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Study of the combustion efficiency of polymers using a pyrolysis–combustion flow calorimeter

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ABSTRACT

The combustion efficiency of various polymeric materials was studied using a pyrolysis–combustion flow calorimeter (PCFC). Decreasing the combustion temperature in a PCFC leads to partial combustion and lower heat release rates. Combustion efficiency versus combustion temperature was modeled using a phenomenological equation and model parameters were related to the chemical structures of eight pure polymers. The flame inhibition effect was evaluated for two classical approaches in flame retardancy by plotting the combustion efficiency versus the combustion temperature. In the first one (the reactive approach), polystyrenes with different chemical groups substituted on the aromatic ring were studied. In the second one (the additive approach), three well-known flame retardants were incorporated into an ABS matrix: ammonium polyphosphate, tetrabromobisphenol A (TBBA), and a TBBA/antimony trioxide system. Results confirm the flame inhibition effect of halogenated compounds in both approaches. Finally, a correlation between peaks of heat release rate (pHRR) in a cone calorimeter and in a PCFC was attempted. Predicting pHRR in a cone calorimeter using a PCFC appears possible when no barrier effect is expected, if PCFC tests are carried out at a precise combustion temperature, for which the combustion efficiencies in both tests are the same.

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1. Introduction

When exposed to an intense heat source, polymers undergo thermal or thermo-oxidative decomposition, leading to release of highly combustible gases. The complete combustion of these gases in the presence of oxygen releases heat, water, and carbon dioxide if the polymer contains only C, H, and O atoms. Nevertheless, combustion is generally only partial and released heat is lower than expected. Combustion efficiency is calculated as the ratio of the real heat release to the maximum heat release (i.e., when combustion is complete).

The main mode of action of halogenated flame retardants is flame inhibition, i.e., the decrease in combustion efficiency. Flame inhibition is partly due to physical effects (dilution and heat capacity, which lead to the cooling of the flame) and partly due to chemical effects (scavenging of highly reactive radicals $H^{\cdot}$, $OH^{\cdot}$ that attack the hydrocarbons [1–3]). Halogenated molecules (such as HBr) react in the gaseous phase by trapping reactive radicals to give less reactive radicals [1]:

$$RX \rightarrow R^{\circ} + X^{\circ} \quad (X = Br \text{ or } Cl) \qquad (1)$$

$$X^{\circ} + RH \rightarrow R^{\circ} + HX$$

$$HX + H^{\circ} \rightarrow H_2 + X^{\circ}$$

$$HX + OH^{\circ} \rightarrow H_2O + X^{\circ}.$$

Therefore, some combustible molecules are not fully oxidized, CO is produced (rather than CO_2), and the heat release is significantly reduced. The efficiency of various compounds in flame inhibition was estimated experimentally or by calculations [1–4]. This efficiency is mainly dependent on specific atoms. Metallic compounds containing Fe, Pb, or Cr are the most effective [1]. Intrinsic inhibition indices were calculated using a Van Krevelen approach for different atoms: C, H, F, Cl, Br, and I. The last two were found to be the most effective [3]. It was highlighted that CF_3Br and CF_3I inhibit flame by chemical action, while other studied additives (fluorinated additives) act mainly through physical effects. Some phosphorus flame retardants could also have a similar action, but their main mode of action is generally considered as char promotion in the condensed phase. Another important characteristic for an efficient flame inhibitor is its ability to be regenerated during the combustion process [2,3].

The pyrolysis–combustion flow calorimeter (PCFC) is an apparatus developed approximately 12 years ago to measure some important flammability parameters of polymers through nonflaming combustion [5]. Since it needs only milligrams of material, it is a powerful method for studying polymers synthesized in the laboratory in small amounts. Some research teams attempted to use

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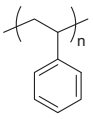
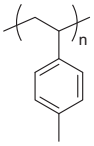
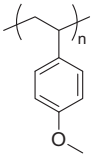
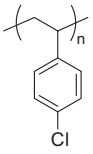
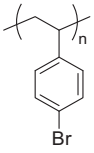
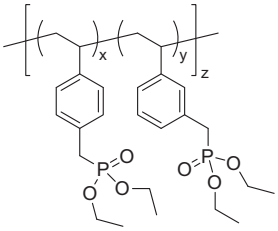
PCFC as a screening tool before performing cone calorimeter tests, which need a greater amount of material [6–8]. But the correlation between the cone calorimeter and the PCFC results is not general, for three main reasons [9]. The first is the barrier effect, which is not efficient in the PCFC, in contrast to the cone calorimeter. The barrier effect becomes effective when an insulating layer could protect the underlying material from the heat source. This layer may be composed of char and/or mineral particles and should be thermally stable. The second is related to thermal stability. Two polymers could exhibit similar peaks of heat release rate but different degradation temperatures in PCFC. In this case, cone calorimeter results could be very different. The third reason is that the combustion is complete in the PCFC standard test while the combustion efficiency could be less than 1 in the cone calorimeter test, even if this test is carried out under well-ventilated conditions.

Nevertheless, it is possible to monitor the conditions (oxygen rate and temperature) in the PCFC combustion chamber to decrease the combustion efficiency, as presented in an article of Schartel et al. [10]. The decoupling between pyrolysis and combustion in the PCFC allows changing the conditions of combustion without modifying the pyrolysis of the sample. This possibility should allow studying the flame inhibition of halogenated flame retardants. But to the best of our knowledge, this possibility has never been exploited. We believe that only the chemical component of flame inhibition could be studied, since the combustion temperature is kept fixed during the test.

In the present article, the combustion temperature in the PCFC was monitored to study the change in combustion efficiency for various polymeric materials. This method was developed to know the role of different elements (Cl, Br, P) as efficient flame retar-

Table 1
Chemical composition of the materials studied.

Series	Designation	Name	Chemical structure
A	PS	Polystyrene	
	$PS\text{-}CH_3$	Poly(4-methylstyrene)	
	$PS\text{-}OCH_3$	Poly(4-methoxystyrene)	
	PS-Cl	Poly(4-chlorostyrene)	
	PS-Br	Poly(4-bromostyrene)	
	PS-P	Poly(diethyl vinylbenzylphosphonate)	
B	LDPE	Riblene FL20 (Polimeri Europa)	
	PMMA	Altuglas V825T (Arkema)	
	PS	Lacqrene 1340 (Arkema)	
	ABS	Terluran GP22 (BASF)	
	PA6	Technyl C216 (Rhodia)	
	PA11	Rilsan (Arkema)	
	EVA (28 wt% vinyl acetate)	Evatane 2805 (Arkema)	
	PVC	EVC Compound	
			FR content (wt%)
C	ABS + APP	Terluran GP22 (BASF) + AP423 (CLARIANT)	3.1, 7.9, 15.7, 31.5, 40
	ABS + TBBA	Terluran GP22 (BASF) + tetrabromobisphenol A	1.6, 15.6, 31
	ABS + TBBA/Sb_2O_3	Terluran GP22 (BASF) + tetrabromobisphenol A/antimony trioxide	1.7/0.6, 4.2/1.5, 8.5/3, 13.6/4.8, 18.6/6.6

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