

# Recommendations on the scientific approach to polymer flame retardancy: Part 2—Concepts

Journal of Fire Sciences

2017, Vol. 35(1) 3–20

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DOI: 10.1177/0734904116675370

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Date received: 2 September 2016; accepted: 19 September 2016

## Abstract

The usage of concepts in scientific communication is critical to our ability to inform the reader about work that has been performed. The significance and thus the quality of scientific discussion rely on the precise use of concepts. In this second part of a two-part paper, concerning the scientific basis of polymer fire retardancy, the proper use of concepts is addressed. Distinct concepts in flame retardancy are discussed, such as fire residue, the correlation of fire performance with char yield according to van Krevelen, catalysis, and wicking. Synergy is discussed in detail, as well as approaches to quantify it, due to its importance for flame retardant polymers. The preceding first paper (part 1) discussed the proper use of scientific terms, thermal analysis, and fire testing. Thus, together these two papers support the community by offering recommendations and addressing some of the most relevant points. They encourage to review scientific practice in the field of flame retardancy of polymers.

## Keywords

Char, synergism, flame retardancy, flammability, fire growth indices, synergy index

## Introduction

Part 1 of this two-part paper gave recommendations on terms and test method procedures to properly evaluate and communicate the fire behavior of polymer materials.<sup>1</sup> These

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guidelines are essential to this part 2, concerning the scientific concepts of polymer fire retardancy, which has become of paramount importance. Indeed, the early technological trial and error approach led to commercial development of successful first generation fire retardants, which, however, proved unacceptable in the long term. This has advanced the typical evolution of industrial development, merging technological know-how with the scientific know-why approach to guide new generations of fire retardant.

Evolution from technology to science in flame retardancy has taken place in the last three decades without any deep contemplation about what flame retardancy concepts require. Thus, today we frequently use such concepts quite freely, neglecting fundamental assumptions and limitations, or in a speculative way without reference to experimental data. At the end of the day, there is a certain lack of quality due to the improper use of such aspects. This article addresses the idea of concepts in flame retardancy of polymers with considerable attention devoted to the concept of synergy. Several important concepts in flame retardancy of polymers are discussed: **fire residue/char**, the correlation of fire performance with char yield according to Van Krevelen, wicking, catalysis, indices covering fire growth, synergism, and the quantification of synergism. Paying attention to details, such as the basic assumptions and limitations in applicability, is proposed to strengthen the significance of any scientific interpretation and conclusions.

Our approach is to address some of the most important points in two-part paper, namely, terms and methods in part 1 and scientific concepts in part 2. Together, the two parts may serve as a tool to strengthen good scientific practice in the field of flame retardancy of polymers.

## **Proper scientific discussion: using concepts according to their precise definition**

### *Fire residue*

The two most important characteristics of a material controlling its fire properties are the amount of fuel released and the effective heat of combustion of this fuel. In practice, very often these characteristics are assessed when discussing the fire residue as the obvious counterpart. Decreasing the amount of fuel released is one of the most successful approaches to flame retardant polymeric materials. Replacing fuel by inert filler as well as increasing carbonaceous charring decreases the released fuel and increases the residue. Thus, in thermal analysis, as well as fire testing, a detailed description of the residue using precise terms provides an essential description of the burning behavior and flame retardancy modes of action. **The term “char” actually designates a carbonaceous material<sup>2</sup> that remains after an organic material has decomposed, while the term residue describes everything that remains at a distinct time or temperature or at the termination of a thermal analysis or fire test, respectively.** One also finds the term “char residue” to describe residue as used above, but just “char” or “carbonaceous residue” is a much better term when the material remaining is carbonaceous. **Inorganic residue may be described as “inorganic residue” or using the proper term “ash”;**<sup>2</sup> if what is left contains both carbonaceous and inorganic residue, or char and ash, respectively, this should be called residue. Furthermore, if the polymer material is loaded with inert, thermally stable inorganic filler, the weight loss compared to that of the virgin polymer at the same temperatures must not be misinterpreted as polymer stabilization. The term “increasing thermal stability” must not be used as a synonym for “increasing residue.”

Indeed, the weight loss curve to be compared with that of the polymer is the calculated weight loss curve on the basis of the real polymer content of the filled material. If the fillers partially decompose upon heating, this should be taken into account in the calculated curve.

### Van Krevelen

One of the most popular concepts to describe the fire behavior of polymeric materials is the relation between char yield ( $\mu$ ) and fire performance. This concept is based on the fact that whatever carbon from the polymer trapped in the thermally stable char will be prevented from feeding the flame, thus reducing the flammability of the polymer. This concept was successfully established in the constitutive work by Van Krevelen<sup>3,4</sup> in the 1970s, proposing the relation between oxygen index (OI) and char yield ( $\mu$ ) in wt% measured in **thermogravimetry under nitrogen** as follows

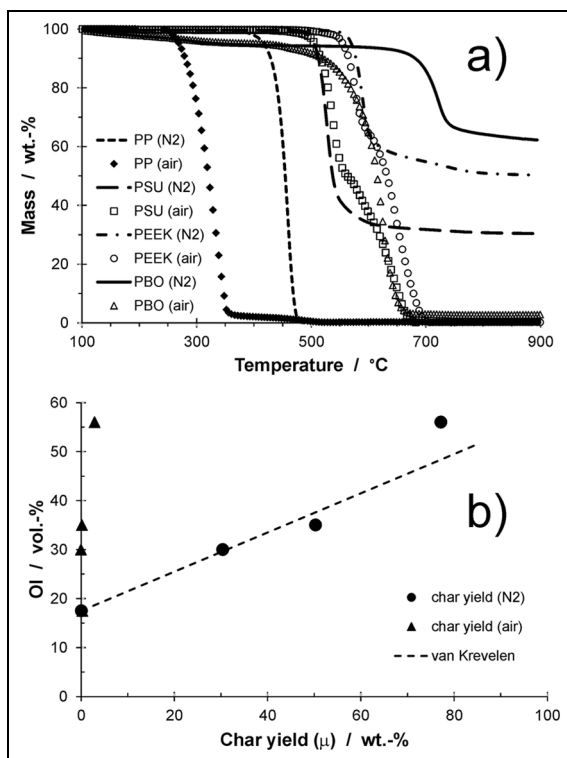
$$\text{OI} = 17.5 + 0.4\mu \quad (1)$$

The reasons why anaerobic pyrolysis rather than thermo-oxidation controls the OI of polymeric materials were discussed in detail in the first part of this guide.<sup>1</sup> It is essential here to use thermogravimetry to evaluate the char yield under anaerobic pyrolysis conditions, in which the polymer decomposes in flaming combustion. Actually, Van Krevelen proposed a general scheme for anaerobic pyrolysis, which represents what occurs in flaming polymer combustion. A pyrolysis step between 350°C and 550°C occurs with production of volatiles and possibly of a residue called “primary char.” A second pyrolysis step could take place between 550°C and 1000°C, when carbon–hydrogen bonds become the weakest bonds; this may be hardly noticeable in thermogravimetry, but it is of paramount importance in terms of the thermal stability of the then highly unsaturated, aromatized structure of residue at higher temperatures. However, carbon atoms are trapped in the residue remaining at 550°C because the carbon–carbon bond dissociation energy is increased by crosslinking, cyclization, or unsaturation occurring during polymer pyrolysis. Exposure of this primary char to oxidative pyrolysis will instead lead to its complete oxidation to volatiles below 600°C, unless heteroatoms like nitrogen or phosphorus are present in the polymer compound to stabilize the residue.

In Figure 1, this basis of the OI–char relation is illustrated by plotting the thermogravimetry results for four distinct materials under air and nitrogen, respectively, and their OI versus the different char yields. Only the char yield obtained under nitrogen is covered by the concept, not the char in air. Strictly speaking, the relation was established for char, not for residue, so the impact of an inert filler, such as decreasing the OI by adding 15–35 wt% glass fibers in technical polyesters and polyamides, is not covered by the equation. What is more, not only did Van Krevelen<sup>4</sup> use char and thermogravimetry under nitrogen, but he also wrote, “This expression is valid for halogen-free polymers only,” meaning that it does not hold for materials that show flame inhibition. Nevertheless, for good reason, the work of Van Krevelen is one of the most cited papers in the field, but unfortunately also often misused for char yields determined by thermal analysis under air or for materials that show considerable deviations from the concept due to inert fillers or flame inhibition.

### Catalytic

One rather frequently encounters the term “catalytic” or “catalyst” in flame retardant papers, in particular, whenever the char yield is increased. Indeed, interactions influencing



**Figure 1.** (a) Thermogravimetry results (mass in wt% versus temperature) under nitrogen (N2) and air for poly(propylene) (PP), poly(sulfone) (PSU), poly(ether ether ketone) (PEEK), and poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) and (b) corresponding OI versus char yield, indicating that the Van Krevelen relation is based on the char yields under nitrogen but not the char yield under air.

decomposition are reported for all kinds of substances containing phosphorus, for metal oxides, zeolites, radical generators, and so on.<sup>5–12</sup> Nevertheless, the common definition of a catalyst is that it is a substance that may participate in a chemical reaction but remains unchanged at the end of the reaction. Thus, not all the reactions increasing char are catalytic, since the actual pyrolysis often changes not only the organic materials but also the so-called catalyst. Although in some systems catalytic reactions occur and play a significant role in flame retardancy, catalytic reactions must be considered speculative, unless the corresponding results or plausible models of the decomposition pathway are available.

### Indices

In various fire tests, the fire behavior of the specimen is monitored over time. Only the measure as function of time, such as the heat release rate (HRR) curve over time, contains the full information. Nevertheless, not only for regulatory purposes but also for comprehensive comparison different indices have been proposed to concentrate the relevant information into a single number, for instance, on fire growth and flame spread, respectively. Some of

the most popular indices are as follows: fire growth rate (FIGRA = maximum value of the ratio  $\text{HRR}/\text{elapsed test time}$ ),<sup>13,14</sup> maximum average rate of heat emission (MARHE),<sup>15</sup> peak heat release rate (PHRR)/ $t(\text{PHRR})$ , fire performance index ( $\text{FPI} = \text{time to ignition } (t_{\text{ig}})/\text{PHRR}$ ),<sup>16,17</sup>  $\text{PHRR}/t_{\text{ig}}$ ,<sup>18,19</sup> parameter  $b$  ( $b = 0.01 \text{ HRR}_{\text{average}} - (1 - t_{\text{ig}}/\text{burning time } (t_{\text{burning}}))$ ),<sup>20</sup> and  $\text{PHRR}^2/t_{\text{ig}}$ .<sup>21,22</sup> Such indices reduce the information crucially, be they empirically deduced from a comparison between different fire tests, such as comparing a bench-scale test with an intermediate-scale test or with a full-scale fire test, or deduced from the analytical description of fire growth or flame spread. The fire development is oversimplified through concentration on the plausible main features or the need to make approximations for an analytical description. The physical meaning is limited with regard to fire behavior and can even be misleading. Nevertheless, such indices are shown to be superior to PHRR for correlation with other fire scenarios.

Keeping in mind that these indices are based on specific comparisons or model descriptions, and that all of them have their individual strengths and limitations, they must not be confused. Unfortunately, quite a lot of papers use the  $\text{PHRR}/t(\text{PHRR})$  observed in cone calorimeter as FIGRA, although strictly speaking this is incorrect. FIGRA is defined as the maximum of the ratio  $\text{HRR}(t)/t$ ,<sup>13</sup> and approximately equals to  $\text{PHRR}/t(\text{PHRR})$  for many cone calorimeter results, but not in general. In particular, for samples that burn for a while and exhibit a PHRR toward the end, the maximum in the ratio  $\text{HRR}(t)/t$  occurs often for the shoulder or local maximum in HRR after the initial increase. The deviation between FIGRA and  $\text{PHRR}/t(\text{PHRR})$  can be considerable. Nevertheless, each of the indices mentioned may be suitable to compare the fire risk of a set of materials always dependent on their HRR curves and assessed fire risk. The assessment of fire behavior may be quite different, so that it is recommended not only to use the correct notation but also to decide which of the indices may be most suitable for the actual task and purpose.

## Wicking

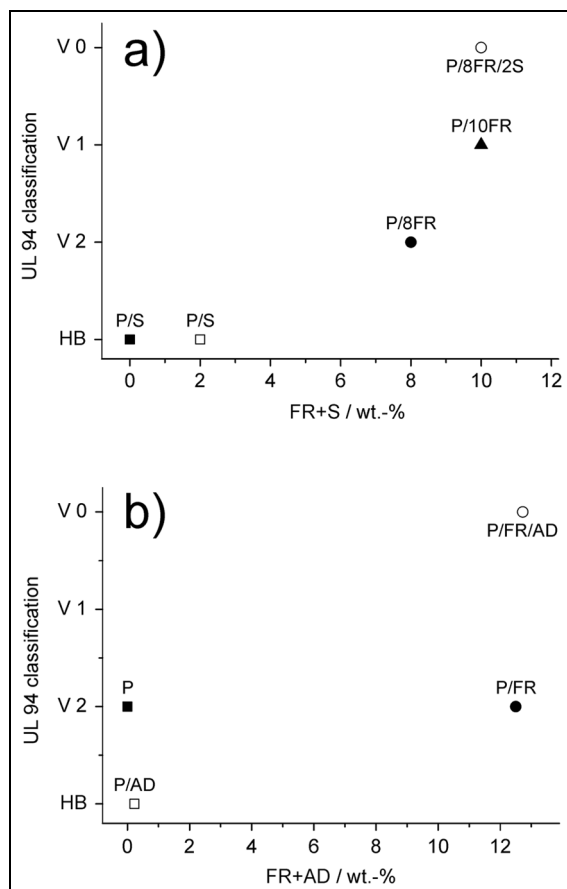
Fillers can influence the fire behavior of polymers through quite a large number of effects, by changing the fire load, specific heat capacity, heat absorption in depth, density, melt flow, and so on. What is more, they change the composition, morphology, and thus properties of the fire residue and the residual surface layer during combustion. Fillers are reported to yield all kinds of effects on the reaction of composites to small flame, such as in OI and UL 94, respectively. Although inorganic fillers reduce the amount of combustibles, they can adversely affect some flammability parameters. For example, OI can decrease, increase, or go through a maximum or a minimum, when increasing the concentration, depending on the morphology and chemical nature of the filler.<sup>23,24</sup> Adding 5–35 wt% short fibers to technical polymers such as polyesters and polyamides decreases the OI and  $t_{\text{ig}}$ , even though HRR and total heat release (THR) decrease due to the reduced amount of combustible polymer. Such somewhat unexpected behavior is often believed to be caused by the effect of wicking. Wicking, by definition, is based on the capillary effect and thus does not describe the generally reduced melt flow and dripping in fiber-reinforced composites. OI and UL 94 are shown to be influenced crucially by melt flow properties and melt dripping,<sup>25–29</sup> but, strictly speaking, true wicking may be rare.

## Synergism

Over recent decades, Ed Weil and Menachem Lewin have reviewed the topic of “synergism” to achieve advanced flame retardancy several times at length.<sup>5,7,10,27</sup> In particular, their conceptual work on how to define and render synergism more precisely is enlightening. Unfortunately, throughout the literature, the term synergism is often used quite freely whenever the combination of flame retardants and an adjuvant, additive, filler, or another flame retardant performs somewhat better than each component alone. Thus, the term synergy is often used when two or more components merely work well together. However, the term “synergy/synergism/synergistic/synergist” must not be used as a synonym for all kinds of benefit, adjuvant, improvement, or advantage. Synergistic effects between additives are defined to be superior to the superposition of the effects of each additive taken independently.<sup>27,30</sup> Antagonism describes the opposite, namely, performance inferior to superposition. Yet, superposition and limited antagonisms are, of course, often valuable improvements compared to the performance achievable when only one of the additives is applied. Even though a particular synergism may be accompanied by surprising performance, being a bargain to get a new patent, any superior performance achieved through the combination of additives—synergistic or not—harbors potential for commercial systems. Using synergistic approaches is the most effective way to reduce the flame retardant content necessary in polymeric materials.

Many synergisms are exploited in the flame retardancy of polymers, reducing the amount of flame retardants needed or increasing the effectiveness of flame retardants:<sup>5,10,27,30,31</sup> metal hydroxides + all kind of synergists, halogen flame retardants + antimony, phosphorus + nitrogen, phosphorus + phosphorus, major flame inhibition + minor charring, flame retardant + anti-dripping agent, flame inhibition + enhanced decomposition/melt flow based on free-radical generators, to mention just some of the most prominent synergistic combinations exploited in actual products. Furthermore, there are several substances used regularly as crucial adjuvants and synergists in flame retardants, such as zinc borates and related substances, metal oxides, silicon compounds/silicate fillers, sulfur compounds, poly(tetrafluoroethylene), and low-melting glasses. Synergism is monitored and defined in the measure of fire performance and can be due to quite different physical–chemical phenomena. In some systems, the synergist improves flame retardancy by optimizing the properties of the residual protective layer, adjusting the temperature range at which radical scavengers are released into the gas phase, or increasing flame inhibition efficiency, all caused by specific chemical reactions or interactions. In other systems, synergy is caused by adjusting the set of material properties controlling the response of a specimen in distinct fire behaviors, for example, by adjusting melt flow and dripping in reaction to small-flame tests. The combination of flame retardancy in the condensed phase and the gas phase has also been proposed as a general route to synergism.<sup>31</sup> Pyrolysis in the condensed phase and combustion within the flame are two sets of chemical reactions. Thus, if one can effectively combine these, so that the condensed phase material slows the rate of combustion, while the vapor phase active material can quench the flame, one may have a quiet effective flame retardant.

In Figure 2(a), two distinct synergistic combinations are shown,<sup>25,32–34</sup> both typical for commercial exploitation focusing on the UL 94 V-0 classification. In the first example, a phosphorus flame retardant is combined with a low amount (2 wt% in the example, often  $\leq 1.5$  wt% in commercial products) of metal oxide as a synergist. The polymer is classified HB; adding the synergist alone does not have any influence on the flammability observed in



**Figure 2.** Synergism in UL 94: (a) polymer/8 wt% flame retardant/2 wt% synergist (P/8FR/2S) showing performance superior to P/10FR and (b) polymer/flame retardant/anti-dripping agent (P/FR/AD) showing superior classification due to adjusting the physical property melt flow.

UL 94. Through the combination, a V-0 classification is achieved, with an overall additive content much lower than what would be needed if only the phosphorus flame retardants were used. Specific chemical interactions are believed to cause changes in decomposition, such as increasing carbonaceous charring, adjusting temperature ranges, and reactions between the additives. The second example (Figure 2(b)), combining a flame retardant with an anti-dripping agent, is quite common for many thermoplastics in order to achieve a non-dripping V-0 UL 94 classification. Many thermoplastics are classified V-2 and HB. Flame retardants, particularly when they also function as plasticizers, reduce viscosity and lead to V-2 behavior. Only in combination with an anti-dripping agent they are able to attain non-dripping V-0 classification. It should be noted that the opposite, combining a flame retardant causing flame inhibition or fuel dilution along with enhanced melt flow or even dripping to remove heat from the pyrolysis front, is also used in commercial products. Melamine cyanurate is used in polyamide for a dripping V-0 classification in UL 94, and

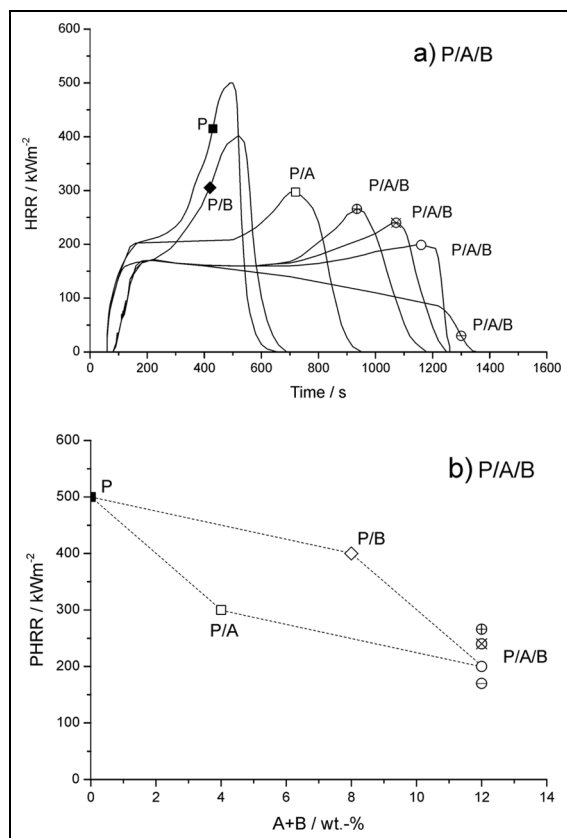
radical generators instead of anti-dripping agents are used in polyvinyl polymers, particularly in thin films and foams.

Most of the synergisms used are rather specific, based on combining distinct flame retardancy effects, adjusting properties such as viscosity or decomposition temperature during pyrolysis, or enhancing an effect through specific chemical reactions. Further synergisms are also specific with respect to the fire property discussed. The same combination may be synergistic in one fire test or fire property but not in another. For instance, the typical synergistic effects discussed between the flame retardant and adjusting the melt flow by radical generator or anti-dripping agents are used to pass reaction-to-small-flame tests such as UL 94, OI, and flammability tests in construction. Yet, these combinations do not work with respect to flame spread in general or in reducing the fire load. Other combinations show impressive synergism in flame spread (reduction in HRR accompanied by a prolonged burning time) but hardly any positive effect on fire load (total heat evolved). Additionally, some fire properties or fire responses in certain fire tests have a quite discontinuous relation to changes in flame retardant content, such that synergism may result when only the performance values are compared.<sup>7</sup> Synergisms observed in a distinct fire test must not be discussed as a general kind of synergy.

Weil<sup>7,27</sup> and Lewin<sup>35</sup> proposed improving the scientific discussion on synergy in flame retardant polymers not only by placing emphasis on the definition but also by quantifying the synergistic effect through a synergistic effect index (SE) for fire risks such as OI. SE is defined through the ratio of the flame retardancy effect of the combination and the effect expected for superposition of the effects of the single components. Thus,  $SE > 1$  marks superior effects through synergism,  $SE = 1$  is obtained for superposition, and  $SE < 1$  indicates inferior effects through antagonism, always compared to the superposition. Although such quantitative discussions have been recently reported by other groups,<sup>35–39</sup> unfortunately, they are rarely used. It should be mentioned that synergy is a mathematical concept in which the effect of two or more additives is greater than the superposition obtained. Thus, synergy should be calculated and not simply asserted.

Quantifying synergy sounds simple, but it is not. The concept of synergy is based on the comparison of the performance observed with results expected for a superposition of the single effects. The main problem is to define what is meant by superposition of the effects or additive effect and to describe it mathematically for the quantification.<sup>7,27</sup> Proper mathematical models are complex, both for describing the reduction in the specific fire response observed and for the relation between concentration and performance. Using just the sum of absolute reductions for any fire property is a quite simple, pragmatic way, but it is not necessarily accurate. The HRR, for instance, is proportional to the product of combustion efficiency ( $\chi$ ), one minus char yield ( $1 - \mu$ ) and the effective heat of combustion of the volatiles. Combustion efficiency ( $\chi$ ) takes into account how completely combustion takes place in the flame, one minus char yield ( $1 - \mu$ ) describes how much fuel and char are produced in pyrolysis, and the effective heat of combustion of the volatiles is a measure of the quality of the released fuel. A reduction in a fire property, such as HRR due to flame retardants yielding flame inhibition in the gas phase, increasing charring in the condensed phase or diluting fuel, may be more like a relative reduction caused by changing these factors. Usually, neither the analytical function is known, namely, how a flame retardant changes a specific measure of fire performance, nor the dependency on the concentration of the flame retardant. Furthermore, the set of materials investigated (polymer “P,” P/flame retardant (P/FR), P/adjuvant, P/FR/adjuvant) is usually limited. Thus, simple assumptions are made, such as

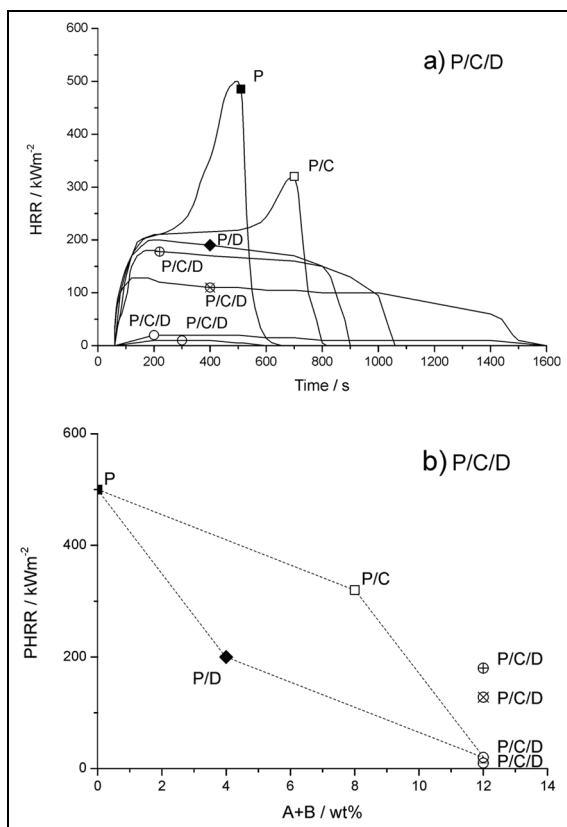




**Figure 3.** (a) Schematic representation of a set of HRR(t) curves in cone calorimeter for a polymer (P), P/4 wt% flame retardant A (P/A), P/8 wt% flame retardant B (P/B) and four different possible HRR(t) curves for P/4 wt% flame retardant A/8 wt% flame retardant B (P/A/B) and (b) corresponding peak heat release rate (PHRR). The parallelogram illustrates an additive effect in the absolute reduction.

absolute or relative flame retardancy effects and linear dependency on the concentration of additive. Assessing the synergy compared to superposition could be based on a calculation based on measured non-linear dependencies of the flame retardant concentration or on assumed linear behavior; the assumption made has a significant impact on the result. The assumptions crucially oversimplify reality, potentially leading to irrelevant expectations or yielding “pseudo-synergism,”<sup>27</sup> a phenomenon discussed in detail in the following paragraphs.

Figures 3 and 4 show two realistic examples illustrating how close fruitful and irrelevant discussions are to each other with reference to the PHRR in cone calorimetry. In the first example, the idealized HRR curves of a polymer (P), P/flame retardant A (P/A), and B (P/B), respectively, and four possible HRR curves for P/A/B are illustrated in Figure 3(a) and the corresponding PHRR in Figure 3(b). The four HRR curves for P/A/B, or more precisely their PHRR values, are constructed to show antagonism, superposition assuming relative reduction in PHRR ( $\text{PHRR}(P/A/B) = \text{PHRR}(P) \cdot \Delta_{\text{rel}}A \cdot \Delta_{\text{rel}}B$ ), superposition in terms of



**Figure 4.** (a) Schematic representation of a set of HRR(t) curves in cone calorimeter for a polymer (P), P/8 wt% flame retardant C (P/C), P/4 wt% flame retardant D (P/D) and four different possible HRR(t) curves for P/8 wt% flame retardant C/4 wt% flame retardant D (P/C/D) and (b) corresponding peak heat release rate (PHRR). The parallelogram illustrates an additive effect in the absolute reduction.

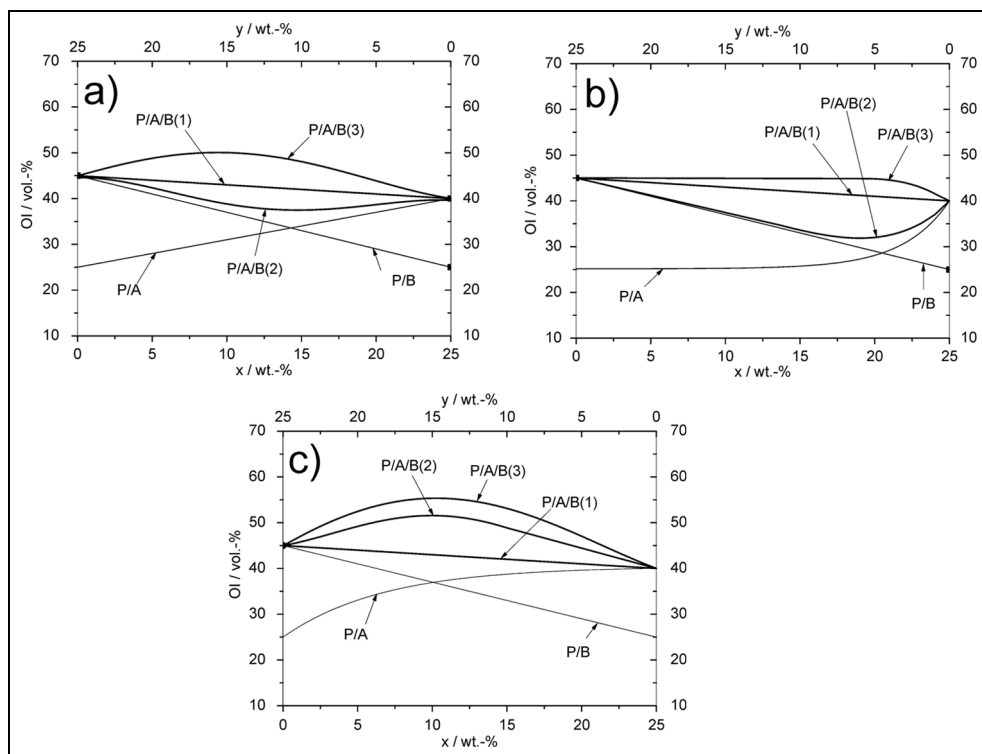
absolute reduction in PHRR ( $\text{PHRR}(P/A/B) = \text{PHRR}(P) - \Delta_{\text{abs}}A - \Delta_{\text{abs}}B$ ), and synergism. All of these idealized HRR curves are quite realistic. The values for assuming superposition of relative reduction (flame retardancy function through a factor such as the combustion efficiency) and the absolute reductions are close to each other. The additional benefit from synergy is obvious.

In the second example (Figure 4), the idealized HRR curves of a polymer (P), P/flame retardant C (P/C), and D (P/D), respectively, and four theoretical HRR curves for P/C/D are illustrated in Figure 4(a) and the corresponding PHRR in Figure 4(b). The four HRR curves for P/C/D, or more precisely their PHRR values, are constructed to illustrate antagonism, superposition assuming relative reduction in PHRR ( $\text{PHRR}(P/C/D) = \text{PHRR}(P) \cdot \Delta_{\text{rel}}C \cdot \Delta_{\text{rel}}D$ ), superposition in terms of absolute reduction in PHRR ( $\text{PHRR}(P/C/D) = \text{PHRR}(P) - \Delta_{\text{abs}}C - \Delta_{\text{abs}}D$ ), and synergism. Only the HRR curves for P, P/C, P/D, and the P/C/D curve showing strong antagonism, but improvement compared to P/C and P/D, are realistic. Even the P/C/D curve based on the superposition of the relative reduction in

PHRR is extremely hard to achieve in reality. The HRR curves for P/C/D assuming superposition of the absolute reductions or synergistic behavior compared to absolute reduction are impossible. Indeed, the example shown here is not as extreme as possible. In cases where the sum of the reduction in PHRR for P/C and P/D is greater than 100%, even negative PHRR values are calculated for the superposition.

The discussed examples based on PHRR in the cone calorimeter are not extraordinary but illustrate the consequences of the basic assumptions typically made when discussing synergy when a limited set of materials is used. The fire property is usually not reduced linearly but non-linearly as the amount of additive is increased. Furthermore, the specific analytical description is not known and may be quite specific and complex. The PHRR at the end of the burning is due to the thermal feedback on the back of the specimen.<sup>19</sup> Usually, non-linear reduction occurs for this PHRR. Furthermore, when it is efficiently reduced, a two-peak behavior, one maximum in HRR at the beginning of burning and one at the end of burning, is observed, and the first maximum in HRR becoming the PHRR. Thus, origin and position of the PHRR changed interrupting any analytical description of the PHRR dependency from the flame retardant concentration. Assuming relative reduction works better when the flame retardancy effect is leveling off, but does not solve the problem of describing the expected flame retardancy effect. Nevertheless, any attempt to quantify synergy improves the practice in scientific work over simply calling every “good” performance of two or more additives synergistic. Quantifying the synergistic effect provides a scientific tool to assess and underline the advantage of synergistic combinations.

Assuming linear dependencies on the concentration of flame retardant when evaluating synergistic effects is a crucially oversimplifying model and can even hide synergistic effects that may arise from exploiting the non-linear dependency of the flame retardancy effect. Indeed, for a wide range of concentrations, a non-linear increase in the flame retardancy effect is quite typical. So the apparent synergism is not only necessarily be related to a reaction or interaction between the two additives, but can also be due to the superposition of relevant non-linear effects. Particularly, when systems with the same amount of additives are compared, for example, a polymer (P) flame retarded with two flame retardants (flame retardant A and flame retardant B) always maintaining the same additive content ( $P/(x + y)A$ ,  $P/(x + y)B$ , and  $P/xA/yB$ ) with  $x$  = the amount of flame retardant A in wt% and  $y$  = the amount of flame retardant B in wt% in  $P/xA/yB$ , the potential of this kind of synergism becomes obvious. Figure 5 shows three idealized examples for the OI of a  $P/xA/yB$  compared to a  $P/A$  and  $P/B$  system, holding the overall amount of flame retardant in the  $P/xA/yB$  constant at  $x + y = 25$  wt% and varying the amount of flame retardant between 0 and 25 wt% for  $P/A$  and  $P/B$ , respectively. The OI of  $P$  is set to 25 vol%, the OI of  $P/25$  wt% A to 40 vol%, and the OI of  $P/25$  wt% B to 45 vol%. In the first example (Figure 5(a)), the increase in OI both for  $P/A$  as well as for  $P/B$  is given by a linear increase.  $P/A/B(1)$  shows the superposition of the absolute change based on a linearly increasing flame retardancy effect of  $P/A$  and  $P/B$ .  $P/A/B(2)$  sketches the OI for antagonism, and  $P/A/B(3)$  for synergy. In the second (Figure 5(b)) and third examples (Figure 5(c)),  $P/A/B(1)$  also indicates the flame retardancy effect calculated for the superposition of the absolute change in OI, assuming a linear increase in  $P/A$  and  $P/B$  when increasing A and B. In the second example (Figure 5(b)), the increase in OI for  $P/A$  is less than linear, as is typical, for instance, for all kinds of hydroxides, whereas in the third example (Figure 5(c)), it is superior to a linear relation, as is typical for many phosphorus flame retardants. The superposition of the absolute OI increase in  $P/A$  and  $P/B$  to calculate  $P/A/B(2)$  reveals strong antagonism



**Figure 5.** OI versus flame retardant concentration for a polymer/flame retardant A/flame retardant B system ( $P/xA/yB$ ), with  $x + y = 25$  wt% illustrating the influence of linear and non-linear dependencies of the OI from the flame retardant concentration. P/A and P/B illustrate the performance when increasing the amount of flame retardant from 0 to 25 wt% for A and B, respectively. P/A/B(1) is always the performance assuming an additive effect for linear behavior, P/A/B(3) synergistic performance assuming an additional phenomenon, and P/A/B(2) illustrates antagonistic behavior in (a). In (b) and (c), P/A/B(2) is the additive effect of P/A and P/B. P/A/B(2) shows strong antagonism in (b) due to the non-linear behavior of P/A and in (c) “pseudo-synergy.”

for the second and strong synergy for the last example. This synergism created by non-linearity is sometimes called “pseudo-synergism”<sup>27</sup> to indicate the difference from the synergism in P/A/B(3) originating from additional phenomena enabled by the combination of substances. Nevertheless, these kinds of synergistic effects are neither artifacts nor imaginary, but real and very often successful routes used to design superior products.

When the non-linear concentration dependencies are known, they can be used to calculate the additive effect and quantify the “real” synergy, which is in most cases different from the results based on the assumption of linearity.<sup>7</sup> However, as mentioned above, the data set is usually limited (e.g. P, P/A, P/B, and P/A/B), and the concentration dependencies are not known in detail. Furthermore, for the usual tasks, such as increasing efficiency or reducing the overall load with additives, the origin of synergism is of minor interest when quantifying it. Thus, calculating the SE based on rather simple, straightforward approach for two additives depends in practice on two predefinitions. These predefinitions control the results and

should be formulated according to the actual task. The first predefinition is whether compounds are compared in which the total amount of additives A and B within the polymer P is kept constant (P/xA/yB compared to P/(x + y)A and P/(x + y)B), or compounds are compared in which the amount of each additive A and B is kept constant (P/xA/yB compared to P/xA and P/yB). x is always the amount of flame retardant A in wt%, and y is the amount of flame retardant B in wt%. The second predefinition is whether the superposition of the property changes  $\Delta M$  is absolute ( $\Delta M(P/A/B) = \Delta M(P/A) + \Delta M(P/B)$ ) or relative ( $\Delta M(P/A/B) = \Delta M(P/A) \Delta M(P/B)$ )

$$SE_{abs}(M)_{x,y=const.} = \frac{\Delta M(P/xA/yB)a}{\Delta M(P/xA) + \Delta M(P/yB)} \quad (2)$$

$$SE_{rel}(M)_{x,y=const.} = \frac{1 - \Delta M(P/xA/yB)}{1 - \Delta M(P/xA) \cdot \Delta M(P/yB)} \quad (3)$$

$$SE_{abs}(M)_{x+y=const.} = \frac{\Delta M(P/xA/yB)}{\frac{x}{(x+y)} \Delta M(P/(x+y)A) + \frac{y}{(x+y)} \Delta M(P/(x+y)B)} \quad (4)$$

$$SE_{rel}(M)_{x+y=const.} = \frac{1 - \Delta M(P/xA/yB)}{1 - \left(1 - \frac{x}{(x+y)} (1 - \Delta M(P/(x+y)A))\right) \cdot \left(1 - \frac{y}{(x+y)} (1 - \Delta M(P/(x+y)B))\right)} \quad (5)$$

where x is the amount of flame retardant A in wt%, and y is the amount of flame retardant B in wt%, respectively.  $\Delta M$  absolute ( $\Delta M_{abs}$ ) or relative ( $\Delta M_{rel}$ ) is the improvement in a specific fire property such as OI, PHRR, and THR.

In the following section, some examples are sketched that illustrate specific processes to quantify synergy; this will include synergy as evaluated in the cone calorimeter, OI and UL 94. In cone calorimeter investigations, a variety of parameters are measured, including HRR(t), PHRR, THR, smoke, time to ignition (TTI), and mass loss rate, and one may ascertain synergy, additivity, or antagonism for each of these measurements independently. Ideally, the PHRR will decrease as will the THR, average mass loss rate (AMLR), CO yield, and smoke production. However, the effect may be quite different in the different fire properties, for example,  $t_{ig}$  (TTI) often changes in different ways for flame-retarded materials; the most obvious desired change is a substantially increased  $t_{ig}$ , but many flame-retarded polymers show the opposite, and, in some cases, a decrease in  $t_{ig}$ , perhaps due to some early decomposition that leads to a thermally more stable structure, may even be advantageous. CO yield and smoke production often increase in flame-retarded systems due to the forced flaming combustion in the cone calorimeter.

As mentioned before, discussing synergy in the cone calorimeter is difficult when considering changes in the PHRR. First of all, reduction in PHRR seems to be non-linear in almost every system, usually leveling off for higher flame retardant concentrations. As one consequence, one must not assume linearity and simple, absolute reduction nor can the reductions observed for two additives be added together (because this may be more than 100% if they offer large reductions). The suggested procedure is for a first approximation: applying the relative reduction in the second additive to that of the first additive. For instance, if a polymer alone has a PHRR of 1000 kW/m<sup>2</sup> and that for polymer plus additive A is 500 kW/m<sup>2</sup>, and polymer plus additive B is 600 kW/m<sup>2</sup>, the 50% reduction in additive A and the 40%

**Table 1.** Cone calorimetric data for PU + adjuvant + APP.

Sample	PHRR (kW/m <sup>2</sup> ) (% reduction)	THR (MJ/m <sup>2</sup> )	ASEA (m <sup>2</sup> /kg)
Polyurea (PU)	1854 ± 65	160 ± 7	452 ± 18
PU + 0.5% PTFE	1450 ± 126 (22)	132 ± 13	493 ± 26
PU + 0.5% graphite	1187 ± 186 (36)	152 ± 4	519 ± 35
PU + 15% APP	720 ± 37 (61)	137 ± 10	500 ± 40
PU + 15% APP + 0.5% PTFE	553 ± 43 (70)	119 ± 12	585 ± 290
PU + 15% APP + 0.5% graphite	536 ± 99 (71)	130 ± 4	641 ± 121

PHRR: peak heat release rate; THR: total heat release; ASEA: average specific extinction area; PTFE:

polytetrafluoroethylene; APP: ammonium polyphosphate.

Source: Adapted from Mariappan and Wilkie.<sup>41</sup>

reduction in additive B require that the PHRR be less than 60% of 500 or 300 kW/m<sup>2</sup> for synergy. If the PHRR is above 300 kW/m<sup>2</sup>, then we have a less than additive response, antagonism; if it equals 300 kW/m<sup>2</sup>, this is superposition. This procedure, of course, amounts to equation (3) for calculating the synergy index. A similar procedure may be appropriate for THR, AMLR, and smoke production, in particular, when flame inhibition or increasing char yield is the main flame retardancy mechanism. Both flame inhibition and charring of the polymer are believed to reduce the heat release by reducing the factors combustion efficiency  $\chi$  and one minus char yield ( $1 - \mu$ ), respectively. However, despite their frequently non-linear effect in PHRR, inert fillers are expected to cause a strongly linear reduction in THR, the fire load, at the same time, through the absolute replacement (in vol%) of fuel (synergy index according to equation (2)); for instance, such different effects on PHRR and THR were reported for layered silicate nanocomposites.<sup>40</sup>

Table 1 provides the cone calorimetric data for polyurea with a fire retardant ammonium polyphosphate (APP) and the adjuvants expanded graphite and polytetrafluoroethylene (PTFE).<sup>41</sup> In the case of the polyurea, one finds a PHRR of 720 kW/m<sup>2</sup> for 15 wt% APP and a 22% reduction in 0.5 wt% PTFE. A 22% reduction in PHRR from 720 is 158 kW/m<sup>2</sup>, which means that additive performance would result in a PHRR of 562 kW/m<sup>2</sup>. The observed value is 553 kW/m<sup>2</sup>, which is certainly within the error bars of the predicted value for additive behavior, the corresponding synergy index according to equation (3)  $SE_{rel} = 1.05$ . In determining synergy, one must bear in mind that in some cases, the two additives may perform the same type of function, for instance, forming a residual protective layer, so that the performance may not even be additive. This situation can be seen when graphite is the adjuvant. Graphite provides a 36% reduction, so, again, using the 720 kW/m<sup>2</sup> of PU + APP, a 36% reduction gives 259 kW/m<sup>2</sup>, and hence, an expected PHRR of 469 kW/m<sup>2</sup>, which is less than the experimental value of 536 kW/m<sup>2</sup>. This must be described as antagonistic behavior.

Considering THR, the reduction is 18% for PTFE alone, 0.5% for graphite alone, and 14% for APP alone; for the combinations, the reduction is 26% for APP + PTFE and 19% for APP + graphite. The superposition values are 113 MJ/m<sup>2</sup> (0.86(132)) for APP + PTFE and 130 MJ/m<sup>2</sup> (0.86(152)). The experimental results are 119 and 130 MJ/m<sup>2</sup>, respectively, and these are very close to superposition and not synergistic. Finally, considering the average specific extinction area (ASEA) as measure of the smoke, one notes that the values for polymer plus additive are always larger than those for the polymer alone, so the additive

contributes to the smoke. The superposition values are  $547 \text{ m}^2/\text{kg}$  for APP + PTFE and  $576 \text{ m}^2/\text{kg}$  for APP + graphite. The experimental values are 585 and  $641 \text{ m}^2/\text{kg}$ . In both cases, the values are greater than the superposition values, which may indicate that the two materials act together to produce more smoke. Thus, the combinations not only show a synergy with respect to smoke production but also an antagonism with respect to the flame retardancy goal of smoke suppression.

It has been noted that synergy must be calculated to compare the observed value with superposition. V-0, V-1, and V-2 classification in UL 94 tests are typical examples for discontinuous characteristics in fire testing and thus, as mentioned above, somewhat tricky in discussing and quantifying synergy. Strictly speaking, the examples in Figure 2 are not well done to unambiguously prove synergy. It should be noted that comparing P/x FR, P/y FR, and P/x FR1/y FR2 always projects synergy when P/x FR1/y FR2 just obtains an UL 94 V-classification. A comparison of P/(x + y) FR, P/(x + y) synergist, and P/x FR/y synergist is a much better way to prove unambiguously synergy in the UL 94 test. To avoid the assessment in the discontinuous UL 94 classes, Weil et al.<sup>42</sup> proposed a regression analysis of the burning times for the first and second ignition and the total burning time, and suggested that the interaction coefficient may be viewed as a measure of synergy.

OI has been used for more than 50 years to monitor dependencies on flame retardant concentrations, to search for synergy in flame retardant combinations, and to quantify synergism.<sup>7,10,27,43</sup> Again, linear approaches were usually reported to assess and quantify synergism, even though it is well known that OI is frequently non-linear with respect to changes in the amount of an additive,<sup>7,44–46</sup> although a non-linear approach has been used.<sup>7</sup> More recently, Horrocks et al.<sup>36</sup> applied a linear methodology, assuming an absolute increase in OI in several polymers using equation (6)

$$SE = \frac{(OI_{FR+S+P} - OI_P)}{((OI_{FR+P} - OI_P) + (OI_{S+P} - OI_P))} \quad (6)$$

where  $OI_{FR+S+P}$  is the OI for the flame retardant + synergist + polymer,  $OI_P$  is the OI for the polymer,  $OI_{S+P}$  is the OI for the polymer + synergist, and  $OI_{FR+P}$  is the OI for the flame retardant in the polymer, all at the same respective amounts. Equation (6) is equation (2) written for OI, of course. In the case of polyester-decabromodiphenyl ether-zinc hydroxystannate,<sup>36</sup> the operative values are  $OI_P = 18$ ,  $OI_{P+S} = 18$ ,  $OI_{FR} = 19$ , and  $OI_{FR+S+P} = 22$ . This yields an SE value of 3. If antimony oxide is the synergist, the SE value is 6 and proves greater synergism. It is clear that the uncertainty of the SE is strongly dependent on the fire performance discussed and the absolute improvements observed. In the OI example here, the uncertainty is in the order of  $\pm 1$ , in other cases,  $< 0.1$ . Furthermore, the obtained SE must be compared with the desired effect; for example,  $SE = 2$  means merely that the change is twice as good as expected. In the case of increasing OI by 2 instead of 1 ( $SE = 2$ ), the synergism is hardly greater than the uncertainty, but increasing OI by 14 instead of 7 ( $SE = 2$ ) is quite considerable.

In sum, the terms “synergy,” “synergism,” “synergistic,” and so on must not be used as synonyms for benefit or improvement but must comply with the definition of a better than “additive” effect. It is recommended to discuss synergy as a specific phenomenon in one or more distinct fire performances and to quantify the synergistic effect, choosing certain models, and approximations. The discussion above may provide some food for thought on how to do this. While synergy due to the combination of fire retardants is a key factor in the

constant search to increase effectiveness and load reduction, the approach available to achieve it is essentially empirical. Mechanistic understanding is required to propose combinations of additives accurately selected, leading to optimized synergy.

## Conclusion

Several scientific concepts in flame retardancy were discussed briefly in part 2 of the two-part paper, such as fire residue/char/ash, the correlation between fire performance and the char yield according to Van Krevelen, catalysis, and wicking, whereas synergy was discussed in detail. The scientific description of flame retardancy and thus the communication within the community benefit crucially from a precise use of these concepts, particularly taking into account their limitations. A series of recommendations are compiled here as follows:

- Discussing the residue obtained in fire testing or thermal analysis in detail, such as determining the carbonaceous char and ash (inorganic residue), opens the door beyond merely measuring the amount of fuel released toward assessing its quality.
- The equation for the OI of Van Krevelen is one of the oldest, easiest, and most powerful concepts in the flame retardancy of polymers but should be used with proper consideration of its applicability.
- Using catalysis and wicking according to their limited meaning: the terms “decreasing the activation energy of a reaction” instead of “increasing charring” and “based on capillary forces” instead of “melt flow–related effects” strengthens the precision of scientific discussion.
- Concluding synergy should be based on the comparison of the performance observed with the one expected for a superposition of the single effects. Synergistic performance should be quantified.

By offering both an introduction to the background and some recommendations, this article sensitizes readers to the topic and, it is hoped, will lead to improved scientific practice.

## Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

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