

Phosphorus-functionalized multi-wall carbon nanotubes as flame-retardant additives for polystyrene and poly (methyl methacrylate)

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Abstract In the present work, we have studied the flameretardant properties of phosphorus-functionalized multiwalled carbon nanotubes (MWCNTs) created by treating oxidized MWCNTs (O-MWCNTs) with phosphoric acid. These phosphorus MWCNTs (P-MWCNTs), along with pristine MWCNTs and O-MWCNTs, were incorporated into polystyrene (PS) and poly (methyl methacrylate) (PMMA) by solution blending at lower concentrations (0.5–10 mass%) than conventional organophosphorus flame retardants (5-30 mass%). Thermal properties of the PS and PMMA polymer nanocomposites were subsequently investigated through thermogravimetric (TG) analysis and microcombustion calorimetry. Scanning electron microscopy was used to evaluate P-MWCNT dispersion in each polymer matrix. P-MWCNTs were welldispersed in PS, improved PS thermal stability during nitrogen pyrolysis in proportion to the phosphorus loading, and led to an improvement in PS flammability properties. In contrast, the P-MWCNTs were more aggregated in

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PMMA and only moderately improved PMMA thermal stability during pyrolysis. In both PS and PMMA, P-MWCNTs were more effective than either MWCNTs or O-MWCNTs at improving each polymer's thermal oxidative stability during combustion in air. Characterization of the P-MWCNT nanoparticles, the PS and PMMA and TG residues indicated that nanocomposites, P-MWCNT flame retardants primarily act in the condensed phase, encouraging char formation of the dispersed MWCNT network as a route to protecting the polymer. By comparing results of polymer composites containing MWCNTs, O-MWCNTs or P-MWCNTs at comparable loadings, data from the current study indicate that phosphorus incorporation can improve the fire-retardant properties of MWCNTs, although optimizing P-MWCNT dispersion in different polymers remains critical to optimizing the flame-retardant effect.

Keywords Carbon nanotube · Phosphorus · Polystyrene · Poly (methyl methacrylate) · Flame retardant · Nanocomposite

Introduction

Most synthetic and natural polymers are highly flammable and require either chemical modification or physical incorporation of flame-retardant additives to improve thermal stability and decrease flammability. Often these additives are incorporated into materials during the manufacturing process, for example in upholstery textiles [1], urethane foams [2], and molded plastics [3, 4]. Many studies have shown how flame retardants can inhibit, suppress, or delay the degradation of a material when it is exposed to the extreme conditions generated by fire [1, 4–8]. While the necessary amounts depend on the nature of the additive and the polymer being protected, typical loadings for common flame retardants are: organophosphorus 5–30 mass%; metal hydroxides 13–60 mass%, and bromine compounds 2–6 mass% [3, 9]. Motivated by the environmental and health hazards of the bromine-based flame-retardant decabromodiphenyl ether (DecaBPE), used heavily in synthetic polymers and textiles, the US Environmental Protection Agency has been assessing the feasibility of using carbon nanotubes (CNTs) as an alternative [9]. This interest derives in large part from the finding that CNTs can be effective flame-retardant additives in many synthetic and natural polymer systems at significantly lower concentrations (0.5–1 mass%) than other commercial flame retardants [10–18].

CNTs are tubular cylinders of carbon atoms with nanometer-scale diameters and micrometer-scale lengths [19]. CNTs comprised of one tube of carbon are called single-walled CNTs (SWCNT), while CNTs with multiple concentric carbon cylinders are referred to as multi-walled CNTs (MWCNT). Many studies have incorporated SWCNTs or MWCNTs into polymers to leverage the extraordinary mechanical, electrical, thermal, optical, and chemical properties of these nanoparticles [20-24]. A series of notable flame-retardant studies spearheaded by the National Institute of Standards and Technology (NIST) revealed how unmodified CNTs can improve the thermal properties of polymer nanocomposites. First, Kashiwagi et al. [17] demonstrated how even small CNT loadings (0.5 mass%) will form CNT nanoparticle networks that reduce the flammability of poly (methyl methacrylate) (PMMA). Cipiriano et al. [11] evaluated how MWCNT aspect ratio impacts flammability reduction of polystyrene (PS) composites. Finally, Kashiwagi et al. [18] evaluated dispersion quality of solution-blended PMMA nanocomposites containing SWCNTs, revealing how the SWCNT/solvent ratio can be tuned to optimize SWCNT dispersion in PMMA to achieve improved thermal stability and reduced flammability. While these early studies investigated both SWCNTs and MWCNTs in model polymer systems (PS and PMMA), most subsequent flame-retardant studies with CNTs in synthetic polymers have focused primarily on MWCNTs, which are more robust and less expensive than SWCNTs.

Many reports have now demonstrated that unmodified MWCNTs can improve a polymer's thermal stability and/ or reduce its flammability, if they are sufficiently welldispersed in the polymer matrix. Improved CNT dispersion can not only be achieved by optimizing the solvent/CNT ratio during solution casting, as demonstrated by Kashiwagi et al. [18], but also by alternative preparation methods (i.e., composite shear mixing, melt mixing, etc.) [25], or by covalent and non-covalent functionalization of CNTs before polymer incorporation [26, 27]. For example, Ballayer et al. [28] used a trialkylimidazolium salt to improve dispersion between MWCNTs and PS, delivering composites with higher thermal stability. Sun et al. [29] achieved a similar result in PS by modifying MWCNTs with а sulfonic acid-based gemini surfactant. Slobodian et al. [30] synthesized more thermally stable PMMA composites with permanganate-oxidized MWCNTs, while Tangtubtim et al. [31] showed how oxidized MWCNTs disperse more effectively in polyethylene to improve that polymer's thermal properties. Siliconfunctionalized MWCNTs have also been added to polypropylene [14], natural rubber [32], and phenolic resins [33] to deliver more thermally stable composites. Most of these studies used SEM, as well as other microscopy techniques, to qualitatively assess CNT dispersion in the polymer matrix.

Although phosphorus-based flame-retardant additives are extremely effective at preventing non-flaming combustion of organic polymers [9], phosphorus-functionalized CNTs have received less attention as flame retardants, most likely due to the difficultly in preparing them. More often, researchers have physically combined CNTs with phosphate flame retardants to prepare more thermally stable polymer composites. Thus, Wesolak et al. prepared flame-retardant textiles by coating them with resins made from polyurethane, MWCNTs and the phosphate intumescents ammonium polyphosphate (APP) and melamine polyphosphate (MPP) [34]. Ebadi et al. [15] studied mixtures of aminated MWCNT and P2O5 in acrylonitrile-butadiene-styrene (ABS). Zhang et al. [35] combined aminated MWCNT and APP to improve the thermal stability of ramie fabric. In 2008, Ma et al. [36] reported a multi-step procedure to graft an intumescent flame-retardant polymer (poly (4,4 diamino diphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB)) to MWCNTs and demonstrated its flame-retardant potential in ABS. More recently, Xing et al. [37] grafted diphenylphosphinic chloride (DPP-Cl) onto aminated MWCNT, again demonstrating how phosphorus-nitrogen containing MWCNTs improve the thermal stability of PS.

A recent thesis by Ortega reported a simpler synthetic route to prepare phosphorus-functionalized MWCNTs (P-MWCNTs) using phosphoric acid [38]. Ortega's method offered an inexpensive way to deliver covalently modified MWCNTs with high thermal stability, using reagents that are readily available and not air sensitive. Motivated by this development, we prepared a series of P-MWCNTs with different phosphorus loadings by modifying Ortega's method. We then incorporated the P-MWCNTs into PS and PMMA, two industrially relevant synthetic polymers whose thermal properties have been well-studied. Our hypothesis was that the P-MWCNT polymer nanocomposites would exhibit improved thermal stability and flammability due to the improved resistance to thermal oxidation exhibited by the P-MWCNT, at lower loadings than required with conventional organophosphorus flame retardants. The polymer nanocomposites were prepared as films through solution blending and casting [39]. To the best of our knowledge, no studies have used phosphoric acid on oxidized MWCNTs (O-MWCNTs) to prepare flame-retardant additives for synthetic polymers. Thermogravimetric (TG) analysis assessed the thermal stability of the MWCNTs, the O-MWCNTs, and the P-MWCNTs, while TG and microcombustion calorimetry (MCC) evaluated the thermal stability and flammability characteristics of the polymer composites prepared with the pristine and functionalized MWCNTs. Materials were further characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron spectroscopy (TEM). Our results show that incorporating P-MWCNTs in PS and PMMA improves the thermal stability of both polymers, while also making PS less flammable. These improvements were achieved at lower MWCNT loadings (0.5-10 mass%) than required for conventional organophosphorus flame retardants (5-30 mass%) and were dependent not only on the amount of phosphorus loaded into the polymer but also on how well the P-MWCNTs were dispersed throughout the polymer matrix.

Experimental

Materials preparation

A full description of chemicals, materials, and methods is provided in the Supporting Information (SI). Each chemical or material was used as received. To prepare P-MWCNTs, pristine **MWCNTs** (Nanolabs, o.d. 15 ± 5 nm, length ca. 5–20 μ m) were oxidized in concentrated HNO₃ and then cleaned via methods previously reported [40]. These O-MWCNTs were treated with 85% H_3PO_4 modeling a strategy published by Ortega [38], where phosphate was first physically adsorbed onto the O-MWCNTs via thermal reflux (4 h at 125 °C), then chemically bonded to the O-MWCNTs by annealing in argon (4 h at 400 °C). The annealed P-MWCNTs were rinsed with copious amounts of ultrapure water to remove any unbound phosphorus prior to characterization or polymer incorporation.

From three batches of similarly oxidized O-MWCNTs (referred to as O1, O2, and O3), a series of four P-MWCNT batches were prepared using slightly different preparative methods to deliver a range of phosphorus functionalization as determined by XPS. These P-MWCNTs are referred to a

P1, P2, P3, and P4: O1 was used to prepare P1, O2 was used to prepare P2, and O3 was used to prepare both P3 and P4. An additional amount of O3 was treated to the same conditions used to incorporate phosphorus (minus H_3PO_4), and used as a study control (referred to as O3-Control).

PS and PMMA polymer nanocomposites were prepared with different loadings of MWCNTs, O-MWCNTs or P-MWCNTs by solution blending and casting. First, the pristine or functional MWCNTs were sonicated in tetrahydrofuran (THF) for 3 h. PS or PMMA was added to the THF-CNT suspension at a polymer/solvent ratio of ca. 20:1 (mg mL⁻¹), and sonicated for 1 h. The CNT-polymer solutions were cast into aluminum weigh dishes and allowed to air-dry. Polymer nanocomposites were vacuumannealed to remove organic solvent prior to thermal analysis.

The following label code is used for polymer composites throughout the manuscript: 'CNT (mass%)_polymer'. PS nanocomposites containing P-MWCNTs (regardless of P-MWCNT type or loading) are labeled P-MWCNT_PS. PMMA nanocomposites with a specific loading of P-MWCNT (i.e., 2 mass%, regardless of P-MWCNT type) are labeled P-MWCNT(2%)_PMMA. When a specific polymer nanocomposite is described (i.e., PS with 2 mass% P3), the appropriate label is P3 (2%)_PS. The SI contains this label code as a reference (Table S1).

Materials characterization

X-ray photoelectron spectroscopy (XPS) identified the surface concentrations and oxidation states of C, O, and P in the MWCNTs and in TG residues; scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/ EDS) examined MWCNT morphology and composition, and qualitatively assessed MWCNT aggregation in the polymer nanocomposites; transmission electron microscopy (TEM) evaluated each MWCNT structure; thermo-gravimetric (TG) analysis evaluated the thermal stability of the pristine MWCNT, O-MWCNT, and P-MWCNT nanomaterials and each polymer nanocomposite; micro-combustion calorimetry (MCC) evaluated the flammability characteristics and thermal stability of the polymer nanocomposites. Specific experimental conditions for these characterization methods are provided in the SI.

Results

Preparation and elemental analysis of functionalized CNTs

Reacting O-MWCNTs with phosphoric acid in accordance with Ortega's method [38] and subsequently annealing the

product under argon reproducibly delivered P-MWCNTs with ca. 0.3 atomic % (at%) phosphorus loading (measured by XPS and EDS), similar to the EDS data Ortega reported in his thesis. A slight modification to Ortega's procedure which did not dilute the H_3PO_4 prior to annealing delivered P-MWCNTs with phosphorus loadings approximately four times higher (1.2 at%). By replacing the 125 °C reflux step with an 8 h sonication at lower temperature (69 °C), P-MWCNT phosphorus loading was further increased to 2.0 at%. This high phosphorus loading was most likely due to continued dispersion of the O-MWCNTs during sonication.

Figure 1 shows the XPS of representative functionalized CNTs; investigating their C(1s), O(1s) and P(2p) photoelectron transitions allowed an assessment of their elemental composition as well as oxidation state. For the pristine MWCNTs, inspection of the C(1s) region revealed the $\pi - \pi^*$ shake-up peak at ca. 291 eV, indicating the presence of a delocalized aromatic structure [40]. No significant amounts of oxygen or phosphorus were detected on the MWCNT surface. Analysis of each O-MWCNT revealed that the HNO₃ oxidation method consistently added between 7.2 and 8.1 at% oxygen to the MWCNT surface. This was accompanied by a slight decrease in the $\pi - \pi^*$ shake-up peak (as compared the pristine MWCNT), indicating that although the surface was covalently functionalized, the extent of sidewall damage was not overwhelming.



Fig. 1 X-ray photoelectron spectroscopy (XPS) of pristine MWCNTs, oxidized MWCNTs (O3 and O3-Control), and phosphorus-functionalized MWCNTs (P1–P4). Oxidized MWCNTs contain the following amounts of oxygen: 8.1 at% before annealing (O3), and 5.9 at% after annealing (O3-control). P-MWCNTs contained the following amounts of phosphorus: 0.3 at% (P1 and P2), 1.2 at% (P3), and 2.0 at% (P4)

XPS of each P-MWCNT again showed C(1s) photoelectron transitions with slightly reduced π - π * shake-up peaks, similar to what was observed on the O-MWCNTs. The P(2p) region showed a single peak centered at 133.5 eV. Peak area integration revealed that the phosphorus concentrations are 0.3 at% for P1 and P2, 1.2 at% for P3, and 2.0 at% for P4. The broadness of the oxygen peak in each of the P-MWCNTs suggests more than one functional species are present, such as -C=O, -C-OH, C-O-P-, etc. It is clear from the P(2p) and O(1s) spectra that the surface oxygen concentrations increase with increasing phosphorus loading. In addition, the phosphorus peak position at 133.5 eV is consistent with phosphorus atoms in a highly oxidized state.

Structural characterization of functionalized CNTs

microscopy of the pristine MWCNTs. Electron O-MWCNTs, and P-MWCNTs (Fig. 2) shows no significant changes in MWCNT morphology upon oxidation or phosphorus functionalization. To obtain resolved SEM images without charging, each sample was Au sputtercoated for 5 min prior to SEM imaging. Based on the sputtering conditions, this coated ca. 15 nm of Au on the nanotube surface, increasing the observed MWCNT diameter by ca. 30 nm. The carbon nanotubes used in this study had an outer diameter of ca. $15(\pm 5)$ nm. Consequently, in each SEM image, the nanotubes had diameters of ca. 40-50 nm (left-side images of Fig. 2). High-resolution TEM (HRTEM) (right-side images of Fig. 2) revealed MWCNTs with the expected outer diameter of 15 ± 5 nm, indicating that in spite of rigorous chemical (i.e., reflux in HNO₃, H₃PO₄, etc.) and physical (i.e., sonication) treatment, the carbon nanotubes maintained their multi-wall structure.

Thermal oxidative stability of functionalized CNTs

Thermal gravimetric (TG) analysis was used to evaluate the thermal oxidative stability of the pristine MWCNTs, O-MWCNTs, and P-MWCNTs (Fig. 3). These analyses were only conducted in air, as purified MWCNTs are thermally stable in an inert atmosphere up to 1000 °C, the upper temperature limit of the TG instrument [41, 42]. The TG plots (Fig. 3a) depict mass loss as a function of temperature; derivative curves (DTG) (Fig. 3b) depict the rate of mass loss as a function of temperature. $\Delta T_{\rm dmax}$ is the difference in peak maxima of the DTG curves between different samples and thereby provides a metric to assess the effect of oxidation or phosphorus incorporation on thermal stability. As compared to pristine MWCNTs, the O-MWCNTs were less thermally stable (O-MWCNTs $\Delta T_{\rm dmax}$ between -3 and -35 °C), and had the same char



Fig. 2 (*Left*) Scanning electron microscopy (SEM) and (*Right*) transmission electron microscopy (TEM) of **a** pristine MWCNTs, **b** oxidized MWCNTs (O3-Control), **c** phosphorus-functionalized

sample P4

yield (ca. 7 mass%). Functionalization of the O-MWCNTs with phosphorus, however, always resulted in higher char yields (ca. 10–18 mass%) and significant improvements in thermal oxidative stability. For example, P-MWCNTs

MWCNT sample P3 and d phosphorus functionalized MWCNT



Fig. 3 a Thermogravimetric (TG) and **b** derivative thermogravimetric (DTG) analyses of functionalized MWCNT powders in air at a rate of 10 °C min⁻¹. $T_{\rm dmax}$ represents the temperature of maximum rate of mass loss; $\Delta T_{\rm dmax}$ represents the difference in $T_{\rm dmax}$ between pristine and functionalized MWCNTs. Figure 3a, b share a common *x*-axis. **c** Thermal stability improvement of P-MWCNTs, with phosphorus concentrations reported in atomic percent (at%), as measured by X-ray photoelectron spectroscopy (XPS)

 $\Delta T_{\rm dmax}$ increased between 98 and 153 °C compared to their corresponding O-MWCNTs, in agreement with results from Ortega [38]. These improvements were directly related to the amount of phosphorus loaded onto the P-MWCNT, as determined by XPS and reported in at% (Fig. 3c).

Surface morphology of polymer CNT composites and CNT aggregation state

SEM was used to assess the surface morphology of solution-blended polymer nanocomposites containing pristine MWCNTs, O-MWCNTs, or P-MWCNTs. Virgin polymer films, as well as PS and PMMA composites, containing 2 mass% P-MWCNT are shown in Figs. 4 and 5, respectively. The SI presents SEM images of the PS and PMMA composites containing 2 mass% pristine MWCNTs (Figs. S1a and S1c) and O3-Control (Figs. S1b and S1d).

SEM images of the virgin PS (Fig. 4a) and PMMA (Fig. 5a) films show smooth surfaces, largely devoid of structural features. When pristine MWCNTs were added to either PS (Fig. S1a) or PMMA (Fig. S1c), the polymer surfaces became rough, and many CNT aggregates were observed at the surface. Poor dispersion of pristine MWCNTs in both PS and PMMA has been observed in previous studies [11, 27, 28]. Functionalization of the MWCNTs with oxygen (O3-Control) improved nanotube dispersion in PS, delivering PS composites with smoother surfaces and less nanotube aggregation (compare Figs. S1a and S1b). PMMA composites containing O-MWCNTs (Fig. S1d), however, still had rough surfaces and some small surface aggregates of CNTs.

In contrast to the SEM of PS composites containing pristine MWCNTs or O-MWCNTs, all SEM images of the P-MWCNT_PS nanocomposites (Fig. 4b–d) reveal smooth



Fig. 4 Scanning electron microscopy (SEM) of polystyrene (PS) films containing **a** PS, **b** P1(2%)_PS, **c** P3(2%)_PS, and **d** P4(2%)_PS. Surface CNT aggregates are highlighted with *white circles*. The *insets* show higher-resolution (500 nm) images of the CNT surface aggregates



Fig. 5 Scanning electron microscopy (SEM) of poly (methyl methacrylate) (PMMA) films containing **a** PMMA, **b** P2 (2%)_PMMA, **c** P3 (2%)_PMMA and **d** P4(2%)_PMMA. Surface CNT aggregates are highlighted with *white circles*. The *insets* show higher-resolution (500 nm) images of the CNT surface aggregates

surfaces, with very few P-MWCNT surface aggregates. The number of surface aggregates (see highlighted regions in Fig. 4) increased slightly as the P-MWCNT phosphorus content increased (for example, compare Fig. 4b, d). Closer inspection of these surface aggregates revealed random tangles of P-MWCNTs dispersed throughout the PS matrix, as seen in the higher-resolution (500 nm scale) SEM images of Fig. 4. In all cases, individual P-MWCNT tube diameters were ca. 40–50 nm, as observed in the SEM images of P-MWCNT nanoparticles (Fig. 2). SEM images also revealed that some P-MWCNTs were shorter than the original MWCNTs (i.e., <5 μ m), most likely a result of the sonication used to prepare the polymer composites [26, 43].

While the surfaces of the P-MWCNT_PS composites were quite smooth with few surface aggregates, the P-MWCNT PMMA composites had a completely different surface morphology. SEM of each P-MWCNT_PMMA composite revealed significantly rougher surfaces than the P-MWCNT_PS composites (compare Figs. 4b-d to 5b-d) the virgin PMMA film (Fig. 5a). In every or P-MWCNT PMMA composite, numerous, micrometerscale surface aggregates were observed (see highlighted regions in Fig. 5). Higher-resolution SEM images revealed that these surface aggregates were bundles of P-MWCNTs. The frequency with which nanotube aggregates were observed on the surface of the P-MWCNT_PMMA composites suggests that the P-MWCNTs did not disperse as well in PMMA as they did in PS.

Thermal stability of polystyrene CNT composites

The thermal stability of PS nanocomposites was assessed with TG in nitrogen gas (N_2) (Fig. 6) and in air (Fig. S2). The metrics used to evaluate and compare the TG data were ΔT_{T5} and ΔT_{dmax} . T5 is the temperature corresponding to 5% mass loss, reflecting the onset of thermal degradation. $T_{\rm dmax}$ is the temperature for the peak mass loss rate, reflecting maximum thermal stability improvement. ΔT_{T5} and ΔT_{dmax} are the differences in these metrics between neat polymer and polymer CNT composites. Table 1 contains the TG metrics for the PS composites. Larger positive values of ΔT_{T5} and ΔT_{dmax} correspond to larger improvements in thermal stability. Differences in char yields, which can be observed as the mass% remaining at the end of each curve, are also used to compare polymer nanocomposite performance in TG.

Pyrolysis of polystyrene CNT composites in N_2

TG of the P-MWCNT_PS composites during pyrolysis (heating to 600 °C in N₂) revealed that P-MWCNTs increased PS thermal stability by as much as 33 °C (ΔT_{dmax}) (Table 1). This improvement scaled with (1) the amount of phosphorus on the P-MWCNTs (see Fig. 6) and (2) P-MWCNT loading in the polymer (see Fig. 6 inset). As a result, P4(10%)_PS (P4 is the P-MWCNT with highest phosphorus content) was the most thermally stable PS nanocomposite analyzed. The positive ΔT_{T5} TG metrics for every P-MWCNT_PS composite analyzed under N₂ (Table 1) indicated that these thermal stability improvements were initiated at the onset of thermal degradation. In contrast, the TG data showed that the O-MWCNTs were less effective than

Fig. 6 Thermogravimetric (TG) analyses of polystyrene (PS) nanocomposites collected in nitrogen at a rate of 10 °C min^{-1} . The primary plots show PS nanocomposites containing 10 mass% of CNT, with the legend indicating the type of CNT loaded in the PS matrix. The *inset* shows TG analysis of PS nanocomposites containing increasing mass% of P4 (P-MWCNT with 2.0 at% phosphorus, as determined by X-ray spectroscopy (XPS))

P-MWCNTs, enhancing PS thermal stability by a maximum of 19 °C ($\Delta T_{\rm dmax}$) and that pristine MWCNTs offered PS the least amount of thermal stability enhancement.

Figure 6 also shows that the P-MWCNT PS composites leave behind more char (mass residual at the end of the analysis) during TG in N₂ than films prepared with pristine MWCNTs or O-MWCNTs. The P-MWCNT(10%) PS composite char yield varied between ca. 20-30 mass% (compared to ca. 9 and 14 mass% for the O3-Control(10%) PS and MWCNT(10%) PS composites. respectively). For the P4 PS series (Fig. 6 inset), the amount of char was directly related to P-MWCNT loading. However, the amount of char was inversely related to P-MWCNT phosphorus content when comparing different P-MWCNT PS composites at the same (10 mass%) loading.

Combustion of polystyrene CNT composites in air

TG of the same representative PS nanocomposites analyzed during combustion (heating to 600 °C in air) is presented in Fig. S2, with corresponding TG metrics presented in Table 1. These data revealed that P-MWCNTs also increased PS thermal oxidative stability more effectively than either pristine MWCNTs or O-MWCNTs, with a maximum improvement of ca. 52 °C (ΔT_{dmax}). During combustion, each P-MWCNT promoted significant char formation in PS. Analysis of the TG plots (Fig. S2) and corresponding metrics (Table 1) did not reveal a clear trend between thermal stability improvement (or char-forming ability) and phosphorus loading/content; however, it was apparent that higher phosphorus loadings deliver the most polymer protection.

In contrast, pristine MWCNTs only moderately improved PS thermal oxidative stability; these



			Auron (a) and (1		
Loading in	Pristine MWC	TN C	03-Control		P1		P3		P4	
PS/Mass%	$\Delta T_{\mathrm{T5}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$	$\Delta T_{T5}/^{\circ}C$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{T5}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{T5}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$	$\Delta T_{\mathrm{T5}}/^{\circ}\mathrm{C}$	$\Delta T_{ m Tdmax}/^{\circ} m C$
(a)										
0	0 (2.3)	0 (0.1)	0 (2.3)	0 (0.1)	0 (2.3)	0 (0.1)	0 (2.3)	0 (0.1)	0 (2.3)	0 (0.1)
0.5	3.6 (0.2)	0.3 (0.3)	9 (0.5)	2.7 (0.4)	2.2 (0.4)	0.3 (0.3)	13.3 (0.6)	5.3(0.3)	6.7 (1.3)	3.9 (0.3)
1	2.7 (0.6)	-2.4 (0.2)	5.6 (1.7)	5.7 (0.4)	6.5 (0.6)	3.4 (0.7)	10.8 (1.4)	5.1(0.8)	14.6(0.6)	8.5 (0.2)
2	5.3 (0.2)	-0.4 (0.1)	8.8 (0.9)	5.8 (0.3)	11.9 (0.4)	11.3 (1.5)	15.9 (0.5)	11 (0.3)	18.2 (0.7)	14.1 (0.5)
10	10.8 (0.1)	3.9 (0.1)	16.8 (0.7)	19.2 (0.6)	17.2 (0.4)	22.3 (2.3)	22.2 (1)	25.7 (0.5)	18 (1.4)	33.3 (0.3)
(q)										
0	0 (1.7)	0 (3.9)	0 (1.7)	0 (3.9)	0 (1.7)	0 (3.9)	0 (1.7)	0 (3.9)	0 (1.7)	0 (3.9)
0.5	4.3 (1.7)	14.3 (8)	8.2 (2.9)	-4.4 (12.4)	-1.7 (0.5)	-1.6 (2.6)	10.1 (1.4)	-4.3 (0.9)	-0.7 (1.4)	7.4 (8.5)
1	-8 (0.4)	5.3 (8)	18.4 (1.6)	25.3 (6.6)	6 (4.1)	12.7 (5.4)	-9.5 (0.4)	-11.2 (0.4)	6.4(1.4)	32.7 (7.3)
2	-9.5(0.7)	-55.4 (3.4)	12.4 (3.8)	24.4 (10.9)	11.3 (4.5)	24.5 (1.6)	0.2 (3.4)	7.3 (4.8)	1.3 (1.4)	29.2 (4)
10	37.6 (1)	18.5 (1.4)	30.3 (14.3)	27 (5.2)	29.4 (7.1)	52 (4.5)	9.1 (2)	40.8 (1)	22.5 (2.7)	36.8 (6.6)
T5 is the tempt CNT_polymer	erature of 5% main composites. Data	ss loss. T _{dmax} repre a represent average	sents the temperature values of sample	ure of maximum ra ss tested in triplicat	the of mass loss. Δ the with standard of	T_{T5} and ΔT_{dmax} ard deviations reported	e the differences i 1 in error bars	in these metrics bet	ween the untreat	ed polymer and

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improvements were inconsistent and did not correlate with MWCNT loading. O-MWCNTs also improved PS thermal oxidative stability, increasing $\Delta T_{\rm dmax}$ by ca. 25 °C with loadings above 1 mass%. The similarity (within error) in the O3-Control PS data suggests that a maximum thermal oxidative stability improvement was reached at low O-MWCNT loadings (ca. 1 mass%).

Thermal stability of PMMA CNT composites

TG was used to assess the thermal stability of PMMA nanocomposites in N_2 (Fig. 7) and in air (Fig. S3). Inspection of the TG plots and the TG data reveal that trends were less clear than those observed in the PS composites. Evaluating the thermal performance of each PMMA nanocomposite required closer inspection of the TG metrics provided in Table 2.

Pyrolysis of PMMA CNT composites in N₂

TG of the P-MWCNT_PMMA nanocomposites pyrolyzed in N₂ reveals that only the high phosphorus content P-MWCNTs (i.e., P4) enhanced PMMA thermal stability (Fig. 7 inset), with P4(10%)_PMMA delivering a modest improvement of ca. 9 °C (ΔT_{dmax}). The corresponding TG metrics for the P4_PMMA series (Table 2) indicated the presence of phosphate imparted stability improvements in the initial stages of thermal degradation (before 300 °C), where modest improvements in the ΔT_{T5} metric correlated with P4 loading in the polymer (Table 2).

Similar to P-MWCNTs, pristine MWCNTs and O-MWCNTs only moderately improved PMMA thermal stability, with maximum $\Delta T_{\rm dmax}$ increases of ca. 7 °C and ca. 8 °C, respectively (Table 2). In contrast to P-MWCNTs, however, these increases were not associated with ΔT_{T5} improvements that would indicate the thermal stability imparted during the early stages of PMMA degradation. Rather, pristine MWCNTs and O-MWCNTs appear to protect PMMA later during the higher temperature degradation events above 300 °C (Fig. 7). In terms of char yield, the pristine MWCNTs consistently delivered the highest char yields in PMMA pyrolysis. Thus, while the MWCNT(10%)_PMMA composite yielded ca. 24 mass% residue at the end of the TG analysis, composites containing similar loadings of P-MWCNTs or O-MWCNTs only left behind ca. 12–15 mass% char (Fig. 7).

Combustion of PMMA CNT composites in air

TG of the same PMMA composites analyzed during combustion in air are presented in Fig. S3 and Table 2. Fig. 7 Thermogravimetric (TG) analyses of poly (methyl methacrylate) (PMMA) nanocomposites collected in nitrogen at a rate of 10 °Č min⁻¹. The primary plots show PMMA nanocomposites containing 10 mass% of CNT, with the legend indicating the type of CNT loaded in the polymer matrix. The inset show PMMA nanocomposites containing increasing mass% of P4 (P-MWCNT with 2.0 at% phosphorus, as determined by X-ray spectroscopy (XPS))



These data show that P-MWCNTs were consistently more effective than MWCNTs or O-MWCNTs in improving PMMA's thermal oxidative stability during the initial stages of PMMA thermal degradation (ΔT_{T5}). For every P-MWCNT_PMMA composite, ΔT_{T5} increased by >11 °C, with a maximum ΔT_{T5} of ca. 36 °C for P2 (10%)_PMMA (Table 2). However, just four of the twelve P-MWCNT_PMMA composites showed a ΔT_{dmax} improvement of >10 °C (Table 2). Only at 10 mass% P-MWCNT loading did the measured ΔT_{dmax} increases correlate with the amount of phosphorus loaded into PMMA, delivering a maximum improvement of ca. 13 °C (Table 2).

While the TG data showed that pristine MWCNTs can also increase PMMA ΔT_{T5} and ΔT_{dmax} by as much 16 °C and 11 °C, respectively (Table 2), no trends were observed with respect to pristine MWCNT loading in the polymer. In contrast, as O-MWCNT loading increases in PMMA, the ΔT_{T5} metric systematically increased from ca. 3 to 23 °C (Table 2); this delay to the onset of PMMA degradation was matched by a systematic decrease in ΔT_{dmax} from ca. 16 to 8.5 °C.

In terms of char formation, char yields for the P-MWCNT(10%)_PMMA series increased from ca. 15–20 mass%, in correlation with phosphorus loading (Fig. S3), indicating that P-MWCNTs enhanced PMMA char formation during combustion in air. The same loading of pristine MWCNTs in PMMA delivered comparable char yields (ca. 21 mass%), while O-MWCNTs did not enhance char formation in the polymer. Of all the PMMA nanocomposites studied, the sample containing the highest phosphorus loading (i.e., P4 (10%)_PMMA) protected PMMA most effectively during combustion, delivering $\Delta T_{T5} = 22.5(\pm 0.5)$ °C, $\Delta T_{dmax} = 13.2(\pm 1.3)$ °C, and ca. 20 mass% char.

Analysis of TG residues from P-MWCNT polymer composites

Analysis of TG residues from eight representative polymer composites (containing 10 mass% P-MWCNT) is presented in Table 3. Each residue was analyzed by SEM, EDS and XPS. Total phosphorus content in each composite was estimated from P-MWCNT mass loadings in the polymer and the P-MWCNT phosphorus content measured by EDS and XPS (both measurements yielded similar values for P-MWCNT phosphorus content). For example, the P4 (10%)_PS composite, which had 10 mass% P4 (with ca. 2 at% phosphorus), contained ca. 0.2 at% phosphorus.

SEM of the TG residues consistently revealed densely packed aggregates of carbon nanotubes (a representative image is presented with Table 3). EDS measurements of each sample indicated that more phosphorus remained in the TG residues than the original phosphorus loading in each respective polymer composite. When the same nanocomposites were combusted in air, the amount of phosphorus was always approximately twice as high as those pyrolyzed in N₂. However, the measured phosphorus content was consistently less than expected had the residues been comprised of just the original P-MWCNTs, suggesting that additional carbon moieties were present.

Flammability assessments through microcombustion calorimetry

Microcombustion calorimetry (MCC) was used to evaluate the flammability characteristics of representative PS nanocomposites (Fig. 8 and Fig. S4a) and PMMA

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Loading in	Pristine MW(CNT	O3-Control		P2		P3		P4	
PMIMA/ Mass%	$\Delta T_{ m T5}/^{\circ}{ m C}$	$\Delta T_{ m Tdmax}/^{\circ} m C$	$\Delta T_{ m T5}/^{\circ} m C$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$	$\Delta T_{ m T5}/^{\circ} m C$	$\Delta T_{\mathrm{Tdmax}}^{\circ}$ C	$\Delta T_{ m T5}/^{\circ} m C$	$\Delta T_{ m Tdmax}/^{\circ} m C$	$\Delta T_{ m T5}/^{\circ}{ m C}$	$\Delta T_{\mathrm{Tdmax}}/^{\circ}\mathrm{C}$
<i>(a)</i>										
0	0 (3.7)	0 (2.7)	0 (3.7)	0 (2.7)	0 (3.7)	0 (2.7)	0 (3.7)	0 (2.7)	0 (3.7)	0 (2.7)
0.5	1.9 (2.3)	2.8 (0.1)	-7.5 (0.9)	5.9 (0.3)	0 (0.4)	1.6 (0.2)	-1.3(1.1)	-3.4(0.1)	1.6 (1.1)	6.8 (0.5)
1	0.5(0.4)	3.3 (0.2)	-12.6 (3.5)	8.2 (0.8)	3.1 (0.5)	2.6 (0.1)	1.6(0.6)	-3.7 (1.2)	3.3 (0.5)	0.1 (0.7)
2	-5.6 (1.4)	3.8 (1)	6.4(0.4)	6 (0.2)	2.4 (0.2)	3.3 (0.3)	-0.1 (1.2)	1.1 (1.5)	6.6(0.2)	2.2 (0.7)
10	-4.1 (7.7)	7.3 (0)	12 (0.2)	7.6 (0.7)	6 (2.5)	4.8 (0.9)	1.2(0.1)	5.1 (1.6)	10.8 (0.7)	9 (0.5)
(q)										
0	0 (5.2)	0 (5.6)	0 (5.2)	0 (5.6)	0 (5.2)	0 (5.6)	0 (5.2)	0 (5.6)	0 (5.2)	0 (5.6)
0.5	10.8 (3.7)	10.9 (0.7)	3.1(0.4)	16.3 (1.9)	14.1 (3.4)	7.7 (2.6)	13.5 (1.4)	-1.2 (1.2)	11.7 (0.7)	-1.7 (0.8)
1	15.8 (1.2)	11.4(1.1)	8.2 (2)	17 (1)	15.4 (1.2)	11.1 (1.4)	13.8 (0.4)	-16.2 (1.7)	23.4 (0.1)	-15 (1.4)
2	3.5(0.9)	10.4(0.6)	14.9 (0.3)	13.9 (0.5)	17.7 (0.8)	12.7 (2)	17.8 (1)	-8.5(0.3)	23.1 (2)	10.5 (2.8)
10	13.6 (2.1)	-8.1 (1)	23.1 (0.5)	8.5 (0.3)	35.8 (0.7)	2.6 (0.7)	21.8 (1.4)	8.1 (1)	22.5 (0.5)	13.2 (1.3)
<i>T5</i> is the temp CNT_polymer	erature of 5% ma: composites. Dati	ss loss. T _{dmax} repre a represent average	esents the temperatu e values of samples	re of maximum rais tested in triplicat	te of mass loss. Δ ie with standard of	$T_{ m T5}$ and $\Delta T_{ m dmax}$ ard	e the differences in	n these metrics bet	ween the untreate	d polymer and

nanocomposites (Fig. 9 and Fig. S4b) containing MWCNT and P-MWCNT. The following MCC measures of effectiveness are presented: heat reduction capacity (HRC), total heat release (THR), char residue reported in mass%, and change in temperature of peak heat release rate (ΔT_{Tpeak}). HRC is a measure of the peak heat release rate, with lower HRC values corresponding to less intense combustion; THR is a measure of the total fuel available in a fire and can be used to indicate the degree that each CNT additive protects the polymer; increases from expected Char Residue indicate that this protection is through the formation of a char layer, while decreases from expected Char Residues may indicate nanoparticle participation in a gas-phase flame-retardant mechanism. Positive increases in ΔT_{Treak} between untreated polymer and the polymer composite are analogous the ΔT_{dmax} increases measured in TG, providing another metric to assess thermal stability improvement.

Flammability characteristics of PS composites

The MCC analysis of PS nanocomposites containing P-MWCNTs (sample P1) or pristine MWCNTs is presented in Fig. 8, with representative MCC plots provided in the SI (Fig. S4a). When low concentrations of the P-MWCNTs (i.e., 0.5-1 mass%) were added to PS, no HRC reductions were observed (Fig. 8a). However, as P-MWCNT loading increased to 1 mass%, the HRC was reduced by 18%. P-MWCNTs continued to lower the intensity of PS combustion as P-MWCNT loadings were increased from 1 to 10 mass%, where the HRC reductions exceeded 35%. No significant reductions in THR were observed (Fig. 8b) as the amount of P-MWCNT in PS was increased from 0.5 to 2 mass%, and char yields correlated with P-MWCNT loading in the polymer (Fig. 8c). However, when P-MWCNT loading reached 10 mass%, THR was significantly reduced by 27%, and char yield increased above 19 mass%, indicating that P-MWCNTs at these concentrations were lowering the composite's flammability by forming a protective char barrier. This is in agreement with the high char yield observed in the TG analysis of the P-MWCNT (10%)_PS nanocomposites (Fig. 6). Regarding thermal stability, ΔT_{Tpeak} improved to ca. 27 °C as P1 loading is increased to 10 mass% in PS (Fig. 8d), in agreement with the ΔT_{dmax} increase (ca. 22 °C) measured during the TG N₂ analysis of the same composite (Table 1).

PS composites with low (0.5 mass%) loadings of pristine MWCNT delivered a 20% reduction in the *HRC* (Fig. 8a) and no significant reductions in *THR* (Fig. 8b), similar to what was observed for P1 (0.5%)_PS. However, increasing MWCNT loading to 10 mass% provided only moderate improvements beyond the initial 20% *HRC* reduction, along with a 14% reduction in *THR* (Fig. 8b).

Polymer composite	Phosphorus content/at%			
	Calculated in Composite*	Measured in residue from N_2 analysis EDS (XPS)	Measured in residue from air analysis	
P3 (10%)_PS	0.1	0.4 (0.3)	0.7 (0.7)	
P4 (10%)_PS	0.2	0.6 (0.4)	1.1 (0.9)	
P3 (10%)_PMMA	0.1	0.4 (0.4)	0.9 (0.6)	
P4 (10%)_PMMA	0.2	0.4 (0.3)	0.9 (0.6)	

Table 3 Energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) of TG residues from P-MWCNT-PS and P-MWCNT_PMMA nanocomposites



* P3 and P4 contained 1.2 and 2.0 at% phosphorus, respectively, as measured by XPS. The total phosphorus content in each polymer composite was estimated from the measured phosphorus content in the P-MWCNTs and the mass percent of P3 or P4 loaded into each polymer

The observed *THR* reductions correlated with increases in char yield (Fig. 8c) closely matching the percentage of MWCNT loaded into the polymer. No significant thermal stability improvements were observed for the MWCNT_PS composites beyond an initial 6 °C (ΔT_{Tpeak}) increase, in good agreement with the ΔT_{dmax} metrics measured in the TG N₂ analysis of the same composites (Table 1).

Flammability characteristics of PMMA composites

The MCC analysis of PMMA nanocomposites containing P-MWCNTs (sample P2) or pristine MWCNTs are presented in Fig. 9, with representative MCC plots provided in the SI (Fig. S4b). When P-MWCNTs were loaded into PMMA, *HRC* steadily decreased as P-MWCNT loadings increased (Fig. 9a). With 10% P-MWCNT loaded into PMMA, more than 42% *HRC* reduction was achieved. However, no significant *THR* reductions were observed (Fig. 9b), and corresponding char yields closely matched the P-MWCNT loading in the polymer (Fig. 9c). Finally, no significant increases in ΔT_{Tpeak} were observed in the

MCC analysis of the P2_PMMA samples, unlike the TG of the same composites, where moderate (>5 °C) ΔT_{dmax} increases were measured (Table 2).

In contrast to P-MWCNTs, even low (0.5 mass%) loadings of pristine MWCNT in PMMA resulted in a 37% decrease in HRC (Fig. 9a). HRC reductions continued to 48% as MWCNT loadings increased, similar to what was observed in MCC of the P2 PMMA nanocomposites. At MWCNT loadings of 0.5-2 mass%, no significant THR reductions were observed (Fig. 9b), and char yields generally matched MWCNT loadings (Fig. 9c). However, when 10 mass% MWCNT was added to PMMA, THR was reduced by more than 20% and char yields increased to 23%, indicating that pristine MWCNTs at this loading satisfactorily protected PMMA by forming a char barrier. Regarding thermal stability, ΔT_{Tpeak} improved to ca. 7 °C as MWCNT loading increased in PMMA (Fig. 9d). The char enhancement and ΔT_{Tpeak} increases observed with MCC of the MWCNT_PMMA composites closely matched analogous metrics measured in the TG N2 analysis of the same composites (compare Fig. 7 and Fig. 9).



Fig. 8 Microcombustion calorimetry (MCC) of representative polystyrene nanocomposites containing pristine MWCNTs or phosphorusfunctionalized MWCNTs, showing **a** heat release capacity (*HRC*), **b** total heat release (*THR*), **c** char residue, and **d** change in

Discussion

Thermal degradation of polystyrene and poly (methyl methacrylate)

To understand the effect of P-MWCNTs, it is first necessary to understand how flame retardants improve the thermal stability and reduce flammability of PS and PMMA. Significant research has been done to determine the thermal degradation mechanisms for both PS [44–50] and PMMA [50–56]. PS and PMMA both begin to degrade by thermal (homolytic) scission at weak links [57], such as the peroxidic linkages that were formed when the polymer was synthesized during radical polymerization. These initial reactions form radical species that cause radical transfer reactions to propagate down the polymer chain, most often via β -scission mechanisms [50].

For PS below 300 °C, the rate of radical recombination exceeds the rate of radical transfer propagations, and very little thermal degradation is observed. Above 300 °C, however, radical transfer rates dominate and the polymer begins to fall apart into volatile fragments. Thermal scission is favored at the carbon atoms bonded to the phenyl



temperature of peak heat release rate ($\Delta T_{\rm Tpeak}$). Data represent average values of samples tested in triplicate with standard deviations reported in *error bars*

ring in the polymer backbone, which act to stabilize these carbon-centered radicals and promote β -scission. PS degradation ultimately yields the styrene monomer (above 40%), as well as styrene oligomers (di, tri, and tetra) [50]. While there are several main scission products in PS thermal degradation, only one event is observed in TG, centered at approximately 410 °C for PS of MW 280,000 heated at 10 °C min⁻¹ in N₂, as shown in the present study (Fig. 6) [50]. Ultimately, all of the PS degrades, leaving behind no char. The presence of oxygen (i.e., combustion in air) lowers the thermal stability of PS by ca. 50 °C [50] due to generation of reactive oxygen species (i.e., •OH) that initiate the radical propagation mechanisms and ultimately unzip the polymer. Figure S2 clearly shows how untreated PS degrades at ca 360 °C during combustion in air. Antioxidants, such as organophosphorus compounds, can serve as flame retardants for PS by reacting with these radicals in the condensed and/or gas phase, thus slowing down the degradation process [50]. Char-forming flame retardants such as MWCNTs can also reduce PS flammability by forming a nanoparticle network to protect the polymer [11], although their effect on PS thermal stability is lessened because PS itself does not char.



Heat release capacity/J g⁻¹ K⁻¹



Fig. 9 Microcombustion calorimetry (MCC) of representative poly (methyl methacrylate) nanocomposites containing pristine MWCNTs or phosphorus-functionalized MWCNTs, showing a heat release capacity (HRC), b total heat release (THR), c char residue, and

Industrially relevant PMMAs (including the PMMA used in this study) are formed via radical polymerization and have a more complex degradation mechanism that begins ca. 190 °C, depending on the heating rate applied during thermal analysis [51-56, 58]. The first degradation event is due to thermal scission of head to head (H-H) linkages in the polymer chain formed during radical combination of PMMA. The second event begins at ca. 240 °C, with scission of unsaturated weak links in the polymer backbone, similar to the weak peroxidic linkages present in PS. The final degradation event is at ca. 350 °C, when random scission occurs throughout the polymer backbone, causing the chain to "unzip" and depolymerize to the monomer (methyl methacrylate) with approximately 95% yield [50]. This three-stage degradation pattern can be seen in the TG of the virgin PMMA sample plotted in Fig. 7.

In the first stage of thermal degradation, oxygen can suppress the low temperature scission of the weak H-H linkages although conversely the presence of oxygen can accelerate the main body scission events by ca. 50 °C and decrease PMMA's thermal stability [51]. Because this second phenomenon is similar to the effect oxygen can have on PS, antioxidant flame retardants, such as



d change in temperature of peak heat release rate (ΔT_{Tpeak}). Data represent average values of samples tested in triplicate with standard deviations reported in error bars

organophosphorus compounds, can also be effective in improving PMMA's thermal stability. While PMMA does not produce significant char during pyrolysis or combustion (ca 3.5 mass% char yield was observed both in Fig. 7 and Fig. S3), CNTs can be effective flame retardants for PMMA, if they are well-dispersed in the polymer and can form a protective nanoparticle network to reduce the polymer's flammability [17, 18].

Carbon nanotubes and phosphorus-based flame retardants

CNTs generally act as a flame retardant by a single mechanism in the condensed phase, forming a char barrier to protect the underlying polymer. To realize this flameretardant effect, it is necessary to achieve good CNT dispersion in the polymer matrix to allow the CNTs to form a CNT network [17, 18]. Phosphorus-based flame retardants (i.e., phosphates or reduced forms of phosphorus) may act in the condensed phase and/or the gas phase, as has been shown by many studies in the literature [4, 7, 35, 59–61]. Phosphates are particularly effective flame retardants when used in conjunction with polymers containing oxygen (i.e.,

PMMA), which they react with to form H_3PO_4 before thermal decomposition [4, 61]. This process impacts the condensed phase by forming a poly-phosphate barrier at elevated temperatures and also dilutes the gas phase when water is released during H₃PO₄ decomposition. In general, reduced forms of phosphorus can oxidize during combustion and be effective in the condensed phase to delay the onset of thermal degradation by reacting with other radicals formed during the depolymerization process [3, 7, 59]. Reduced forms of phosphorus may also form free-radical species in the gas phase, which can delay ignition or reduce heat release during combustion. Red phosphorus, arguably the most widely used form of phosphorus in flame-retardant applications, has been shown to act in both the gas phase as a radical inhibitor and in the condensed phase to promote char formation [3]. While conventional phosphate flame retardants are required in high concentrations (5–30 mass%) [3, 9], our hypothesis was that phosphorusmodified MWCNTs might impart a synergistic flame retardant effect in synthetic polymers at significantly lower loadings.

Characterization of the phosphorus functionalized carbon nanotubes

Our P-MWCNTs were prepared by reacting H₃PO₄ with MWCNTs that had been oxidized with HNO₃. Based on previous studies investigating this oxidation method, the O-MWCNTS contained a distribution of carboxyl (COOH), carbonyl (C=O), and hydroxyl (C-OH) functional groups [62]. XPS analysis of the P-MWCNTs suggests that phosphate was present at the P-MWCNT surface, as had been proposed by Ortega [38]. This was most likely due to phosphate esters formed by a condensation reaction between the phosphoric acid and the hydroxyl and/or carboxyl groups on the O-MWCNTs during annealing. TG of the P-MWCNTs clearly demonthat phosphorus functionalization of strated the O-MWCNTs increased their thermal oxidative stability, as was observed by Ortega [38]. This thermal stability appears largely due to phosphate enhancing char formation of the P-MWCNT during combustion, which delivered significantly higher char yields in the P-MWCNTs as compared to the pristine MWCNT or O-MWCNTs (Fig. 3a). By preparing a series of P-MWCNTs with different phosphorus loadings, we further demonstrate that this effect correlates with the amount of phosphorus bonded to the P-MWCNTs (more phosphorus delivers higher thermal stability). In spite of the physical and chemical treatments, the structural integrity of the P-MWCNTs was maintained, leaving them as good candidates for incorporation into the polymer films.

Thermal stability and flammability of polystyrene CNT composites

Our TG analysis clearly indicated that PS nanocomposites containing P-MWCNTs were more thermally stable than composites prepared with pristine **MWCNTs** or O-MWCNTs. P-MWCNTs improved PS thermal stability and thermal oxidative stability by a measure directly related to the amount of phosphorus loaded into the polymer matrix (Fig. 6, S2 and Table 1), and corresponding MCC analysis of the P1 PS composites (Fig. 8 and Fig. S4a) showed how higher phosphorus content also made PS less flammable. Combined with an analysis of P-MWCNT PS TG residues (Table 3), our data indicate that as the P-MWCNT PS nanocomposite matrix thermally degraded, P-MWCNTs were able to form the nanoparticle network required to provide a condensed-phase flame-retardant effect [17].

During pyrolysis of the P-MWCNT PS composites, thermal stability improvements were measured in eleven of the twelve PMWCNT_PS composites tested, with a maximum improvement of 33 °C (ΔT_{dmax}) (see Table 1) and significantly higher than expected char yields. These improvements were most likely due to the thermally stable P-MWCNTs forming a condensed phase network that protected the underlying PS and delayed thermal decomposition. During combustion in air (Fig. S2), PS thermal oxidative stability was enhanced by more than 52 °C ($\Delta T_{\rm dmax}$): an improvement that also increased with P-MWCNT loading (Table 1) and was associated with higher than expected char yields (Fig. S2). Each result highlights the importance of phosphorus in achieving the flame-retardant effect. In contrast, pristine MWCNTs offered no significant improvement to PS thermal stability, in agreement with previous studies [11]. Although O-MWCNTs were less thermally stable than pristine MWCNT or P-MWCNTs, they did improve PS thermal stability (to a lesser degree than P-MWCNTs), but did not promote any additional char formation. Their impact was most likely due only to improved dispersion in PS as a result of the functionalization, an effect demonstrated in previous studies [26, 27, 63]. Our SEM analysis supports this conclusion, as the O3-Control (2%) PS composite (Fig. S1b) had smoother surfaces and less CNT aggregation than those containing pristine MWCNTs (Fig. S1a).

Although MCC was conducted to investigate the flammability characteristics of the polymer composites, it also validated the thermal stability improvements observed in TG. The similarities between ΔT_{Tpeak} and ΔT_{dmax} data of the same composites confirmed the degree to which P-MWCNTs were better than pristine MWCNTs at improving PS thermal stability. The MCC data also indicated how PS flammability was reduced at the highest

P-MWCNT loading. At low concentrations (<2 mass%), the trends in HRC and THR reductions for the P1_PS and MWCNT_PS composites were similar (Fig. 8b) and were likely only due to the presence of an incombustible filler. However, as loadings increased to 10 mass%, HRC and THR reductions were larger for the composites containing P-MWCNTs, and their corresponding char residues increased above 19%, as was observed in TG. These effects were also clearly seen in the raw MCC data (Fig. S4a), which illustrated the advantage of using phosphorus-functionalized MWCNTs to reduce polystyrene flammability. At these higher phosphorus loadings, the flammability reductions were most likely due to the presence of phosphorus on the P-MWCNT acting in the condensed phase forming a barrier to protect the polymer. In contrast, MCC showed that pristine MWCNTs reduced PS HRC by generally the same amount at each loading above 1 mass% (Fig. 8a), consistently lowering the intensity of PS combustion by providing a heat and mass transfer barrier, even though they did not improve PS thermal stability. These data were similar to what Cipiriano et al. [11] reported in their study of PS composites containing pristine MWCNTs. The corresponding reductions in THR (Fig. 8b) and expected char yields were due to the stability of pristine MWCNTs, which do not pyrolyze in inert gas at temperatures below 1000 °C [41]. Since PS is a non-charring polymer, any char-enhancing features of the pristine MWCNTs could not be exploited to further reduce the composites' THR. Only at the highest MWCNT loading was there evidence of some polymer protection, when the THR decreased and the amount of char residue was slightly higher than the amount of MWCNT added.

Together, the TG and MCC analyses indicate that phosphorus played an important role in the P-MWCNT flame retardant mechanism. It is known that phosphates can form a condensed phase poly-phosphate protective barrier at elevated temperatures and can enhance char formation when acting as a flame retardant [7, 61]. While char yields of the MWCNT_PS composites matched MWCNT loading for each composite analyzed, higher P-MWCNT content in PS delivered significantly more char compared to the P-MWCNT loading in the polymer. Since PS itself is not char-forming, we conclude that the flammability reduction was primarily a result of the phosphorus inducing further char formation from the P-MWCNTs loaded into the PS, enhancing the P-MWCNTs ability to form a protective char barrier. The phosphate may also have reacted with oxygen moieties on the P-MWCNT surface, enabling H₃PO₄ formation and subsequent decomposition at high temperatures, a process which can promote more char in the condensed phase and impact the gas phase through water evolution. The underlying polymer can be protected by excess char during pyrolysis, delaying the onset of thermal degradation, increasing thermal stability and lowering flammability; each of these phenomena were observed in the TG and MCC of the P-MWCNT_PS composites in our study.

The phosphorus content in the TG residues (Table 3), and the excess char observed in the TG and MCC analyses all support the idea that P-MWCNTs act via a char enhancement mechanism. As the phosphorus in the P-MWCNTs enhanced the carbonaceous char yield, the amount of phosphorus present in TG residue was diluted. The result was a lower phosphorus content (at%) in the TG residue than expected had the char consisted only of the original P-MWCNTs (see Table 3). During combustion in air, some of this char was oxidized, increasing the total amount of phosphorus measured in the TG residue, compared to what was measured after the same sample was pyrolyzed in N₂. While the evidence for the condensedphase mechanism is clear, the inverse relationship between phosphorus content and char yield in the P-MWCNT (10%)_PS composites (Fig. 6) also suggests that some phosphorus may have volatized during pyrolysis and participated in a gas-phase flame-retardant mechanism in addition to providing fire protection in the condensed phase. Thus, it is likely that the phosphate impacted both the condensed-phase (char formation/enhancement) and gas-phase (POx volatilization and/or H₃PO₄ formation/decomposition) mechanisms.

Thermal stability and flammability of PMMA CNT composites

TG of the P-MWCNT_PMMA composites showed that P-MWCNTs can improve PMMA's thermal stability by suppressing the initial degradation events at temperatures below 240 °C. This early protection was evident in the TG N_2 analysis (Fig. 7) and was more significant during combustion in air (Fig. S3), where each P-MWCNT showed a significant improvement in the ΔT_{T5} metric (Table 2). In the best case (P2 (10%)_PMMA), ΔT_{T5} increased by ca. 36 °C; MCC of this same composite (shown in Fig. S4b) also clearly showed how the phosphorus-functionalized MWCNTs protected PMMA during this initial stage of degradation. In general, the TG air plots (Fig. S3) show that the second decomposition stage (which begins around 240 °C in virgin PMMA) began later for the P-MWCNT PMMA composites, but proceeded faster than the composites containing either pristine MWCNTs or O-MWCNTs. The TG and MCC data indicated that although P-MWCNT incorporation inhibited the initial formation of free radicals in the early stages of PMMA decomposition (below 240 °C), they did not slow the final propagation of PMMA decomposition. Therefore, in most cases, a significant improvement to the $\Delta T_{\rm dmax}$ was not observed for the P-MWCNT_PMMA composites. However, in four of the twelve P-MWCNT_PMMA composite systems (Table 2), $\Delta T_{\rm dmax}$ did increase by more than 10 °C, indicating P-MWCNTs have more potential to improve PMMA than what was realized in this study. These inconsistencies were most likely due to the poor dispersion of P-MWCNT in PMMA observed in the SEM analysis (Fig. 5).

Similarly, both pristine MWCNTs and O-MWCNTs offered PMMA limited thermal stability improvement. Although some thermal oxidative stability was observed in the TG air analysis of the O3-Control_PMMA series, it was not associated with any significant char enhancement or increases in $\Delta T_{\rm dmax}$. The improvement was most likely due to improved dispersion of the O-MWCNTs in PMMA, as was observed with O-MWCNTs in PS. While the SEM images of PMMA composites containing pristine MWCNTs or O-MWCNTs (Figs. S1c–d) did show rough surfaces and aggregation, the aggregates were much smaller than the micron-sized aggregates seen in the P-MWCNT_PMMA composites (compare Figs. 5b–d to Figs. S1c-d).

The MCC of the P2_PMMA composites showed that high *HRC* reductions (>42%) could be achieved with P-MWCNTs (Fig. 9a). However, these high *HRC* reductions were not accompanied by *THR* reductions or increased char yields beyond the amount of P-MWCNT loaded into the polymer. In fact, char yields were approximately half of what was expected based on P-MWCNT loadings, suggesting that some of the P-MWCNT had pyrolyzed during the MCC analysis to engage in a gasphase mechanism and that the P-MWCNTs did not completely form a protective char barrier in PMMA. While it should be noted that phosphorus often acts in both the condensed and gas phases of a fire, it is difficult to capture gas-phase flammability reductions using TG or conventional MCC [64].

The limited effectiveness of P-MWCNTs to protect PMMA in the condensed phase appears most likely due to poor P-MWCNT dispersion in the polymer. This not only limited P-MWCNTs potential to consistently improve PMMA's thermal stability (i.e., deliver higher ΔT_{dmax}), but also hindered their ability to form the nanoparticle network required to lower PMMA's flammability. Poor dispersion also contributed to MCC data variability, which was slightly higher than expected in the P-MWCNT PMMA composites where CNT agglomerations were regularly in SEM. In contrast, MCC observed of the MWCNT PMMA composites indicated that pristine MWCNTs at the highest loadings did form a char barrier to protect PMMA. It can be seen from the TG plots (Figs. 7 and S3) that virgin PMMA did produce some char (ca. 3.5%) during analysis in both N₂ and in air. Therefore,

unlike what was observed with the MWCNT_PS composites, the char-enhancing ability of MWCNT could be exploited in PMMA, increasing PMMA char formation, delivering the lower *THR*, higher char yield, and slightly improved thermal stability.

Our TG and MCC data showed how each nanoparticle (i.e., MWCNTs, O-MWCNTs, and P-MWCNTs) interact with PMMA during thermal degradation, participating in condensed-phase and/or gas-phase mechanisms. We conclude that the P-MWCNTs can be effective flame retardants for PMMA, but their potential was not fully realized due to poor dispersion within the PMMA matrix. CNTs need to be well-dispersed to form a uniform network/char layer in a polymer, and producing a uniform composite material remains a constant challenge. In their study of PMMA composites containing SWCNTs, Kashiwagi et al. showed how dispersion was the critical factor in maximizing many material properties including thermal stability and flammability [18]. All of our polymer composites were prepared by solution blending and casting. Though it is the most readily available laboratory method, polymer dispersion quality could be improved by adjusting many variables, including evaporation rate, solvent type, concentration, solvent/solute interactions, and sonication temperature/time [26].

MWCNT dispersion in polymer matrices can also be improved through MWCNT functionalization, which can decrease the significant Van der Waals forces holding the CNTs together. This effect has been shown in several studies of polymer composites that contain covalently modified MWCNTs, for example with silicon [32, 65] or nitrogen [66]. The SEM images in the present study qualitatively showed that the P-MWCNT dispersion was better in PS than it was in PMMA. This is plausible considering that PS and MWCNTs both have extended aromatic structures and delocalized pi orbitals. While the phosphorus functionalization of O-MWCNTs disrupted the CNT– CNT intermolecular bonding enough to facilitate better P-MWCNT dispersion in the PS matrix, it was not as effective in PMMA.

Our promising results highlight the importance of achieving good CNT dispersion in the polymer matrix in order to maximize P-MWCNTs flame retardant potential. This was reflected not only in the performance of the P-MWCNT nanocomposites, but also in how the MWCNT and O-MWCNT composites performed. Despite the fact that O-MWCNTs had lower thermal stability than pristine MWCNTs (Fig. 2), their functionalization allowed for more effective dispersion in both PS and PMMA, delivering more thermally stable composites containing pristine MWCNTs. The phosphorus functionalization highlighted in this study provides a route to significantly improve the

flame-retardant properties of MWCNTs, if dispersion can be optimized in the polymer matrix. Additionally, the maximum thermal stability improvements achieved with P-MWCNTs required a very small amount of P-MWCNT (0.5-10 mass%), whereas conventional organophosphorus flame retardants are used in higher loadings (5–30 mass%) [3, 9]. Using MWCNTs to support the flame-retardant phosphorus heteroatom allows one to take advantage of the P-MWCNTs improved thermal properties, as well as other CNT benefits (i.e., structural reinforcement, viscoelastic) when added to the polymer. Improved methods to increase phosphorus loading on P-MWCNTs would allow P-MWCNT to be used in polymers at lower loadings, most likely improving dispersion while delivering higher thermal stability.

Conclusions

In this study, phosphorus-functionalized MWCNTs (P-MWCNTs) were shown to be effective flame-retardant additives in polystyrene (PS), increasing PS thermal stability in a manner directly related to phosphorus loading, and decreasing PS flammability. P-MWCNTs also showed potential to increase the thermal stability of poly (methyl methacrylate) (PMMA) with improved dispersion in the polymer matrix. Thermogravimetric (TG) analysis demonstrated that when phosphorus was bonded to oxidized MWCNTs, their thermal oxidative stability improved by 98-153 °C in proportion to phosphorus loading. TG demonstrated that P-MWCNTs improved PS thermal stability by 33 °C during pyrolysis in N₂, and by 52 °C during combustion in air. Microcombustion calorimetry (MCC) showed that P-MWCNTs also improved the flammability characteristics of PS at high phosphorus loadings, lowering heat release capacity by more than 35% and decreasing total heat release by 27% while doubling the char yield. P-MWCNTs acted primarily by delaying the onset of thermal degradation, enhancing char formation of the MWCNTs, and forming a protective char barrier within the PS composite. These effects were achieved at lower loadings than typically required for commercial phosphate flame retardants. When P-MWCNTs were loaded into PMMA, they improved the thermal oxidative stability of PMMA by more than 40 °C, and offered moderate improvements to PMMA thermal stability during pyrolysis in N2. MCC of the P-MWCNT_PMMA composites indicated that significant reductions in the polymer's heat release capacity could be achieved, but that P-MWCNTs did not form the network char barrier required to protect PMMA in the condensed phase. The observation that the flame-retardant effects of P-MWCNTs were less in PMMA

than in PS indicates a strong correlation between dispersion quality and flame-retardant effectiveness.

This study demonstrates the potential for using phosphoric acid functionalized MWCNTs as flame retardants in synthetic polymers. More importantly, it shows how specifically modifying carbon nanotubes with flame-retardant functional groups, and incorporating them into synthetic polymers can impart synergistic flame-retardant effects. Realizing the full potential of this approach will require optimized CNT functionalization strategies as well as improved polymer-CNT dispersion methods to maximize their impact upon scale-up. With the right approach, functionalized carbon nanotubes can become more effective flame retardants, maximizing their potential at lower loadings. Not only do functionalized MWCNTs represent a viable alternative to current commercial flame retardants, but they can enhance a diverse range of properties (thermal and structural) when incorporated into polymer systems.

Supporting information

The supporting information is available free of charge at DOI: XXX. SEM images of polymer composites (Fig. S1), TG air analysis of CNT_PS composites (Fig. S2), TG air analysis of CNT_PMMA composites (Fig. S3), Representative MCC plots (Fig. S4), Label codes (Table S1).

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest. Any opinions, findings and conclusions, or recommendations expressed in this manuscript are those of the authors and do not reflect the views of the US Air Force or the US Navy.

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