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Flammability of polyesters

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ABSTRACT

The flammabilities of a series of polyesters, varying both the diol length and the degree of aromaticity of the diacid units were evaluated using cone calorimetry. Addition of inorganic additives, copolymerization with sulfoisophthalate ionomeric units and with the phosphorous flame retarding agent, phospholane, were also examined. A strong, linear relationship between the polymer carbon:hydrogen ratio and various flammability indicators was established. The phospholane was demonstrated to produce only a modest reduction in flammability, whereas the isomeric comonomer produced an unexpectedly strong reduction in all aspects of flammability tested. Addition of inorganic modifiers resulted in varied, and relatively modest changes in polyester flammability.

1. Introduction

Polymer flammability is a key property for commercial products ranging from textiles and home furnishings, electronics, transportation, and other consumer and industrial applications. The polyesters, especially poly(ethylene terephthalate), PET, are an important family of polymers which transcend these applications, with sales in the billions of pounds per year. The traditional means of flame retarding polyesters, use of bromoaromatic compounds in tandem with antimony oxide is becoming non-viable, the subject of legislative actions across the world. In the search for alternative means of flame retarding polyesters, *Y. Wang and coworkers,* [1] examined the use of a phosphorous-modified liquid crystal copolyester, PLCP, as an additive for PET, finding that 15 wt% addition of the modifier decreased flammability while enhancing the mechanical properties compared to virgin PET. The limiting oxygen index (LOI) for this PET blend increased from 21.3 to 32.4 and there was no dripping found during burning. In such a blend the PLCP short fibrils behave as a reinforcing agent, much like glass fibers in polymer composites. *Y. Wang and coworkers,* [2] then studied a phosphorous-containing copolyester/montmorillonite nanocomposite incorporating 2-carboxyethyl(phenylphosphinic) acid, HPPA, as the char-catalyzing active component. By introducing a small amount of organoclay, there was an improvement in both the thermal stability and the flame retardancy of the PET-co-HPPA. The LOI of the PET-co-HPPA increased 34.0 with 1 wt% of organoclay (27.0 without the addition of clay [3]); 2 wt% of organoclay was required in order for the nanocomposite to achieve a UL-94 V-0 rating. The increase in organoclay from 1 to 2 wt% did not increase the LOI, but did increase the viscosity of the polymer as a means of retarding dripping during the burning event. Copolymerization of PET with bis(4-carboxyphenyl phenyl phosphine oxide), BCPPO, was investigated by the same workers. By incorporating 5 wt % of BCPPO, the copolymer exhibited good fiber-forming properties, improved flame retardancy (LOI of 31.6), and a high glass transition temperature and enhanced thermal stability [3]. Other approaches to flame retarding PET have made use of combinations of triaryl phosphine oxide, [4] red phosphorous/aluminum oxide, [5] and dichlorobromophenyl phosphate [6]. Modification of polymer flammability by the addition of non-halogenated additives and inorganic fillers has been well reviewed [7].

The present work examines the flammability of a wide range of polyesters, in an effort to develop fundamental understanding of how composition affects their flammability, hopefully providing guidance to workers who then will integrate flame retardant systems to these polymers.

2. Experimental

2.1. Materials

Commercial polyester samples (intrinsic viscosities in units of dL/g) were obtained from KoSa (now Indorama, Spartanburg SC) and include: poly(ethylene terephthalate) (PET; 0.86), PET/0.35 wt% titanium dioxide (0.68), poly(butylene terephthalate) (PBT; 0.80), poly(trimethylene terephthalate) (PTT; 0.70), poly(ethylene

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Table 1
Cone calorimetry results.

Polymer		Heat released (KW/m^2)		(MJ/m^2)	% Char	Time (s) to
		Peak	Average	Total	Yield	Sustained burn
PET		1018	594	80.4	15.2	68.7
		990	576	86.7	15.2	69.6
		1017	554	78.4	14.6	74.5
	Mean	*1008*	*575*	*81.8*	*15.0*	*70.9*
	SD	*16*	*20*	*5.0*	*0.3*	*1.1*
PET/TiO_2		1154	430	78.8	16.5	61.6
		1089	549	77.4	18.8	64.5
		1266	536	82.3	15.3	71.9
	Mean	*1170*	*502*	*79.5*	*16.9*	*66.0*
	SD	*90*	*63*	*3.0*	*1.8*	*3.1*
PTT		1989	885	95.7	10.2	60.9
		2020	867	96.4	10.0	60.9
		2024	888	96.1	10.9	74.3
	Mean	*2011*	*880*	*96.1*	*10.4*	*65.2*
	SD	*19*	*11*	*0.4*	*0.5*	*7.9*
PBT		2058	977	108.6	8.2	55.2
		2018	969	107.7	8.3	57.5
		1924	959	106.7	8.5	53.0
	Mean	*2000*	*968*	*107.7*	*8.3*	*55.2*
	SD	*69*	*5*	*1.0*	*0.2*	*2.3*
PEN		503	298	61.1	39.7	76.8
		484	275	58.9	40.2	74.2
		491	274	54.5	43.4	83.8
	Mean	*493*	*282*	*58.1*	*41.1*	*78.3*
	SD	*10*	*14*	*3.0*	*2.0*	*5.0*
PETBB		845	256	70.7	25.8	82.8
		778	288	70.9	25.0	69.4
		889	313	73.4	23.8	73.4
	Mean	*837*	*286*	*71.7*	*24.9*	*71.9*
	SD	*56*	*29*	*1.0*	*1.0*	*2.1*
PET/5% clay		883	500	82.8	18.4	47.2
		833	521	83.0	18.5	48.5
		890	551	82.8	18.4	58.5
	Mean	*869*	*524*	*82.9*	*18.4*	*58.5*
	SD	*31*	*26*	*0.1*	*0.1*	*6.2*
PET/5% clay/POSS		690	469	84.7	19.6	35.4
		770	494	90.6	13.5	40.2
		701	472	85.2	18.2	34.7
	Mean	*720*	*478*	*86.8*	*17.1*	*36.8*
	SD	*43*	*14*	*3.2*	*3.2*	*3.0*
PET/C-nanofiber		719	382	72.4	22.2	71.0
		763	403	72.1	22.4	63.4
		780	411	71.8	22.3	62.9
	Mean	*754*	*399*	*72.1*	*22.3*	*65.8*
	SD	*31*	*15*	*0.2*	*0.1*	*4.5*
PET/P-ester FR #1		778	441	56.0	18.3	72.4
		912	433	59.9	16.3	72.1
		842	425	60.1	25.5	72.7
	Mean	*847*	*433*	*58.7*	*20.0*	*72.4*
	SD	*62*	*8*	*2.3*	*4.0*	*0.3*
PET/P-ester FR #2		998	472	62.2	16.2	72.5
		1002	358	67.0	14.2	81.9
		925	468	62.0	16.7	74.3
	Mean	*975*	*433*	*63.8*	*15.7*	*76.2*
	SD	*43*	*65*	*2.8*	*1.3*	*4.5*
PET/P-ester FR #3		1062	502	65.0	15.4	75.7
		1098	514	62.6	16.8	77.1
		869	469	60.3	15.4	77.7
	Mean	*1010*	*495*	*62.6*	*15.9*	*76.8*
	SD	*123*	*23*	*2.4*	*0.8*	*1.0*
PET/P-ester FR #4		837	469	59.4	29.0	72.1
PET/SIPE		640	339	67.2	23.2	67.9
		614	357	76.2	22.5	69.6
		826	439	70.0	26.3	61.2
	Mean	*693*	*378*	*71.1*	*24.0*	*66.2*
	SD	*116*	*53*	*4.6*	*2.0*	*4.4*
PET/SIPE/P-ester		462	312	65.8	24.3	65.4
		613	407	63.7	24.3	65.2
		559	358	65.7	21.9	73.4
	Mean	*545*	*359*	*65.1*	*23.5*	*68.0*
	SD	*76*	*48*	*1.2*	*1.4*	*4.7*