}, α_i) yields:

$$\Delta t_i = t_i - t_{i-1} = \frac{1}{A_i \exp(-E_i/RT)} \quad (7)$$

where Δt_i is a time increment required to increase the conversion from

α_{i-1} to α_i at temperature T ; the parameters A_i and E_i are identical to those appearing in Eq. (2). Summing up the individual terms given by Eq. (7) allows to predict absolute isothermal times t_α or inversely the corresponding $\alpha(t)$ curve. The main advantage of isothermal isoconversional times, compared to kinetic parameters or isoconversional temperatures, resides in their intuitive interpretation as a direct measure of thermal stability. Moreover, instead of directly plotting the predicted t_α curves, the data can be normalized to neat polymers. Such relative measures tend to be more robust in general since potential biases (introduced both experimentally and by kinetic analysis) are at least partially canceled out [34]. The results can further be simplified by choosing a fixed conversion at which isoconversional times would be mutually compared; a sensible basis for comparison could be $t_{0.5}$, i.e., the reaction half-time. Ratios of degradation half-time for blended polymers to neat ones for PLA and PHBV are graphically depicted in Fig. 10 for all four investigated blends. In order to minimize potential bias introduced by extrapolation, the comparison was done in the temperature region where the degradation process was experimentally observed by TG. Noteworthy is the effect of temperature on the $t_{0.5}(\text{blend})/t_{0.5}(\text{neat})$ ratio, especially in case of PLA. Within the temperature range in which PLA degradation was observed (300–375 °C), the blended PLA is less stable than the neat polymer while extrapolation to lower temperatures implies stabilizing effect. However, this observation is not supported by direct comparison of isoconversional temperatures where $T_\alpha(\text{blended PLA}) < T_\alpha(\text{neat PLA})$ holds universally (see Fig. 9). Extrapolations based on kinetic parameters are very sensitive to any bias as already mentioned; thus, sound comparison can only be done within the temperature range of measurements. The effects of blending on polymer stability are routinely assessed by TG; frequently, the peak temperature (T_{\max}) evaluated from a DTG record [35] or decomposition onset [36, 37] is taken as a measure of stability. For a similar blend of PLA with PHB (poly(3-hydroxybutyrate), a gradual decline of $T_{\max}(\text{PLA})$ from 360 °C to 355 °C was observed for 95:5 and 80:20 blends, respectively [38]. These results are in line with $t_{0.5}(\text{blend})/t_{0.5}(\text{neat}) < 1$ for PLA:PHBV 60:40 and 40:60 blends above ca. 300 °C. Thermal stability data for PLA:PHBV system are relatively scarce. In [39] blends with 75:25 to 25:75 composition were studied and $T_{0.05}$, $T_{0.10}$ and $T_{0.50}$ were determined. All these temperatures increased with the proportion of PLA; however, the indicated percentages pertain to overall mass losses and thus do not specifically reflect decomposition of a single component within the blends. In cases where stepwise decomposition of polymer blend is observed, the temperature-based criteria evaluated at fixed overall conversion can potentially be misleading. For example, if the least stable component represents only 10% of a mixture, then $T_{0.50}$ is a very insensitive parameter with regard to thermal stability. PLA:PHBV blends in a wide range of ratios were studied by TG in [40]; all the blends were found to exhibit lower thermal stability than PLA, but higher thermal stability than PHBV. In this case, the effect of blending was assessed by comparing the DTG peak temperatures (T_{\max}). Such approach eliminates the aforementioned problems with insensitivity of parameters based on constant mass loss; however, the resulting shifts in T_{\max} are relatively hard to interpret in practical terms. On the other hand, the method presented here offers the advantage of assessing the effect of blending for each component independently of its amount in a given mixture on a well-defined quantitative basis such as isothermal isoconversional time.

Conclusions

Thermogravimetry, if not supported by supplementary data, cannot provide mechanistical insight into the processes taking place during thermal decomposition of polymers and their blends. However, isoconversional kinetic analysis coupled with mathematical deconvolution of measured $\alpha(T)$ envelope provides kinetic parameters which can be used for estimating the effect of blending on thermal stability of constituents. Compared to classical parameters such as degradation onset temperature or peak temperature determined from DTG curve, the

deconvolution analysis allows to determine stability of all components of a mixture regardless of their proportions. Here we also show that deconvolution analysis can be carried out directly on integral $\alpha(T)$ curves, thus bypassing the work with differential data da/dt . Subsequent isoconversional analysis of deconvoluted $\alpha(T)$ curves allows to calculate various parameters for assessing the potentially accelerating or inhibiting effect of blending on thermal degradation, for example, by means of decomposition half-time $t_{0.5}$. The results can be made more robust if relative criteria such as $t_{0.5}(\text{blend})/t_{0.5}(\text{neat polymer})$ are determined. Using this approach, detrimental effect of PHBV and PBAT on thermal stability of PLA above 300 °C was confirmed. On the other hand, stability of PHBV in both binary and ternary mixtures was improved compared to neat polymer.

Conflict of interest

The authors have no conflict of interest. The funding was acknowledged properly.

CRedit authorship contribution statement

Tibor Dubaj: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. **Stefano Vecchio Cipriotti:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **Jacopo Tirillo:** Writing – review & editing, Writing – original draft, Investigation. **Fabrizio Sarasini:** Writing – review & editing, Writing – original draft, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2024.179761](https://doi.org/10.1016/j.tca.2024.179761).

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