Green Application of Flame Retardant Cotton Fabric Using Supercritical Carbon Dioxide

SeChin Chang*, Brian Condon, and Jade Smith

Cotton Chemistry & Utilization (CCU) Research Unit, Southern Regional Research Center (SRRC), United States Department of Agriculture (USDA)-Agriculture Research Service (ARS), 1100 Robert E. Lee Blvd., New Orleans LA, 70124, USA. (Corresponding author: sechin.chang@ars.usda.gov)

ISSF 2012, May 13-16, 2012, San Francisco, CA

Mission

To increase cotton's consumption by inventing products and processes that demonstrate preferred use of cotton over competing fibers in needed and emerging applications involving plastics, textiles, and composites

Why and How Do We Use Flame Retardants

Resistance to ignition by specific sources such as cigarette or small open flames

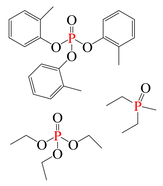
Fire behavior of materials used in the manufacture of following items are very important:

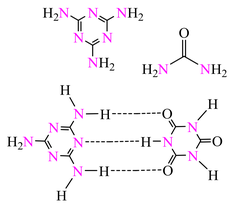
Wearing apparel (clothing), Upholstered furniture, Beds and bedding (mattresses), Curtains and draperies, Textile floor coverings (carpets)

- It can be achieved by the application of chemicals to the fibers before processing into a textiles
- The trend in the newly emerging chemistry is to develop of halogen (Cl and Br)-free flame retardant:
  Environmentally friendly and Non or reduced toxicity
- Current project is aimed evaluating the control of various organophosphorus, nitrogen and silicon precursors

Advantages of Flame Retardants Based on Phosphorous or Nitrogen Compounds

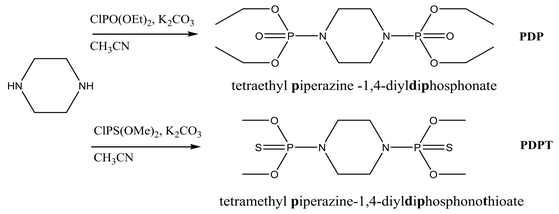
- **Phosphorous FRs:** tri-o-cresyl phosphate, dimethyl methyl phosphonate, triethyl phosphate…
  - applications: plastics, polyurethane foams, thermosets, coatings, and textiles
  - low toxicity: do not produce toxic smoke, toxic dioxins and furans.
  - environmentally friendly
- **Nitrogen FRs:** melamine cyanurate, urea, melamine…
  - low toxicity: absence of dioxin and halogen acids as well as low evolution of smoke.
  - *condensed phase - char formation
  - *gas phase - release of N_2
  - recyclability: less corrosive gases during combustion.
  - moderate price



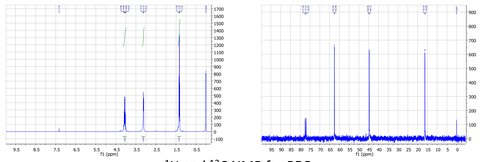


*Liang HB, Shi WF (2004) Polym Degrad Stab 84:525; Zhu SE, Shi WD (2003) Polym Degrad Stab 80:217; Horacek H, Grabner R (1996) Polym Degrad Stab 54:205

Synthesis and Characterized of Novel Flame Retardant Containing P and N



	PDP	PDPT
Yield (%)	96% (light yellow oil)	93% (white solid)
^{1}H NMR ($CDCl_3$), ppm	δ1.25 (t, 12H,-CH_3), δ3.38 (s, 8H, -CH_2-N), δ3.88 (m, 8H, -CH_2O-)	δ3.23 (t, 8H,-CH_2N), δ3.64 (d, 12H, -CH_3)
^{13}C NMR ($CDCl_3$), ppm	δ 16.4 (d, J_{C-P}=28 Hz), δ 40.2 (s), δ 61.5 (d, J_{C-P}=20 Hz)	δ 45.5 (t), δ 53.5 (d, J_{C-P}=20 Hz)
^{31}P NMR (H_3PO_4), ppm	-0.4 (s)	78.1 (s)



^{1}H and ^{13}C NMR for PDP

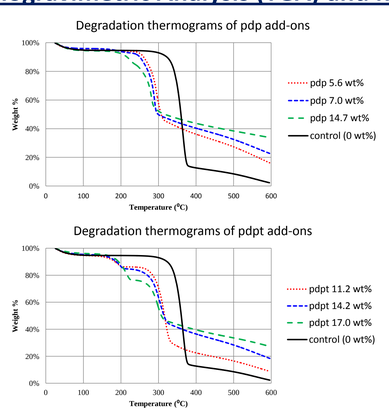
Innovative Method by Supercritical Fluid Assisted

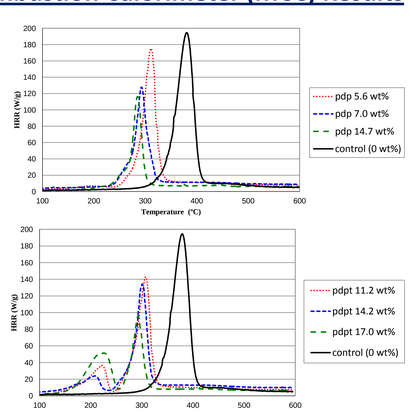
- ✓Target FR chemical synthesis by organic or inorganic reactions
- ✓Fabric treatment: scCO2 with co-solvent and Cure
- ✓Penetration or hydrogen bonding
- ✓Semi-durability

	Pressure (psi)	Temp,^{o}C	Time, h
Urea & $Na_3PO_4.12H_2O$	2000 - 3700	65 - 100	3 - 10
PDP	1800-2800	60 - 100	3 - 10
PDPT	1600-3100	80 - 95	3 - 10

Critical temperature (T_c): **32.1 ^{o}C**
Critical pressure (C_p): **1,070 psi** (73.8 bar)

Thermogravimetric Analysis (TGA) and Micro-scale Combustion Calorimeter (MCC) Results



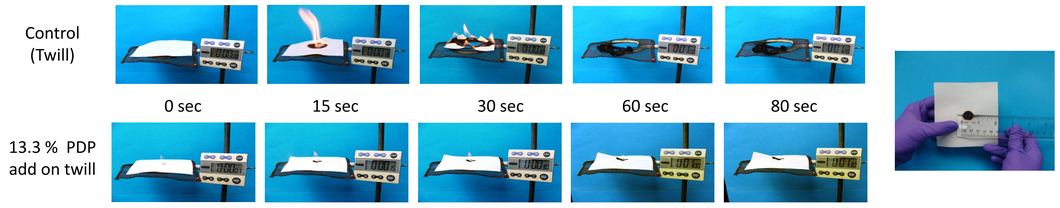


Samples add-on (%)		Onset of degradation (^{o}C)	Char % yield at 600 ^{o}C
Control	0	333.1	2.3
PDP		188.6, 271.9, 456.7	9.7
PDP w/fabric	5.6	276.3	16.2
	7.0	275.2	22.8
	14.7	268.6	33.7
PDPT		178.2, 300.6, 452.1	23.4
PDPT w/fabric	11.2	171.1, 295.9	8.8
	14.2	175.9, 281.8	18.5
	17.0	190.5, 279.9	27.3

Fabric add-ons (%)		THR (kJ/g)	HRR (J/g-K)	pHRR (w/g)	T_{max} (^{o}C)	Char yield (%)
Control twill		8.5 ± 0.1	178.0 ± 4.4	185.0 ± 5.7	366.6 ± 1.2	13.3 ± 0.4
PDP w/fabric	5.6	5.5 ± 0.3	146.3 ± 11.0	146.4 ± 11.6	304.2 ± 4.3	23.1 ± 2.1
	7.0	4.1 ± 0.1	121.0 ± 11.1	120.9 ± 10.7	293.0 ± 2.1	28.1 ± 0.6
	14.7	3.2 ± 0.1	103.3 ± 4.2	104.6 ± 3.1	282.5 ± 3.4	32.2 ± 0.8
PDPT w/ fabric	11.2	5.8 ± 0.4	113.3 ± 7.6	112.6 ± 7.7	302.7 ± 0.7	21.4 ± 1.4
	14.2	4.6 ± 0.1	115.0 ± 1.0	114.5 ± 0.8	300.6 ± 0.1	26.3 ± 3.3
	17.0	5.1 ± 0.4	83.0 ± 4.0	82.6 ± 2.9	291.6 ± 1.6	27.2 ± 3.9

Flammability Test (Modified pill*, Limiting Oxygen Index (LOI, ASTM D2863-00), and Vertical (ASTM D6413-08)

- Diameter of pill ~ 7 mm; diameter of the burn zone ~11 to 15mm << 25mm all pass
- The easiest flammability test is the pill test with a fabric placed on a ring stand so both sides of the fabric are equally exposed to air

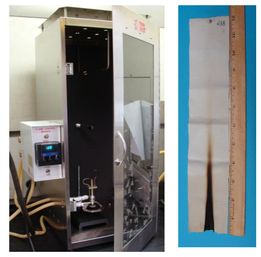


*Method of Blanchard, E.J.; Graves, E.E.; Salame, P.A. J. Fire Sciences, **2000**, *18*, 151-163

- The minimum amount (%) oxygen needed to sustain a flame when a sample is burned in an atmosphere of nitrogen and oxygen
- LOI values describe the flammability potential materials

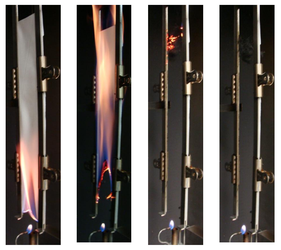
- LOI < 21 ⇒ flammable in air (18% O_2) upon ignition
- 21< LOI < 28 ⇒ slow burning
- LOI > 28 ⇒ self extinguishing
- 28 < LOI < 100 ⇒ intrinsically non-flammable
- **26 < LOI < 100 ⇒ textiles are considered to be flame retardant**

Bajaj, P. Chapter 10, Heat and Flame Protection, in *Handbook of Technical Textiles,* Horrocks, A.R.; Anand, S.C. Eds. Woodhead Publishing, **2000**, 223-263.



Vertical flammability test chamber (left side) and result for treated fabric after flame testing (right side)

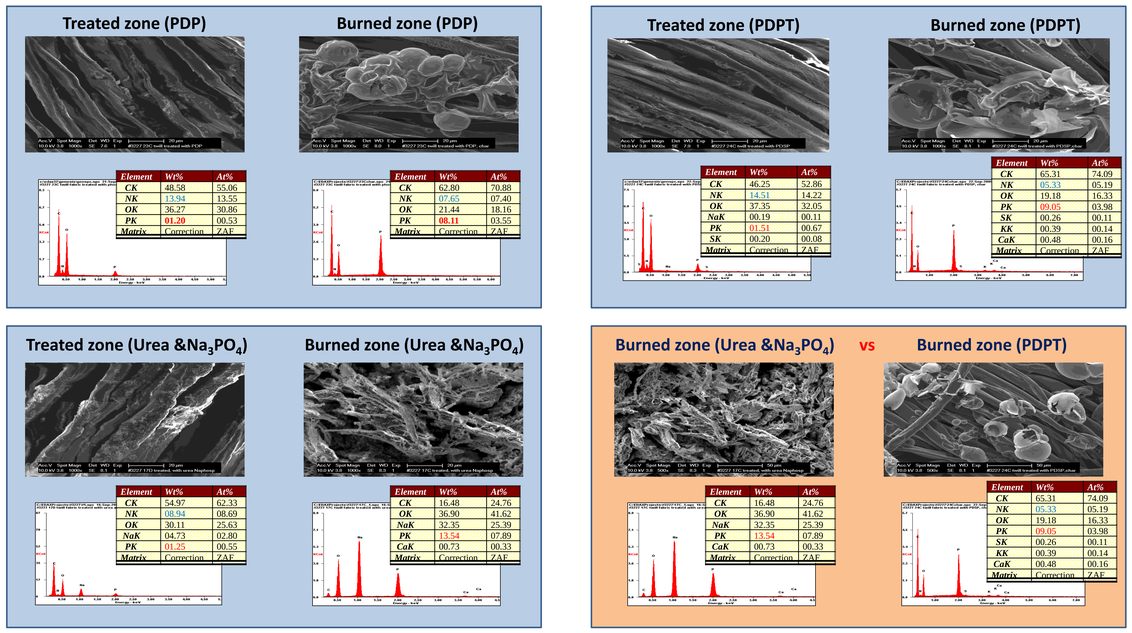
- Vertical flammability test (ASTM D 6413-08) : 12 sec exposure to flame and measure after-flame time (AFT), after-glow time (AGT), and char length (CL).



Ignition after-flame after-glow char

Treated chemical w/	Add-ons (%)	Pill test	After-flame (sec)	After-glow (sec)	Char length (cm)	Final result for vertical test	LOI (%)
Control twill	0	Failed	10	30	NA	Failed	18.5
Urea/Na_3 PO_4	13.2	Failed	8	40	NA	Failed	27
	14.6	Failed	10	35	NA	Failed	29
	15.4	Failed	10	39	NA	Failed	29
PDP	6.5	Passed	4	5	12	Passed	26
	9.8	Passed	3	6	10	Passed	27
	13.3	Passed	1	5	6	Passed	29
PDPT	11.4	Passed	2	3	8	Passed	28
	13.6	Passed	1	3	7	Passed	30
	22.4	Passed	0	0	7	Passed	34

Scanning Electronic Microscopy (SEM) and EDAX Studies



Conclusions and Acknowledgements

- A new environmentally friendly halogen-free and cost effective chemicals, piperazine phosphonates (PDP) and phosphonothionates (PDPT) FR derivatives shows improved flame retardant properties, and ^{1}H , ^{13}C, ^{31}P NMR and GC-MS spectrometry confirmed its chemical structure
- New FR were treated on cotton fabrics by using innovative supercritical carbon dioxide method
- FT-IR, TGA, and SEM confirmed its chemical structure, thermal decomposition properties, char % and morphology of char formation
- Preliminary modified pill, LOI and vertical flammability tests showed that the PDP and PDPT FRs provides satisfactory flame resistance to the treated fabrics
- Since both phosphorus and nitrogen stays in char residue, there is better flame retardant properties than phosphorus content only
- Advanced semi-durability of new piperazine phosphonothionates (PDPT) FR crosslinkers with cotton fabrics were successfully done

- Funding from USDA-ARS, CRIS:6435-41000-085-00D
- Express thank you for Mr. Bruce Ingber (SEM and EDAX), Dr. Mien Nguyen (NMR) and Ms. Crista Madison (LOI)