A NEW SUSTAINABLE POLYMERIC FIRE SAFETY SOLUTION FOR THERMOPLASTICS AND ELASTOMERS

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Abstract: A new generation of High Performance Polymeric flame-retardants has been developed at Albemarle Corporation. Designed for use in a broad range of plastics, these products are made via a break-through technology. The flexibility of this technology allows the products to be tailored to offer a unique set of physical and flame retardant properties in a "single-package" solution. Thanks to their non-bio accumulative, non-toxic and excellent recyclability these products are ideal for a polymer industry striving for more environmentally friendly and sustainable fire safety solutions.

Introduction: Brominated compounds continue to be the most efficient and cost effective classes of flame retardants. While they are very effective in imparting flame retardancy, often times some of these FR's fall short on meeting other requirements in terms of the physical and mechanical properties of the polymers to which they are added. There is also a growing need for effective flame retardant solutions that are more environmentally friendly, sustainable and recyclable. Polymeric flame retardants are especially gaining more interest due to their larger molecular structure. Polymeric materials that have a molecular wt greater than 1000 are not expected to bio-accumulate or possess toxicity. Researchers at Albemarle have developed a new technology to make stable low molecular weight brominated polymers (OECD definition) using readily available raw materials. These polymers were found to have a wide range of properties that can be tailored to offer specific physical and flame retardant performance in any given resin system. GreenArmor™ is the first of this new generation polymers and has high bromine content, better FR efficiency, is melt-blendable and can be used in both thermoplastic and thermoset polymers. Polymers flame retarded with GreenArmor™ have excellent mechanical and electrical properties, offer better thermal and color stability and have excellent recyclability. This presentation summarizes the performances of GreenArmor™ in a number of different polymer systems.

Experimental:

Materials:

HIPS	High-impact polystyrene
ABS	Acrylonitrile-butadiene-styrene terpolymer
EVA:	Ethylene-vinyacetate copolymer
PP	Polypropylene ethylene copolymer
TPE	Thermoplastic elastomer
GF PA 6/6	Glass-filled Polyamide 6,6

GF PBT	Glass-filled polybutyleneterephthalate
GF PET	Glass-filled polyethyleneterephthalate
GreenArmor™	New Brominated polymer
Saytex 102E®	Decabromodiphenyl ether
Saytex 8010® & Saytex 8010ZD®	Ethylene-bis-pentabromophenyl
TTBPT	Tris-tribromophenoxy triazine
BEO	Brominated epoxyoligomer
TBBPA	Tetrabromo-bis-phenol-A
Saytex HP-3010®	Brominated polystyrene from Albemarle Corporation
Saytex HP-7010®	Brominated polystyrene from Albemarle Corporation
Saytex PBT620®	Brominated polystyrene from Albemarle Corporation
Saytex BT-93® & Saytex BT-93W®	Ethylene-bis-tetrabromophthalimide
Saytex 120®	Tetradecabromodiphenoxybenzene
BrPS-1 thru BrPS-6	Brominated Polystyrene Products from other commercial sources
FR-1	Brominated Carbonate oligomer
FR-2	Polybrominated benzylacrylate
FR-3	Higher molecular weight brominated epoxyoligomer
Sb_2O_3	Antimony trioxide

Compounding, Molding and Testing:

Various resins and flame-retardants were hand mixed in a plastic bag prior to extrusion. The compounding was conducted on a Werner & Pfleiderer ZSK30 twin-screw extruder. The extruded strand was pelletized on-line. All formulations were injection molded at a Battenfeld BA350 CD injection-molding machine.

Testing was performed on samples according to the following ASTM test standards: Tensile Strength (D638) specimen type 1; Flexural Strength (D790) method 1; Heat Deflection Temperature under Load (D648) 1/8" at 264 psi; Vicat softening temperature (D1525) 1/8" at 1 Kg; Notched-Izod Impact Strength (D256) method A; Gardner Impact Strength (D3029) method G; and Melt Flow Rate (D1238) procedure A, Conditions as noted. The UL-94 flammability test was performed on 1/8", 1/16" and 1/32" bars as noted. The color measurements were made using Hunter Lab scale, D65 illuminant, 10° observer, and integrated-sphere geometry.

Results and Discussions

Styrenic Polymers: GreenArmor™ as well as three other commercially available flame retardants were compounded in HIPS and their performances

were compared. The physical, mechanical, impact, thermal, rheological, and flammability properties data of these formulations are summarized in Table-1.

Saytex 8010 has the highest bromine content and is the most efficient FR for HIPS. However as it is a non-melting material, the impact properties and MFI are not as good as TTBPT or BEO. They however offer better MFI and impact properties but suffer form lower bromine content resulting in reduced FR efficiency. These flame retardants are typically blended together to balance the performance. GreenArmor™ on the other hand offers the best properties overall as a single FR solution so that no blending is required.

Table-1

FR			**GreenArmor**	**TTBPT**	**Saytex 8010**	**BEO**
Br %			10.0	10.0	10.0	10.0
Antimony Trioxide %			4.0	4.0	4.0	4.0
Properties		Units				
UL-94, 1/8"	UL-94		V-0	V-0	V-0	V-0
$t_1 + t_2$		sec.	12	11	8	9
MFI, 200°C/ 5kg	ASTM D1238	g/10 min	14.7	18.1	9.7	25.8
HDT	ASTM D648	°C	70.6	70.1	71.4	66.5
Vicat	ASTM D1525	°C	97.2	94.8	96.8	90.1
N-Izod Impact Strength	ASTM D256	ft-lb/in	1.63	1.66	1.03	1.21
Tensile Strength	ASTM D638	psi x10^3	3.2	3.1	3.0	3.0
Tensile Modulus	ASTM D638	psi x10^5	2.9	2.8	3.1	2.9
Elongation at yield	ASTM D638	%	1.3	1.2	1.1	1.2
Elongation at Break	ASTM D638	%	19.3	28.2	7.8	18.6
Flexural Strength	ASTM D790	psi x10^3	6.8	6.6	5.7	6.4
Flexural Modulus	ASTM D790	psi x10^5	3.3	3.3	3.4	3.4

A similar study carried out with current solutions for ABS and GreenArmor™ clearly shows that GreenArmor™ has the best overall performance. The results are summarized in Table-2

Table-2

FR			**GreenArmor**	**TTBPT**	**TBBPA**	**BEO**
Br %			12.0	12.0	12.0	12.0
Antimony Trioxide %			4.5	4.5	4.5	4.5
Properties		Units				
UL-94, 1/8"	UL-94		V-0	V-0	V-0	V0
$t_1 + t_2$		sec.	8	8	7	8
MFI, 230°C/3.8kg	ASTM D1238	g/10 min	9.1	13.8	25.4	20.9
HDT	ASTM D648	°C	74.0	74.0	66.3	72.5
Vicat	ASTM D1525	°C	103.1	100.8	90.1	97.3
N-Izod Impact Strength	ASTM D256	ft-lb/in	1.86	1.70	1.27	1.12
Tensile Strength	ASTM D638	psi x10^3	4.9	4.7	4.3	4.4
Tensile Modulus	ASTM D638	psi x10^5	3.1	3.1	3.3	3.3
Flexural Strength	ASTM D790	psi x10^3	9.2	9.0	7.9	9.0
Flexural Modulus	ASTM D790	psi x10^5	3.2	3.0	3.3	3.3

Thermal and Color Stability studies: Recycle studies done using multi-pass injection molding as well as humid-aged recyclates show that GreenArmor™ is thermally very stable and exhibits excellent recyclability. HIPS containing GreenArmor™ retains its properties after six injection-molding cycles and after 168-hr humidity aging. (Fig 1 and Fig 2).

Figure-1

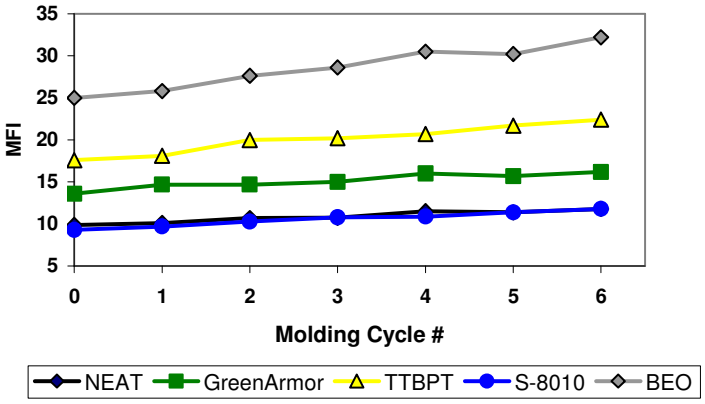
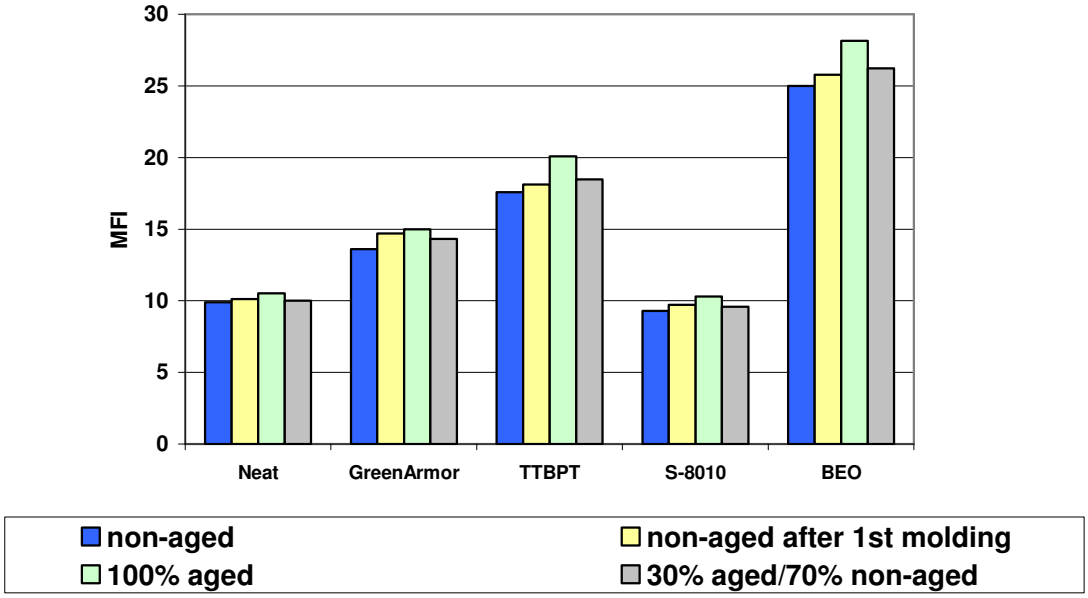
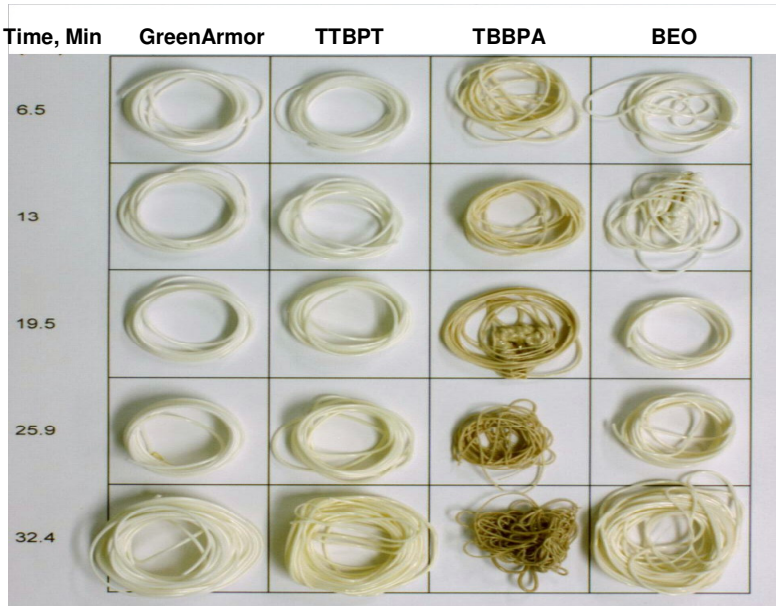


Figure-2



ABS extrudates from capillary rheometer @ 250°C for varying residence times show the excellent color retention of GreenArmor™ compared to TTBPT, TBBPA and BEO (Fig 3)

Figure-3



GreenArmor™ is well suited for use in HIPS and ABS. It imparts high melt flow as it is melt-blendable, imparts great impact strength, provides great thermal resistance and melt stability, has excellent mechanical properties, performs well in various HIPS and ABS grades and exhibits excellent recyclability

Polyolefins: The performance of GreenArmor™ was compared with other flame retardants in three different types of polyolefin resins. Table-3 summarizes properties for PP formulations for e.g. similar performances were seen in an EVA system.

Table-3

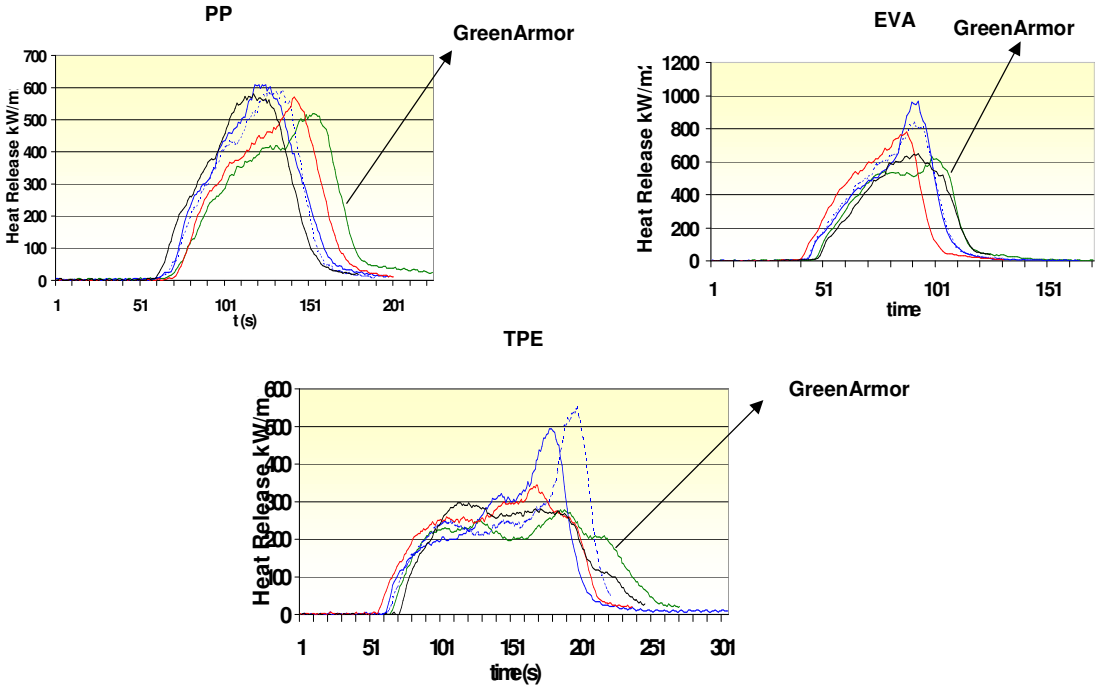
Ingredient		Saytex 102E	Saytex 8010	Saytex 8010ZD	Saytex BT-93	GreenArmor
PP Copolymer		56.8	56.8	56.8	56.8	56.8
FR Loading (wt%)		22.0	22.0	22.0	22.0	22.0
Sb2O3		7.0	7.0	7.0	7.0	7.0
Talc		14.0	14.0	14.0	14.0	14.0
Ethanox 310		0.1	0.1	0.1	0.1	0.1
Ethaphos 368		0.1	0.1	0.1	0.1	0.1
Specific Gravity		1.27	1.27	1.26	1.26	1.25
Tensile Strength	psi X 10^3	2.5	2.3	3.5	2.8	2.7
Tensile Modulus	psi X 10^5	4.4	4.2	4.1	4.4	4.5
Elongation @ Yield	%	3.3	3.2	4.5	2.3	2.3
Elongation @ Break	%	30.6	25.5	42.1	8.7	7.5
Flexural Strength	psi X 10^3	6.3	6.2	5.9	6.6	6.6
Flexural Modulus	psi X 10^5	3.3	3.3	3.0	3.2	3.5
Izod Impact	ft-lb/in	0.52	0.51	0.75	0.38	0.42
GLOSS		21.3	25.1	24.5	24.4	27.8
Melt Flow Index	g/10 min	4.0	3.9	3.6	3.4	6.2
HDT	℃	119.5	120.8	114.7	118.7	115.3
VICAT	℃	154.2	154.3	152.1	153.9	148.2
Dielectric Constant		2.51	2.49	2.50	2.55	2.49
Dissipation Factor	%	1.47	1.81	3.14	1.84	3.60
Volume Resistivity	10^16	1.0	1.4	0.9	1.5	1.5
Surface Resistivity	10^16	3.8	4.6	3.3	10.2	6.4
Dielectric Strength	v/mil	534	533	541	561	647

Table-4 summarizes the comparison of GreenArmor™ with other flame retardants in a thermoplastic elastomer system (TPE).

Table-4

Ingredient		**Saytex 102E**	**Saytex 8010**	**Saytex 8010ZD**	**Saytex BT-93**	**GreenArmor**
PP Copolymer		45.4	45.4	45.4	45.4	45.4
Ethylene-Octene copolymer		11.4	11.4	11.4	11.4	11.4
FR Loading (wt%)		**22.0**	**22.0**	**22.0**	**22.0**	22.0
Brightsun HB		7.0	7.0	7.0	7.0	7.0
Mistron Vapor Talc		14.0	14.0	14.0	14.0	14.0
Ethanox 310		0.1	0.1	0.1	0.1	0.1
Ethaphos 368		0.1	0.1	0.1	0.1	0.1
Specific Gravity		1.28	1.26	1.26	1.24	1.24
Tensile Strength	psi X 10^3	3.1	3.0	3.0	3.3	3.3
Elongation @ Yield	%	5.5	5.8	6.8	5.6	3.0
Elongation @ Break	%	113	360	362	14	67
Flexural Strength	psi X 10^3	5.5	5.7	5.3	5.8	5.9
Flexural Modulus	psi X 10^5	2.6	2.2	2.0	2.6	3.5
Izod Impact	ft-lb/in	0.61	0.74	1.03	0.52	0.54
GLOSS		16.5	19.4	22.5	21.4	24.6
Melt Flow Index	g/10 min	3.7	3.7	4.1	3.2	6.7
HDT	℃	102.7	99.6	94.5	102.6	104.5
VICAT	℃	154.2	154.3	152.1	153.9	148.2
Dielectric Constant		2.48	2.49	2.46	2.49	2.46
Volume Resistivity	10^16	0.8	0.8	6.7	1.2	1.6
Surface Resistivity	10^16	3.4	2.6	2.8	5.1	5.9
Dielectric Strength	v/mil	526	525	533	552	636

Cone Calorimetry data shows that GreenArmor™ has the lowest heat release rate compared to other FRs tested in all three polyolefin systems.



Overall, GreenArmor™ is an excellent FR in Polyolefins and provides good physical properties, comparable FR properties at lower Br content, lower Peak HRR vs. other FR's, equivalent or better electrical properties, improved process ability translating to higher throughput

Engineering Thermoplastic Resins:

Polyamide 6,6: Table-5 summarizes the comparison of GreenArmor™ with a number of brominated polystyrene flame retardants available commercially. With the highest bromine content, GreenArmor™ has the best FR efficiency and overall physical and mechanical properties. With its lowest melt-viscosity, it offers the best MFI and high gloss.

Table-5

FR		GreenArmor	HP 3010	HP 7010	BrPS-1	BrPS-2	BrPS-3	BrPS-4	BrPS-5	BrPS-6
Br %		74%	68%	68%	59%	64%	64%	64%	66%	66%
% FR with 6.3 % Sb2O3		19%	20.7%	20.7%	23.6%	22.9%	22.9%	22.9%	21.5%	21.5%
LOI	% Oxygen	36.8	36.4	36.1	35.4	36.5	37.5	37.3	36.7	38.1
UL-94	Pass/Fail	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
	seconds	7	20	26	17	24	16	24	9	8
Melt Flow Index	g/10 min	29.0	23.2	11.5	29.9	27.5	25.8	24.0	10.2	14.3
HDT	℃	240.7	243.4	238.0	240.6	243.0	242.9	242.0	238.8	222.9
Specific Gravity	g/cm3	1.63	1.65	1.62	1.66	1.66	1.66	1.66	1.67	1.66
Gloss	n/a	29.2	22.6	20.3	23.2	22.9	21.8	23.4	19.6	20.2
Tensile Strength	psi X 10^3	15.4	15.2	12	12.4	13.2	15.9	16.6	15.2	10.8
Tensile Modulus	psi X 10^5	14.5	14.6	16	14.9	15.8	15.4	15.3	14.7	15.3
Elongation at yield	%	1.49	1.49	1	0.98	1	1.35	1.47	1.47	0.84
Elongation at Break	%	3.52	3.47	3.34	2.54	3.06	2.86	3.03	3.15	1.75
Flexural Strength	psi X 10^3	33.6	33.6	30.9	32	33.9	34.4	35.7	33.7	30.1
Flexural Modulus	psi X 10^5	13.1	13.8	12.3	13.6	14	14.2	14.6	13.9	14.3
Izod Impact	ft-lb/in	1.79	1.71	1.54	1.34	1.55	1.49	1.62	1.41	0.85
Gardner Impact	in.lb/in	88	89	69	49	66	51	61	62	21
Dielectric Strength	V/mil	17.363	15.783	20.354	17.378	17.321	17.921	17.295	17.933	17.279
Dielectric Constant		3.884	3.874	3.807	3.842	3.847	3.84	3.828	3.829	3.743
Comparative Tracking Index	Volts	200	250	350	275	275	275	275	350	200
Volume/Surface Resistivity	ohm	11.7 / 7.85	8.34 / 10.2	4.07 / 8.06	9.30 / 11.7	9.86 / 10.7	9.71 / 14.6	9.67 / 8.91	4.72 / 8.61	4.57 / 1.19
Dissipation Factor		0.008	0.007	0.008	0.009	0.016	0.013	0.015	0.016	0.002

Polyesters: A similar study was conducted in both 30% glass filled PBT and PET and again GreenArmor™ meets or exceeds the performances of other flame retardants (Table –6 and 7)

Table-6

FR		GreenArmor	PBT-620	S-8010	BT-93W	BrPS-1	BrPS-2	BrPS-3	FR-1	FR-2	S-120	FR-3
Br %		74%	54.4%	82.3%	67.2%	59%	64%	64%	58%	71%	81.8%	
% FR with 6.3 % Sb2O3												
LOI	% Oxygen	33.1	31.8	33.5	32.9	32.0	31.2	31.5	33.6	32.6	32.4	33.3
UL-94	Pass/Fail	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
	seconds	7	8	8	8	8	9	8	8	10	9	9
Melt Flow Index	g/10 min	18.0	18.3	13.3	12.9	15.4	14.4	13.2	7.9	16.2	12.9	9.9
HDT	℃	170.1	180.2	188.2	194.2	176.1	181.5	179.4	160.8	179.5	189.9	174.8
Specific Gravity	g/cm3	1.68	1.67	1.70	1.73	1.70	1.69	1.69	1.72	1.67	1.72	1.67
Gloss	n/a	29.1	14.3	14.7	15.2	13.7	11.8	11.3	22.1	21.5	17	13.8
Tensile Strength	psi X 10^3	12.7	11.8	12.0	11.6	11.9	11.9	12.0	13.2	12.6	12.0	12.6
Tensile Modulus	psi X 10^5	11.4	12.1	12.4	12.4	12.3	12.2	13.1	11.9	12.2	12.0	11.7
Elongation at yield	%	1.13	0.98	1.30	1.49	1.47	1.45	1.31	1.49	1.17	1.00	1.16
Elongation at Break	%	2.88	2.74	3.44	3.29	2.86	2.81	2.32	3.40	2.97	3.29	3.07
Flexural Strength	psi X 10^3	23.4	21.1	23.6	21.7	21.7	22.7	21.4	24.7	23.4	22.0	22.8
Flexural Modulus	psi X 10^5	11.2	11.4	12.1	11.4	12.0	12.3	11.6	11.5	11.4	11.0	11.1
Izod Impact	ft-lb/in	0.6	0.9	0.9	0.9	0.6	0.8	0.7	0.9	0.8	0.9	0.6
Gardner Impact	in.lb/in	32	28	46	42	22	27	28	34	33	49	35
Dielectric Strength	kV/mm	16.0	20.5	16.6	18.6	20.8	20.9	20.4	16.8	19.2	17.3	18.2
Dielectric Constant		3.7	3.7	3.8	3.7	3.7	3.7	3.9	3.7	3.8	3.8	3.8
Comparative Tracking Index	Volts	200	200	175	175	225	275	250	175	175	200	150
Volume Resistivity	ohm	1.91	0.93	1.08	1.36	1.04	1.05	9.45	1.50	0.93	1.36	1.75
Surface Resistivity	ohm	1.6 E17	7.7 E16	8.4 E15	1.7 E15	6.9 E16	6.8 E16	3.8 E16	2.1 E17	1.9 E16	6.3 E16	8.7 E16
Dissipation Factor		0.013	0.023	0.016	0.033	0.059	0.046	0.028	0.011	0.023	0.026	0.028

Table-7

		Saytex HP-3010	Saytex HP-7010G	Saytex BT-93W	Saytex 120	BrPS-1	BrPS-2	FR-1	GreenArmor
45% GF PET		34	34	34	31	37	36	34	33
30 % GFPETPET		48.6	48.6	48.6	53.6	43.8	45.8	49.1	50.6
FR Loading		12	12	12	10	13.8	12.8	11.5	11
Sodium Antimonate		5	5	5	5	5	5	5	5
PTFE		0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
LOI		27.5	27.5	31.7	31	29.3	29.6	30.1	30.6
UL-94, 1/32"		V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
t1+t2		13.5	11.32	10.62	12.56	33.61	13.07	8.29	10.95
Melt Flow Index	g/10 min	7.7	5.8	6.8	8.7	8.6	7.3	7.4	11.7
HDT	℃	206.1	201.8	216	210.9	203.7	204.1	204.6	203.1
Gloss	n/a	81	73.8	82.4	77.8	81.4	81.2	82.5	78.1
Tensile Strength	psi X 10^3	17.9	16.8	17.1	17.2	18	17.8	17.8	17.9
Tensile Modulus	psi X 10^5	16.4	15.8	16.5	16.5	16.7	16.2	16	16.2
Elongation at yield	%	2.08	2.46	2.01	2.26	1.86	2.05	1.99	2.03
Elongation at Break	%	2.1	2.5	2.04	2.28	1.89	2.08	2.01	2.06
Flexural Strength	psi X 10^3	26.8	27.2	28.2	28.2	27	28	28.1	27.5
Flexural Modulus	psi X 10^5	15.9	15	16.1	15.2	16.5	16.5	16.3	16.5
Izod Impact	ft-lb/in	0.972	0.989	0.861	1.043	0.928	0.92	0.879	0.806
Gardner Impact	in.lb/in	23	30	19	30	12	19	12	12
Dielectric Strength	kV/mm	19.49	20.084	18.4	17.667	19.496	19.287	17.771	16.074
Dielectric Constant	N/A	3.649	3.757	3.846	3.787	3.727	3.728	3.78	3.78
Comparative Tracking Index	Volts	225	200	200	200	200	200	175	200
Volume Resistivity	ohm-cm	1.00x10E15	1.02x10E15	7.84x10E14	8.62x10E14	1.32x10E15	1.12x10E15	1.01x10E15	1.18x10E15
Surface Resistivity	ohm-cm	1.19x10E16	2.52x10E15	4.24x10E15	1.07x10E16	1.65x10E16	1.19x10E16	3.89x10E15	6.15x10E15
Dissipation Factor	N/A	0.0126	0.0181	0.0057	0.0032	0.0055	0.0067	0.0161	0.0176

GreenArmor™ is an excellent FR in Polyamides and polyesters and provides comparable or better mechanical properties, low melt viscosity i.e. higher MFI, comparable FR properties at lower loadings than other BrPS products, better Impact properties, better Gloss, equivalent or better electrical properties and improved process ability resulting in higher throughput

Summary:

GreenArmor™ is a high performing polymeric fire safety solution that is versatile and can be used in almost every polymeric system. It is melt blendable, easy to process, has excellent FR efficiency, is thermally stable (no degredation products), color stable (Aesthetics!), and recyclable. The polymeric nature of GreenArmor™ makes it an environmentally friendly and sustainable fire safety solution for a wide range of polymeric systems.