Pyrolysis and Combustion of Polymer Mixtures. Is the Heat Release Rate an Additive Quantity?

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ABSTRACT

The microscale combustion calorimetry study of polymer mixture pyrolysis is presented. Binary mixtures of HDPE with a number of massively produced polymers (LDPE, PET, PS, PC, PVC, PMMA), binary PMMA-PVC mixtures, and the ternary mixture composed of HDPE, PC, and PS are considered. The extent of interaction between the mixture components in pyrolysis is assessed by comparing the shapes of the measured temperature dependencies of the heat release rate in volatile oxidation with those for the curves obtained by the mass-weighted summation of the individual contributions of the pure polymers constituting the mixture. The strongest interaction is observed in HDPE-PET, HDPE-PS, HDPE-PS-PC, and in PMMA-PVC mixtures. A destabilizing interaction occurs in mixtures containing polyethylene and polystyrene, while the presence of polyvinylchloride has a stabilizing effect.

Except for PMMA-PVC mixtures, in all binary mixtures considered in this work the heat of volatile combustion and the char yield were found to be additive quantities and varied almost linearly with the variation of the component mass fractions. Dissimilar to that, the PMMA-PVC mixtures produced a higher amount of charring residue and a lower heat of combustion of volatiles compared to the component-based predictions assuming additivity.

KEYWORDS: Pyrolysis, microscale combustion calorimetry, polymer, flammability.

INTRODUCTION

Predicting the heat release rate generated by a multi-component fire load as well as in the design of equipment for incineration of municipal solid wastes justifies the need to consider pyrolysis of plastic mixtures. Although both the fire load and the plastic wastes normally consist of the mixture of combustible materials, a majority of the previous studies of material pyrolysis have been mainly focused on individual polymers. Additivity of the heat release rates in burning the volatiles generated by the individual mixture components is a common assumption used in the engineering simulations. This assumption implies that no chemical interaction occurs neither in the solid phase nor in the gas volatiles.

Current literature offers rather controversial conclusions on the importance of the interaction effects in polymer mixture pyrolysis. Indeed, the interaction between the components of the plastic mixture in the pyrolysis was found (or assumed) to be insignificant in some of the previous studies [1, 2], while a more thorough investigation may demonstrate such an interaction to occur in certain mixtures [3, 4]. Furthermore, a demonstration of the synergetic effect (even though it is claimed in a number of papers) is not always convincing since the experimental errors and repeatability are rarely assessed and reported.

The interaction mechanism in a polymer mixture is essentially attributed to the formation of active radicals in thermal decomposition of an individual polymer, radical migration across the component

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interfaces, and the subsequent reactions of such radicals with the polymers in the mixture and with other radicals [4]. In its turn, radical consumption by a particular mixture component proceeds along with the radical production, and the outcome of this competition determines whether the synergy has a stabilizing or destabilizing effect.

A possible reason of the controversial conclusions is that the pyrolysis and combustion of polymer mixtures might be affected not only by the polymer type, but also by the heating rate, proportion of the components in the mixture, and the degree of mixture homogeneity. Depending on how the components are combined, we will distinguish the blends and the mixtures. The polymer blends are prepared as an (almost) homogeneous sample, normally by melting and molding [4, 3]. Alternatively, a combination of materials that is heterogeneous on the macroscopic level shall be termed as a mixture.

In the two practical cases listed above, the polymers are never perfectly mixed, and the degree of heterogeneity may vary. Spatial separation of and the interface between the mixture components crucially affects the intensity of potential interaction. Quality of mixing is difficult to control, and it might be a possible reason for controversial conclusions on the interaction effects observed in the mixtures with the same polymers.

In this work, we consider the mg-scale samples and mix the powder components at the inter-particle level, i.e. more thoroughly than they are mixed in practice. Therefore, if additivity (absence of interaction) is confirmed here, it will work even more so in practice. At the same time, mechanical mixing is not as fine as that in polymer blends, and the interaction effects in the blends should be more pronounced than those in the relatively coarse mixtures.

One of the most convincing studies of the effect of the mixing quality on polymer interaction in pyrolysis is the study undertaken by Faravelli *et al.* in Ref. [5]. The experimental (TGA) and modeling results obtained in this study for PE-PS mixtures confirm that in poor mixing the decomposition of each polymer behaves independently. However, when the polymers are finely mixed, a co-pyrolysis and interaction occur. As such, the measurement data (either TGA or MCC) depend on mixing quality, and a possible interaction should be taken into account in data interpretation.

As shown, for example, in Ref. [7], the interaction between two components can be approximately quantified by a single adjustable parameter. However, the interaction complexity rapidly increases with the number of interacting components, and it motivates the authors of Refs. [6, 7, 8] to neglect any interaction between the molecular groups and to assume additivity of the group contributions in evaluating flammability properties of the polymers.

With the component interaction taken into account, the degradation behavior of either blends or mixtures cannot be theoretically predicted, both due to the incomplete knowledge of chemical degradation roots and the interactions at the interfaces controlled by morphology. This highlights the importance of getting new experimental evidence of the effects of mixing on polymer thermochemical stability and flammability. An example of *a posteriori* formulation of the interactive kinetic model of mixture pyrolysis is Ref. [10], in which both binary and ternary mixtures of PE, PP, and PET plastics are investigated by TGA. The interaction effects have been observed (although not systematically investigated) and then included in the kinetic model using the quadratic expressions with the cross-product terms.

Previous studies of the blend and mixture pyrolysis have mainly been undertaken by using thermogravimetric analysis (TGA) or, more rarely, using the isothermal methods. In this work, we apply an alternative experimental methodology, microscale combustion calorimetry (MCC) [11]. Rare examples of previous MCC studies considering a combination of distinct polymers are Refs. [7] and [9], where no visible interaction was observed in pyrolysis of the PC-ABS blend. At the same time, analysis of molecular group contribution to the flammability properties undertaken in Refs. [6, 7, 8] focuses on the individual polymers, not on mixtures or blends. To the current knowledge by the authors, this work as well as Ref. [12] represent the first systematic study of commingled plastics pyrolysis undertaken by MCC. Similar to the TGA, a mg-scale sample is exposed to the constant heating rate, while, dissimilar to the TGA, additional information on the heat of combustion of pyrolysis volatiles is also produced in MCC. Collection of the new MCC measurement data for the mixtures composed of most widely used plastics (LDPE, PET, PS, PC, PVC, PMMA) and evaluation of the interaction effects is the objective of this work. Based on these measurement data, the quantitative indicators of mixture thermochemical stability and flammability (heat of combustion of pyrolysis volatiles, char yield in anaerobic pyrolysis, heat release capacity, and characteristic pyrolysis temperature) are evaluated, and the additivity of these quantities is assessed.

MCC STUDY OF POLYMER MIXTURES

Methodology

Commercially available flammable polymers (Scientific Polymer Products Inc.) listed in Table 1 have been studied in this work. In the MCC apparatus, the mg-scale samples were exposed to the constant rate heating (from 0.25 to 1 K/s) in the nitrogen flow of 80 cc/min. Oxygen flow of 20 cc/min is added to the volatile-nitrogen flow to replicate the oxygen-to-nitrogen ratio characteristic of air. Pyrolysis volatiles are then completely oxidized in the combustion chamber at the temperature of 900 °C, and the oxygen consumption rate, $\dot{m}_{O_2}$, is measured. Based on the assumption of the constant heat of combustion per unit mass of oxygen consumed (taken equal to Δq_{O_2} = 13.1 kJ/g O_2), the specific heat release rate, $\dot{q}$, is recorded as a function of time, t, and of the sample temperature, $T = T_0 + \beta t$, where T_0 is the initial temperature, and β is the heating rate.

Table 1. Material properties provided by the manufacturer

Designation	Name	Molecular weight, kg/mol	Appearance	Density, kg/m^3	Melting/ softening point, °C
LDPE	Low density polyethylene	50	Pellets	920	107-135
HDPE	High density polyethylene	125	Pellets	950	121
PET	Poly(ethylene terephthalate)	N/A	Pellets	1385	252
PS1.2	Polystyrene	1.2	Granular	1060	74
PC	Polycarbonate	45	Pellets	1200	151
PMMA	Poly(methyl methacrylate)	35	Beads	1200	N/A
PVC	Poly(vinyl chloride)	350	Powder	1400	285

The individual polymers in Table 1 have already been studied by MCC in Refs. [13, 14, 15], and the measurement data for the heating rates of 0.25, 0.5, 1, and 1.5 K/s are summarized in Ref. [13], where the kinetic models of the polymer decomposition are also provided as well as the comparisons with the published data. Two types of polyethylene (HDPE and LDPE) are considered here. As shown in Ref. [13], thermal decomposition of HDPE and LDPE proceeds quite similarly, and its quantitative characteristics are also similar. Note, that the low molecular mass polystyrene PS1.2 (1.2 kg/mol) is rather different from the high molecular mass polystyrenes, considered, for example, in Refs. [14, 15]. Thermal decomposition of PS1.2 produces much lower peak heat release rate, wider pyrolysis temperature range, and higher peak temperature value [13]. As a result, PS1.2 has a lower heat release capacity.

The pellets and beads were crunched and the small pieces of the polymers were manually mixed in the sample cup as uniformly as possible. Each small particle had the mass of 0.3-0.4 mg and the size of about 0.6 mm. Additional measurements with very large particles (5 mg, 2-3 mm) produced very similar results. The weak effect of the initial particle size is due to melting and mixing the components before the pyrolysis starts (see the melting points in Table 1). To repeat identical runs, sufficiently large amounts of the mixtures were prepared. In binary mixtures (except PMMA-PVC), the following initial component mass fractions are considered: 20, 40, 50, 60, and 80%. In ternary mixtures, equal masses of all three components were taken.

To ensure the prescribed proportions of the mixture components in a sample, the samples with the sufficiently large mass (normally about $m_0 \approx 10$ mg) were used in the MCC measurements for the mixtures. It is worthy of note that, for the given initial sample mass, the maximum heating rate exists (about 0.5 K/s for the mixtures with prevalence of PE) beyond which the oxygen flow becomes insufficient to completely oxidize all the volatiles.

Alternatively, several single runs were performed with the PMMA-PVC mixture having various component proportions, which were not exactly prescribed in advance. This enabled using of a smaller sample mass and a higher heating rate, albeit at the expense of impossibility to repeat identical tests with the same mixture composition.

The measurement procedure for each heating rate follows that described in ASTM D7309-07a [16] with the exception of multiple heating rates. The detailed description of the measurement procedure and data processing is provided in Refs. [13, 14]. Each measurement was performed 2–5 times to ensure repeatability of heat release rate-temperature curves and to assess the average value and standard deviation. The measured dependencies of heat release rate (per unit sample mass) on sample temperature, $\dot{q}(T)$, were pre-processed by applying the following operations: (i) interpolation to the sample temperature values aliquot 1°C; (ii) subtracting the baseline (straight line between the sample temperature before the onset and after completion of the process); (iii) averaging over identical runs and evaluating standard deviation. Pre-processing of the MCC measurement data included evaluating transient (conversion, reaction rate), integral (total heat release, effective heat release capacity) and other (peak temperature, 10%, 50%, and 90% conversion temperatures) characteristics of material decomposition.

If volatile oxidation proceeds in an excess of oxygen (this is controlled by limiting the sample mass and the heating rate), then the heat release rate per unit sample mass is

$$\dot{q} = -\Delta q_{O_2} \frac{\dot{m}_{O_2}}{m_0} = -\Delta q_{O_2} \sigma_{O_2} \frac{\dot{m}}{m_0} = -\Delta q \frac{\dot{m}}{m_0}, \quad (1)$$

where m_0 is the initial sample mass, σ_{O_2} is the stoichiometric oxygen to fuel mass ratio, $\dot{m}$ is the sample mass loss rate, and $\Delta q_{O_2} \sigma_{O_2} = \Delta q$ is the heat of combustion per unit mass of volatiles. In the MCC apparatus, oxygen consumption and sample temperature are synchronized by allowing for the residence time of the gas reactants in the combustor. Due to complete volatile oxidation and synchronization of oxygen consumption rate with the sample temperature, the dependence $\dot{q}(T)$ measured in MCC characterizes the rate of sample decomposition, similar to the mass loss rate $\dot{m}(T)$ measured in TGA.

Let the relation (1) holds for the i-th mixture component: $\dot{q}_i = -\Delta q_i \left(\dot{m}_i / m_{0,i}\right)$. In case of independent pyrolysis of and oxidation of volatiles produced by each component (no interaction neither in condensed nor in gas phase), the additivity principle holds for the multicomponent mixture:

$$\dot{q} = \frac{1}{m_0}\sum_i \dot{m}_i \Delta q_i = \frac{1}{m_0}\sum_i m_{0,i}\dot{q}_i = \sum_i y_{0,i}\dot{q}_i \ , \tag{2}$$

where $y_{0,i} = m_{0,i}/m_0$ is the initial mass fraction of the i-th component, and $m_0 = \sum_i m_{0,i}$ is the initial mass of the mixture. Thus, the heat release rate produced by the mixture of independently reacting (non-interacting) components can be evaluated as the mass-weighted sum of the individual component contributions. Deviation from the additivity principle is an indication of the component interaction in pyrolysis. An interaction in the gas phase is also possible but is not expected to be important due to complete volatile oxidation.

In processing the MCC measurement data, we use the heat release-based global conversion,

$$\alpha = \frac{1}{\overline{\Delta q'}}\int_{T_0}^{T} \dot{q}(T)\,dT \ , \tag{3}$$

where T is the current sample temperature, $T_{\max}$ = 800 °C is the final temperature at which pyrolysis is complete. By definition, $0 \le \alpha \le 1$.

The heat of combustion per unit sample mass, $\overline{\Delta q'}$, is evaluated by integrating the heat release rate over the entire process:

$$\overline{\Delta q'} = \int_0^{t_{\max}} \dot{q}dt = \frac{1}{\beta}\int_{T_0}^{T_{\max}} \dot{q}dT \ . \tag{4}$$

Note, that $\overline{\Delta q'} = \left(1-\nu_r\right)\overline{\Delta q}$, where $\nu_r = m_\infty/m_0$ is the solid residual mass fraction. If additivity holds, then according to Eq. (2) the heat of combustion is also an additive quantity:

$$\overline{\Delta q'} = \sum_i y_{0,i}\overline{\Delta q'_i} \ . \tag{5}$$

The integral in Eq. (4) can be represented as a product $\int_{T_0}^{T_{\max}} \dot{q}dT = \langle \dot{q} \rangle \Delta T_{pyr}$, where ΔT_{pyr} is the pyrolysis temperature interval, and $\langle \dot{q} \rangle$ is the characteristic heat release rate in this interval. Substituting this product in Eq. (4) yields:

$$\overline{\Delta q'}/\Delta T_{pyr} = \langle \dot{q} \rangle / \beta \ . \tag{6}$$

The ratio on the left-hand side of Eq. (6) is called the heat release capacity and is used as an indicator of the material thermochemical stability and flammability [11, 16]: $\eta = \overline{\Delta q'}/\Delta T_{pyr}$.

The heat release capacity is often evaluated as $\eta_p = \dot{q}_p/\beta$, where $\dot{q}_p$ is the peak heat release rate [11]. This definition (which is formally derived for the special case of a single-step reaction) is not suitable in case of multi-peak dependencies $\dot{q}(T)$, particularly when a lower (and wider) peak contains more heat release. Following Refs. [13, 14], we, therefore, define the effective heat release capacity as $\eta_{10-90\%} = \overline{\Delta q'}/\Delta T_{10-90\%}$, where $\Delta T_{10-90\%}$ is the temperature interval between 10% and 90% conversion.

Thermochemical stability of a material is also quantified by the characteristic temperature at which pyrolysis reaction attains its maximum rate (the peak temperature, T_p). In addition to the peak temperature, we use in this work the temperature corresponding to 50% conversion (the median temperature, $T_{50\%}$), which is less sensitive to the experimental errors and can be used in multi-reaction scenarios represented by multiple peaks. For the polymers decomposing in a single step (for example PE, PP, PS980 etc.), the dependencies $\dot{q}(T)$ are nearly symmetric, and the peak and median temperatures are close to each other (the difference is few degrees only).

Thus, three quantities, $\overline{\Delta q'}$, $\eta_{10-90\%}$, and $T_{50\%}$, along with the shape of the $\dot{q}(T)$ curve, will be used in this work to characterize material thermochemical stability and flammability. A material is regarded as more stable and less flammable in case of lower heat of combustion and heat release capacity ($\overline{\Delta q'}$ and $\eta_{10-90\%}$) and higher pyrolysis temperatures ($T_{50\%}$ and T_p). If components in the mixture react independently, then the heat of combustion, $\overline{\Delta q'}$, (as well as the solid residual mass fraction, ν_r) is the additive quantity, while the heat release capacity and the median temperature, $\eta_{10-90\%}$, and $T_{50\%}$, are not. Indeed, according to the definition

$$\eta = \frac{\overline{\Delta q'}}{\Delta T_{pyr}} = \frac{\sum_i y_{0,i}\overline{\Delta q'_i}}{\Delta T_{pyr}} = \sum_i \frac{\Delta T_{pyr,i}}{\Delta T_{pyr}} y_{0,i}\eta_i \ , \tag{7}$$

where $\Delta T_{pyr,i}$ and $\eta_i = \overline{\Delta q'_i}/\Delta T_{pyr,i}$ are the pyrolysis temperature interval and the heat release capacity of the i-th component. Since $\Delta T_{pyr} > \Delta T_{pyr,i}$ (the pyrolysis temperature interval of a mixture is wider than that for an either of the components), the heat release capacity of the mixture (defined by Eq. (7)) is lower than the weighted sum of the heat release capacities of the components: $\eta < \sum_i y_{0,i}\eta_i$. Note, that this conclusion is dissimilar to the additivity assumption used for the heat release capacity in Ref. [7].

For a binary mixture with $y_{0,1} + y_{0,2} = 1$, the simplest approximation of a non-additive quantity is (see Eq. (4) in Ref. [7]):

$$\psi = y_{0,1}\psi_1 + \left(1 - y_{0,1}\right)\psi_2 + \lambda\left(y_{0,1}\left(1 - y_{0,1}\right)\right)^{1/2}\left(\psi_1 + \psi_2\right), \tag{8}$$

where the first two terms represent the additive part, and the last term approximates the deviation from additivity, which is quantified by parameter λ. This parameter can be regarded as the degree of interaction only if Eq. (8) is applied to $\overline{\Delta q'}$ or ν_r but not to $\eta_{10-90\%}$ or $T_{50\%}$. In the latter case, parameter λ is non-zero even in case of independently reacting components.

RESULTS AND DISCUSSION

The individual polymers were investigated first, and the results are summarized in Table 2. As established in Ref. [12], thermal decomposition of most of the polymers presented in Table 2 is of an autocatalytic type.

The binary compositions considered in this work include the mixtures of HDPE with PC, PS1.2, PET, PVC as well as the mixture of PMMA with PVC. As expected and in agreement with Ref. [17], no interaction effects were observed in HDPE-LDPE mixtures. The absence of a visible interaction between HDPE and LDPE supports the assumption that the presence of other polymers should have a similar effect in the mixture with either HDPE or LDPE.

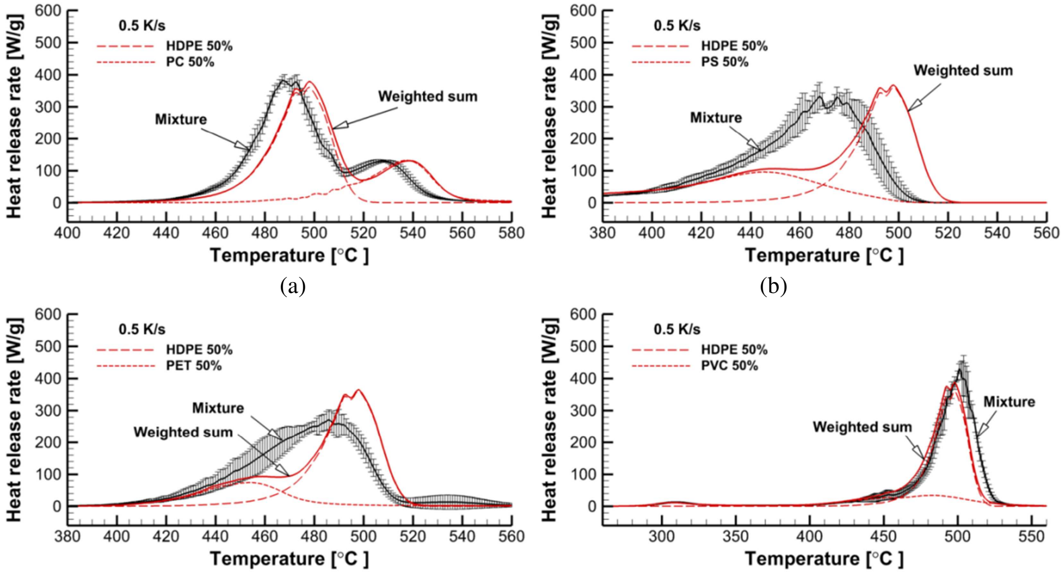
Table 2. MCC measurement data for pure polymers[a]. Pyrolysis in a nitrogen flow at 0.5 K/s

Polymer	$\overline{\Delta q'}$, MJ/kg	ν_r, –	$\eta_{10-90\%}$, kJ/(kg K)	$T_{50\%}$, °C	E_a, kJ/mol[b]
			Non-charring		
HDPE	41.3±0.1	0	1245	494	229±7
LDPE	41.5±0.6	0	1012	486	227±7
PS1.2	33.9±0.3	0	237	429	167±10
PMMA	24.9±0.2	0	433	393	212±18
			Charring		
PC	20.0±0.2	0.234±0.005	417	533	233±13
PET	14.3±0.6	0.09±0.03	168	453	217±23
PVC	13.8±0.2	0.057±0.001	73.9	464	268±50c

a Average values and standard deviations obtained in several tests

b Conversion-averaged apparent activation energy evaluated by the iso-conversional method of Friedman (see Ref. [12] for details) using three heating rates 0.25, 0.5, and 1.0 K/s. Standard deviation is also given

c Strong variation with conversion in the multi-step pyrolysis



(a) (b)

(c) (d)

Fig. 1. MCC measurements $\dot{q}(T)$ for the binary mixtures (solid lines with vertical bars), contributions of the individual polymers $y_{0,i}\dot{q}_i(T)$ (dashed lines) and the weighted sum $\sum_i y_{0,i}\dot{q}_i$ (solid line, no bars) at the heating rates of 0.5 K/s. Vertical bars show the standard deviation in multiple measurements. a) – HDPE-PC; b) – HDPE-PS1.2; c) – HDPE-PET; d) – HDPE-PVC

Thermal decomposition of binary mixtures with equal initial mass fractions of the components is further represented by the MCC measurement data in Fig. 1 (various component proportions have also been investigated). For the HDPE-PC binary mixture (see Fig. 1, a), the maximum deviation from the mass-weighted average is observed at $y_{0,i}$ = 0.5. In the mixture measurement, the HDPE peak is shifted to lower temperatures compared to that in the mass-weighted average at any mixture composition, which implies destabilization of HDPE in presence of a sufficiently large amount of PC. The PC peak exhibits the same trend at $y_{0,i}$ = 0.5. When either component dominates, the heat release rate recorded for the mixture is quite close to that predicted by the mass-weighted average. For the HDPE-PS1.2 binary mixture (Fig. 1, b), a very strong deviation from the mass-weighted average is observed at any mixture composition, and the HDPE peak of the mixture occurs at remarkably lower temperatures compared to those in the mass-weighted average. This implies that decomposition of HDPE is strongly facilitated by the presence of PS regardless of its amount. This observation is in agreement with the results of Ref. [17]. A similarly strong destabilizing interaction effects are also observed in Fig. 1, c, for the HDPE-PET binary mixtures.

The interaction effects in the joint decomposition of HDPE and PVC are not crucial and hardly exceed the experimental uncertainty (see Fig. 1, d), although HDPE decomposition is slightly delayed in presence of PVC. In spite of the weak interaction in HDPE-PVC mixture, the presence of PVC causes a much more pronounced delay of PMMA decomposition. This is clearly visible in Fig. 2, which shows that the reaction peak is shifted significantly towards higher temperatures. Thus, the stabilizing effect of PVC, albeit of different strength, can be concluded for the binary mixtures with PE and PMMA.

Such a stabilizing effect, demonstrated here by MCC, has already been observed in earlier non-isothermal (TGA) and isothermal studies (see Ref. [18] and the review in Ref. [4]). In these studies, it has been concluded that combination of the radicals produces by both PMMA and PVC may produce some cross-linked structures, which are more difficult to destroy. A possible mechanism of the stabilizing effect introduced by PVC is also discussed in Ref. [17].

Consistent with the above observations, decomposition of the ternary mixture considered in Fig. 3 is strongly affected and destabilized by the presence of polystyrene.

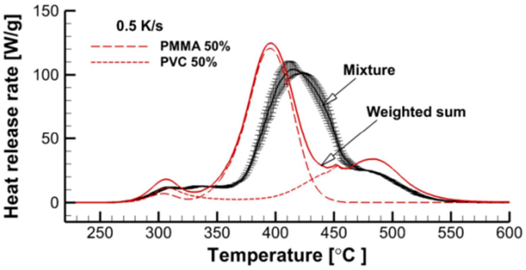


Fig. 2. MCC measurements $\dot{q}(T)$ for the 50%PMMA+50%PVC binary mixture (see the caption in Fig. 1).

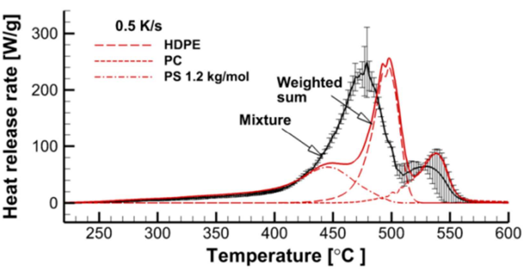


Fig. 3. MCC measurements for the HDPE-PS1.2-PC ternary mixture, $y_{0,i}$ = 1/3 (see the caption in Fig. 1).

To formally quantify the degree of deviation from the additivity rule, we evaluate the following non-additivity indicator:

$$\zeta = \frac{1}{\langle \Delta q \rangle} \int_{T_0}^{T_{\max}} \left| \dot{q}_{add} - \dot{q}_{mixt} \right| dT , \qquad (9)$$

where $\dot{q}_{add}$ is the heat release rate evaluated as the weighted sum of the measured component contributions, $\dot{q}_{mixt}$ is the heat release rate measured in the mixture, and $\langle \Delta q \rangle$ = $\left(\int_{T_0}^{T_{\max}} (\dot{q}_{add} + \dot{q}_{mixt}) dT \right) / 2$. The value of ζ was found to be weakly sensitive to the heating rate.

The above analysis and evaluation of the non-additivity indicator, ζ, indicates a various degree of component interaction in mixture decomposition:

1. Strong interaction in HDPE-PS1.2 (ζ = 0.69), HDPE-PS1.2-PC (ζ = 0.51), HDPE-PET (ζ = 0.5) and PMMA-PVC (ζ = 0.52) mixtures. The shape of the MCC curves is very different, and the peak temperatures differ greatly compared to those predicted by the weighted sum of the individual component contributions. Decomposition of the most flammable component (HDPE or PMMA) is destabilized in HDPE-PS1.2, HDPE-PS1.2-PC, and HDPE-PET mixtures, and, in contrast, stabilized in the PMMA-PVC mixture. Destabilization of the HDPE-PS1.2 mixture observed in this work is qualitatively consistent with the conclusions of Ref. [5], where the increased reactivity of PE-PS mixture is explained by the attack of radicals coming from the PS.
2. Moderate interaction is observed in HDPE-PC (ζ = 0.42), HDPE-PP (ζ = 0.3) mixtures. The shape of the MCC curves is qualitatively similar to that predicted by the weighted sum of the individual component contributions, albeit some shift of the peaks to lower temperature occurs.
3. The interaction is weak and is of the order of the experimental uncertainty in HDPE-PVC (ζ = 0.27) and PC-PS1.2 (ζ = 0.26) mixtures. No interaction in HDPE-LDPE mixtures (ζ = 0.08).

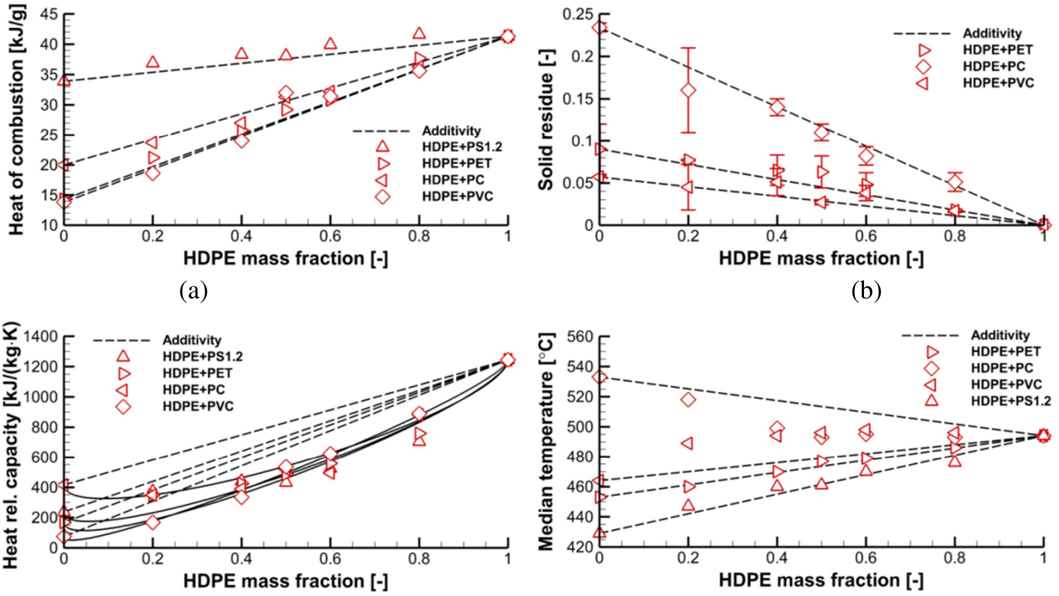
Note, that the statistical variation of multiple identical measurements (repeatability error) causes the value of ζ to be below 0.1. Weak, moderate, and strong interactions correspond to ζ in the ranges 0.1–0.3, 0.3–0.4, and 0.5–0.7, respectively. The interaction effect can be either stabilizing or destabilizing, and it can also be quantified by comparing the median temperatures evaluated for both $\dot{q}_{add}$ and $\dot{q}_{mixt}$. This comparison is presented in Table 3.

As shown in Fig. 4, a, the integral heat of combustion (which is evaluated as the total oxygen consumption in the combustor multiplied by 13.1 MJ/kg O_2, see Eqs. (4) and (1)) remains to be the additive quantity regardless of the extent of the interaction during the process. Indeed, the MCC measurements for the mixtures presented in Fig. 4, a, correspond to the mass-weighted sum of the component HOCs, to within the experimental uncertainty. The same conclusion applies to the char yield demonstrated in Fig. 4, b. As discussed above, the heat release capacity is the non-additive quantity, and the measurement data for the mixtures are well below the mass-weighted values (Fig. 4, c), as expected. The measurement data can be approximated by Eq. (8), and the best fit is achieved with λ = 0.25 for HDPE-PVC and λ = 0.35 for the binary mixtures of HDPE with PET, PS1.2, and PC. Data shown in Fig. 4, d, indicate that the deviation from (or agreement with) the mass-weighted values of the median temperature is different in the considered mixtures. The interaction parameter corresponding to the best fit with Eq. (8) is λ = -0.03 for HDPE-PC, λ = 0.035 for HDPE-PVC, and λ = 0 for HPDE-PS1.2 and HDPE-PET.

Alternatively, for the PMMA-PVC mixture, it can be concluded that the solid residual mass fraction in mixture pyrolysis is observably greater than the mass-weighted value, and this deviation exceeds the experimental uncertainty (see Fig. 5, b). This observation correlates with the measured HOCs in the mixture being lower than the mass-weighted values (see Fig. 5, a). Therefore, the chemical interaction between PMMA and PVC, which is quite pronounced in this mixture (see also Fig. 2), also facilitates excessive char formation and suppresses volatile production.

Table 3. Overview of the interaction effects

Mixture	Interaction	ζ	$T_{50\%}$, °C, mixture	$T_{50\%}$, °C, weighted sum	$\Delta T_{50\%}$, K
			0.5 K/s		
Strong interaction					
HDPE-PS1.2	Destabilizing	0.69	461	477	–16
HDPE-PS1.2-PC	Destabilizing	0.51	473	488	–15
HDPE-PET	Destabilizing	0.5	477	490	–13
PMMA-PVC	Stabilizing	0.52	419	403	16
Moderate interaction					
HDPE-PC	Destabilizing	0.42	493	500	–7
HDPE-PP	Destabilizing	0.3	477	482	–5
Weak interaction					
HDPE-PVC	Stabilizing	0.27	496	491	5
PC-PS1.2	Stabilizing	0.26	464	454	10
HDPE-LDPE	Non	0.08	489	489	0



(a) (b)

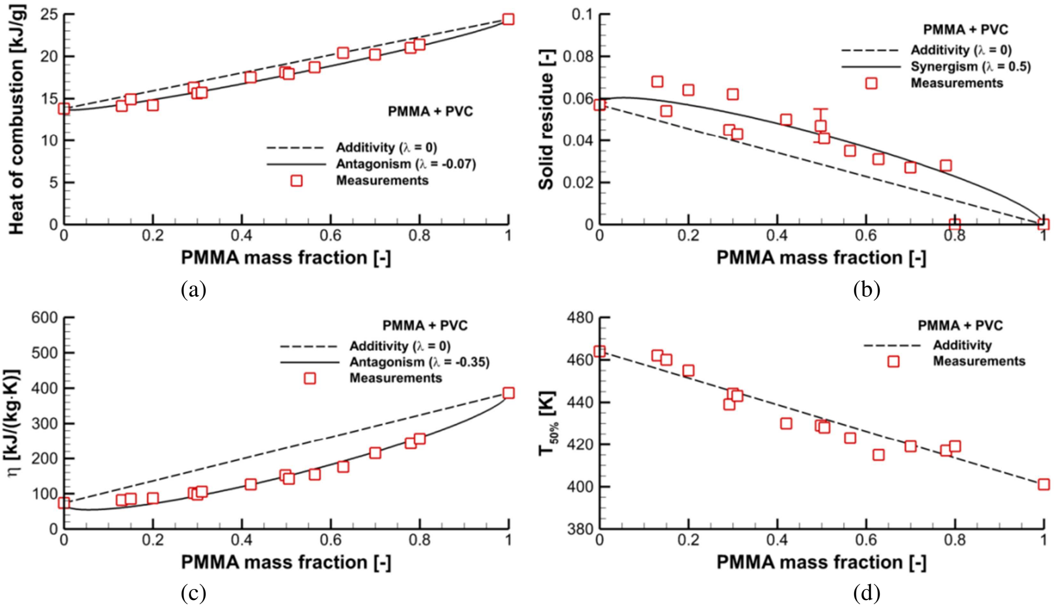
(c) (d)

Fig. 4. The effect of HDPE mass fraction on flammability properties of the binary mixtures: a) – heat of combustion; b) – solid residue mass fraction; c) – heat release capacity (solid lines correspond to Eq. (8) with λ = -0.35 for all the mixtures except HDPE+PVC for which λ = -0.25); d) – median temperature.

CONCLUSIONS

Binary mixtures of HDPE with a number of most widely produced polymers (LDPE, PET, PS, PC, PVC, PMMA), binary mixture of PMMA with PVC, and the ternary mixture composed of HDPE, PC, and PS have been studied by means of microscale combustion calorimetry.

These mixtures are shown to exhibit a various degree of component interaction in mixture pyrolysis. The interaction degree was assessed by comparing the shapes of the measured temperature dependencies of the heat release rate in volatile oxidation with those for the curves obtained by the mass-weighted summation of the individual contributions of the pure polymers constituting the mixture.



(a) (b)

(c) (d)

Fig. 5. The effect of PMMA-PVC mixture composition on flammability properties: a) – heat of combustion; b) – solid residue mass fraction; c) – heat release capacity; d) – median temperature.

The strongest interaction was observed in HDPE-PET, HDPE-PS1.2, HDPE-PS1.2-PC and in PMMA-PVC mixtures. Decomposition of the most flammable component (HDPE or PMMA) is destabilized in HDPE-PS1.2, HDPE-PS1.2-PC, and HDPE-PET mixtures, and, in contrast, stabilized in the PMMA-PVC mixture as determined by the shift of the reaction peaks to the lower and higher temperatures, respectively. The interaction observed in HDPE-PC mixture is moderate albeit it, nevertheless, exceeds the experimental uncertainty. In this interaction HDPE-PC mixture is destabilized, while the HDPE-PVC mixture is weakly stabilized. No interaction effects exceeding the experimental uncertainty were observed in HDPE-LDPE and PC-PS1.2 mixtures. It can, therefore, be concluded that the destabilizing interaction occurs between PE and PS, while the presence of PVC has the stabilizing effect.

Except for PMMA-PVC mixtures, in all binary mixtures considered in this work the heat of volatile combustion and the char yield were found to be additive quantities and varied almost linearly with the variation of the component mass fractions. Dissimilar to that, the PMMA-PVC mixtures produced a higher amount of charring residue and a lower heat of combustion of volatiles compared to the component-based predictions assuming additivity.

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