Peer-reviewed version available at *Fibers* **2018**, *6*, 31; doi:10.3390/fib6020031

Article

Environmentally sustainable flame retardant surface treatments for textiles: the potential of a novel atmospheric plasma/UV laser technology

A. Richard Horrocks*, Sara Eivazi, Maram Ayesh and Baljinder Kandola

IMRI, University of Bolton, Bolton, UK; a.r.horrocks@bolton.ac.uk; sara.aivazi@gmail.com ; mwa1res@bolton.ac.uk; b.kandola@bolton.ac.uk
* Correspondence: a.r.horrocks@bolton.ac.uk; Tel.: +44 1204 903831

Abstract: Conventional flame retardant (FR) application processes for textiles involve aqueous processing which is resource intensive in terms of energy and water usage. Recent research using sol-gel and layer-by-layer chemistries, while claimed to be based on more environmentally-sustainable chemistry, still require aqueous media with the continuing problem of water management and drying processes being required.

This paper outlines the initial forensic work to characterise commercially produced viscose/flax, cellulosic furnishing fabrics which have had conferred upon them durable flame retardant (FR) treatments using a novel, patented atmospheric plasma/UV excimer laser facility for processing textiles with the formal name - Multiplexed Laser Surface Enhancement (MLSE) system. This system (MTIX Ltd., UK), is claimed to offer the means of directly bonding of flame retardant precursor species to the component fibres introduced either before plasma/UV exposure or into the plasma/UV reaction zone itself, thereby eliminating a number of wet processing cycles.

Nine commercial fabrics, pre-impregnated with a semi-durable, proprietary FR finish and subjected to the MLSE process have been analysed for their flame retardant properties before and after a 40 °C 30 min water soak. For one fabric, the pre-impregnated fabric was subjected to a normal heat cure treatment which conferred the same level of durability as the plasma/UV-treated analogue. TGA and LOI were used to further characterise their burning behaviour and the effect of the treatment on surface fibre morphologies were assessed. Scanning electron microscopy indicated that negligible changes had occurred to surface topography of the viscose fibres occurred during plasma/UV excimer processing.

Keywords: surface; textiles; flame retardant; plasma; ultraviolet; durability, phosphorus, nitrogen, polyurethane, thermal analysis, scanning electron microscopy

1. Introduction

1.1 Background

It is almost 30 years ago that environmental concerns were raised with regard to flame retardants, originally in respect to the potential release of polybrominated dioxins during the incineration of polybrominated diphenyls and diphenyl ethers [1]. Since that time these concerns have increased to the extent that in recent years there has been much interest in developing environmentally sustainable, surface flame retardant treatments to textiles as potential replacements for those currently used based on halogen or formaldehyde-based chemistry [2, 3]. Coincidently, these concerns have overlapped with the regulatory UK demand that since 1988 all domestic furnishing fabrics shall be resistant to both a lighted cigarette and a simulated match [4]. In the latter case, the furnishing fabric must be exposed to flame over a specified unmodified, polyurethane foam and the fabric should be sufficiently flame retardant to resist ignition of both fabric and foam. During the intervening period, back-coating fabrics with organobromine/antimony III oxide formulations has become a principal means of enabling fabrics comprising all fibre types to pass the regulatory requirements [4]. Not surprisingly, given the associated environmental concerns pressures to move away from such treatments continue to mount.

Recent interest has focussed on a number of novel surface technologies based on nanoparticle, sol-gel and layer-by-layer, as well as atmospheric plasma surface depositions fully reviewed elsewhere [5] . The potential success of these surface treatments depends on a number of factors including whether the textile behaviour is thermally thin or thermally thick, what the minimal flame retardant, active species (e.g. phosphorus, nitrogen, silicon, etc.,) levels are required to yield an acceptable level of flame retardancy with acceptable durability requirements. Any successful treatment should have minimal influence on other desirable fibre and fabric properties and of course be cost-effective.

While intumescent treatments have received considerable attention in the past, like those based on sol-gel treatments are often challenged by having poor wash durability [5, 6]. Layer-by-layer treatments applied to cotton and cotton/polyester blends, however, have recently demonstrated acceptable self-extinguishing properties during vertical fabric strip testing after a defined washing procedure. Notable among these are the recently published results of Grunlan et al [7, 8]. All the above recent surface technologies are based on aqueous precursor treatment with the associated need for energy-intensive drying processes.

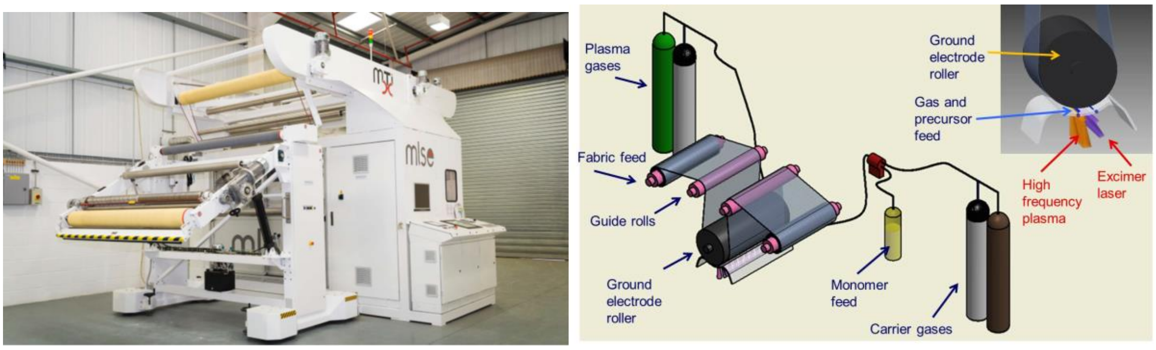
1.2 Atmospheric plasma treatments

In attempts to develop continuous processes requiring lower need for water-based processing, the advent of atmospheric plasma to continuous, open-width fabric processing equipment offers the opportunity of “dry” textile finishing with the consequent minimization of water requirements, effluent production and expensive drying processes [9]. This has created interest in its application to conferring flame retardancy in addition to other novel effects, such as improved fabric handle and increased dye uptake [10].

Of the little work published to date using atmospheric plasma, work in our laboratories has shown that deposition of silicon-based species on textile surfaces can significantly improve their flame retardancy defined in terms of improved flash fire resistance [11]. This improvement of flash fire resistance was observed on pure cotton, Proban®-treated cotton and Nomex® aramid fabrics. Subsequent work of Tata et al. [12] showed that polyester fabrics could be etched initially by cold oxygen plasma and then finished with hydrotalcite, nanometric titania and silica aqueous suspensions to give improved fire performance levels, even after washing in demineralised water at 30 °C for 30 min. A subsequent study [13] used plasma surface activation combined with nano-montmorillonite clay deposition to improve the thermal stability of fabrics in air. Totolin et al. [14] have reported grafting/crosslinking of sodium silicate layers onto viscose and cotton flannel substrates by using atmospheric pressure plasma which increased fabric burning times during 45° testing, although as recognised also by Edwards et al. [15] additional phosphorus as a phosphoramidate was necessary to achieve better levels of flame retardancy. Unfortunately, while char levels were increased, flame self-extinguishability during vertical fabric testing was not achieved and correlated with the still low phosphorus levels present.

1.3 A Combined atmospheric plasma/UV laser or Multiplexed Laser Surface Enhancement (MLSE) system

A recently developed and patented, available as a full commercial process by MTIX Ltd., UK [16], exploits the simple principle that atmospheric plasma treatment alone is insufficient to activate adjacent fibre and flame retardant species and that a second high energy source sufficient to form strong FR-fibre chemical bonds, offers a means to this. In the MLSE process, this latter is a 308 nm UV excimer laser able to break single covalent bonds (C-C, C-O, C-N, etc.) in both flame retardant precursor and fibre thereby increasing the chance of interaction. In principle, this system offers the means of eliminating a number of wet processing cycles normally associated with textile finishing processes [17] since the whole process is undertaken under dry conditions with no washing off requirements or other liquid effluents. The patent [16] also identifies the ability of the MLSE system to introduce properties of hydrophilicity, hydrophobicity, improved dyeability and anti-microbial properties to textiles as well as specifically claiming that flame retardancy may be introduced either by pre-impregnating/coating prior to plasma/UV or by introduction of volatile/aerosol flame retardant precursors into the plasma zone. Current commercially-available equipment based enables textile fabrics up to 2 m in width to be continuously processed up to speeds of 20 m/s. Figures 1(a) and 1(b) show a typical machine based on this technology and a schematic view of the process respectively.



(a) (b)

Figure 1: Multiplexed Laser Surface Enhancement (MLSE) system for open-width, textile fabric processing *(reproduced with permission from MTIX Ltd., Huddersfield, UK)*

The process exploits a number (typically up to four) of dielectric barrier discharge (DBD) plasma heads located so that one or both sides of a fabric may be treated simultaneously. Associated with each head is a UV laser beam traversing the reaction zone created by the plasma discharge across the fabric. Figure 1(b) and the right hand insert shows schematically the fabric pathway travelling over one plasma/UV head assembly. Plasma atmospheres may comprise nitrogen, argon and carbon dioxide alone, mixed together or compositions containing small amounts (e.g. up to 20%) of oxygen.

Exploratory work to date has shown that attempts to research and develop novel FR treatments that may replace conventional back-coatings and chemically-based flame retardant treatments for both cotton and wool fabrics (and respective blends) have met with some success but have been based entirely on trial and error processing. However, there has been no research into process at a scientific level and this paper presents the first part of recent work at the University of Bolton in which we attempt to undertake a forensic analysis of a range of successful, commercially processed fabrics to analyse the quality of flame retardancy being introduced by the MLSE system in order to better understand the process and compare their behaviour with similar, more conventionally treated fabrics.

This paper will analyse a number of proprietary viscose/linen, cellulosic blend, furnishing fabrics in terms of the levels of flame retardancy achieved and their durability to the statuary durability requirement of being able to withstand a 30 min, 40^{o}C water soak durability test [4]. The potential surface morphological changes occurring to surfaces of the viscose majority fibres are examined by scanning electron microscopy, which are considered to be the more sensitive of the two fibres present because of the absence of lignin present in the flax fibres [18].

doi:10.20944/preprints201804.0094.v1

Peer-reviewed version available at *Fibers* **2018**, *6*, 31; doi:10.3390/fib6020031

2. Materials and Methods

2.1 Materials and preparation

Nine jacquard woven, cellulosic-blended, commercial fabrics (see Table 1) were pre-impregnated with a phosphorus-and nitrogen containing flame retardant (FR) formulation prior to plasma/UV treatment (2 kW and 208 nm) under an inert atmosphere (see below) at various add-ons. The cellulosic fabrics varied in terms of the jacquard design (e.g. check versus stripes), fabric construction and area density and were believed to comprise blended yarns of viscose and flax fibres with the former in the majority. Subsequent scanning electron micrographs confirmed this assumption (see Section 3.3). When normally applied by a pad-dry process, the proprietary flame retardant (FR) formulation is not durable to water soaking, although if heat-cured some level of water soak durability is achieved. This was demonstrated by applying the commercial flame retardant at a nominal 6% add-on using a laboratory pad-mangle system to an untreated sample 2 fabric via a simple pad-dry process (sample 2a) and a pad-dry-cure (3 min at 150°C) process (sample 2b). Percentage add-ons of the flame retardant formulation of fully treated fabrics were calculated by comparing the area densities of respective fabrics that had no FR pre-impregnation with those that had been plasma/UV-exposed before the water soak. Fabric types, respective area densities and flame retardant add-ons are presented in Table 1.

Table 1: Area densities and percentage add-ons of flame retardant

	Treatment	**Sample**	**Area density, g/m^2**	**Plasma/UV-exposed fabric add-ons, % (before water soaking)**
1.	Pad/dry/plasma	Cellulosic, woven twill	413	13.8
2.	Pad/dry/plasma	Cellulosic, woven twill	417	12.7
2a	Pad/dry	"		6.0*
2b	Pad/dry/cure (150°C)	"		6.0*
3.	Pad/dry/plasma	Cellulosic, woven twill	406	12.1
4.	Pad/dry/plasma	Cellulosic, woven twill	421	8.5
5.	Pad/dry/plasma	Cellulosic, woven	410	13.4
6.	Pad/dry/plasma	Cellulosic, woven twill	388	11.1
7.	Pad/dry/plasma	Cellulosic, woven chenille	332	27.7
8.	Pad/dry/plasma	Cellulosic, woven twill	337	23.0
9.	Pad/dry/plasma	Cellulosic, woven twill	447	14.0

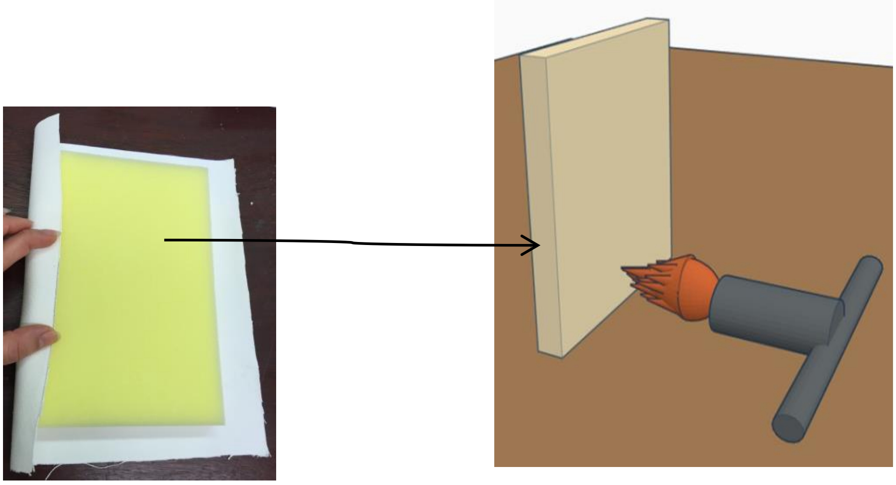
Note: * add-on is a nominal value calculated during pad application

2.2 Atmospheric plasma/UV laser (MLSE) conditions

For the commercial fabrics, the plasma power was 2 kW and plasma gas 95% nitrogen/ 5% CO_2. The excimer laser power was 650 mJ. The process speed was 20m/min. Plasma/UV-exposed on both sides of the fabrics using one single head each side (see Figure 1(b)). Since the plasma beam has a width of 30mm [16], then it may be calculated that the time of exposure of a given area of fabric will be only about 0.1 s.

2.3 Flammability testing

Plasma/UV exposed fabrics were examined for their ability to pass the Source 1 (simulated match) ignition requirements of BS 5852: 1979:Part1 as required by the current UK regulations for furniture and furnishing fabrics [4]. In this paper we have used a simulation of this test, first devised in industry over 25 years ago and described in full elsewhere [19]. In summary, this test combines the fabric and foam sample dimensions of the BS5438: 1989: Test 2 vertical strip method with a 20s front face, flame application time as defined in BS5852: Part 1: Source 1 (see Figure 2).



Foam dimensions:
220 x 150 x 22 mm

Fabric/foam composite exposed for 20s
to BS 5438: Test 2A, butane flame

Figure 2: Schematic diagram of the simulated match test for BS 5852: 1979: Part 1: Source 1 using a modification of BS 5438: 1989: Test 2A.

In this simulated test, a piece of non-flame retardant, flexible polyurethane (PU) foam of 220 x 150 x 22 mm (density of $22 kg/m^3$) is covered by a flame retarded fabric sample with the foam adjacent to the reverse side. This composite is mounted in the Test 2 sample frame with the fabric face towards the gas burner in the horizontal mode (Test 2A, face ignition condition) with its tip 17 mm from the fabric surface. With a vertical flame height adjusted to 40mm as specified in BS 5438, the flame is applied to the composite face for 20 s and then removed. If the composite yields afterflame times (AFT) > 2 min or produce externally detectable amounts of smoke, heat or afterglow 2 min after removal of the ignition source, a "fail" is recorded for the test result, otherwise a "pass" result is reported. All FR-treated, plasma/UV-exposed samples (including samples 2a and 2b) were subjected to this test before and after the mandatory 40 °C, 30 min water soak requirement [4]. Fabric damaged lengths (FaDL) were determined by simple measurement as were the depths of foam damage (FoDD) after each test.

Limiting oxygen index values were recorded using a Fire Testing Technology (UK) test equipment according to the ASTM D2863 method for thin materials including textiles.

2.4 Thermal analysis

TGA experiments were performed using a SDT 2960 Simultaneous DTA-TGA (TA Instruments). Samples with weights in the range 5-10 mg were placed in an open platinum pan heated from 50 to 700 °C in air with a heating rate of 10 °C min-1. Temperatures of onset of mass loss (determined at 5% mass loss), T_{onset}, were determined as were temperatures of maximum mass loss during volatilisation, T_{max1}, and char oxidation, T_{max2}. Residues at 400 and 550 °C were recorded, which respectively indicated maximum char yields prior to their oxidation and after oxidation in air.

2.5 Scanning electron microscopy and EDX

Samples of commercial sample 6 in untreated and flame retardant impregnated, plasma/UV laser-treated fabrics, before and after a water soak were coated with gold using a Quorum Technologies SC7620 sputter coater and then examined using a Hitachi S-3400N scanning electron microscope at a beam voltage of between 2 and 5kV.

3. Results

3.1 Flammability testing

The percentage add-on results are listed in Table 1 before water soaking. All results for fabric/foam composite testing and respective fabric LOI results are listed in Table 2. All fabrics without any pre-impregnation with the flame retardant formulation failed the simulated match test over unmodified PU foam in that after extinction of the igniting flame, all fabrics continued to burn together with the underlying foam and the composites required to be extinguished using a water spray. The LOI values of these untreated fabrics (Non-FR) are listed in Table 2 and not surprisingly are typically in the range 19.8-19.3 vol% observed for 100% cellulosic fabrics.

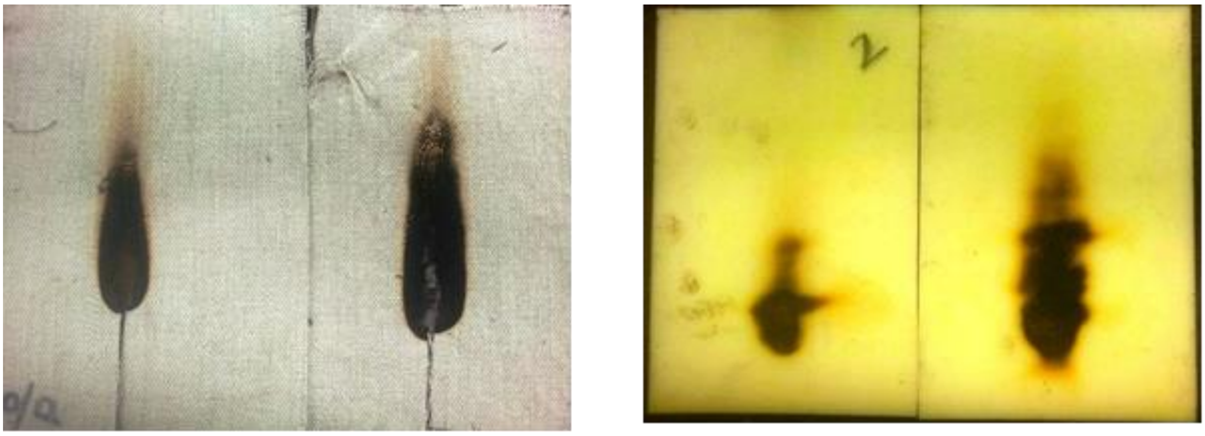
Table 2: Simulated match test (Source 1, BS 5852) and LOI results

Fabrics	**Initial area density (g/m$^{2)}$**	**Simulated match test over PU foam before**			**Simulated match test over PU foam after water soaking**			**LOI, vol% vol %**		
		AFT ,	**FaDL, mm**	**FoDD, mm**	**AFT, s**	**FaDL, mm**	**FoDD, mm**	**Non FR**	**FR/Plasma/UV**	
									Before	**After**
1.	413	0	105	5	5	119	10	18.9	28.4	22.8
2.	417	0	84	9	7	116	9	19.3	29.8	24.7
2a.		2	85	5	Fully burnt	-	-	19.3	31.2	19.7
2b.		0	72	2	13	110	10	19.3	31.2	21.9
3.	406	0	69	9	15	165	9	19.0	29.7	22.5
4.	421	0	73	14	11	120	9	18.8	29.6	23.2
5.	410	0	78	10	23	170	8	18.9	29.9	22.9
6.	388	0	94	9	11	125	9	18.9	29.5	23.3
7.	332	0	92	9	1	112	12	19.1	32.1	25.4
8.	337	0	82	8	1	110	9	19.2	32.2	25.6
9.	447	0	102	9	18	156	14	19.0	29.8	22.9

Key: AFT = Afterfame time; FaDL = fabric damaged length; FoDD = Foam damaged depth

The results for sample 2a show that a simple pad-dry FR application is not durable to the 40^{o}C water soak as expected, since the fabric when tested over PU foam before soaking passes the simulated match test and has LOI = 31.2 vol%, whereas afterwards it fails and LOI reduces to 19.3 vol%, the same as the untreated fabric. However, the application of a 3 min, 150^{o}C cure shows that a degree of water soak durability has been achieved since sample 2b after soaking passes the simulated match test with LOI = 21.9 vol%.

All flame retardant, plasma/UV-treated fabrics passed the simulated match test before water-soaking with afterflame times (AFT) of 0 s and damaged lengths (FaDL) ≤ 102 mm. After water soaking, all samples once again passed with afterflame times ≤ 23s and damaged lengths ≤ 165 mm, which reflect the partial loss of flame retardant during the 30s, 40°C water soak. However, the fabric/foam composites still were deemed to have passed the simulated match test (and hence BS 5858: 1979: Source 1) since afterflame times were ≤ 120s and damaged lengths did not extend to the edges of the fabric sample, 180 mm above the impinging flame centre. Typical images of all burnt fabric/foam composite samples impregnated with the FR, plasma/UV- treated and then subjected to a 30 min, 40°C water soak are represented by that for sample 6 fabric shown in Figure 3(a) for damaged lengths before and after soaking and in Figure 3(b) for PU foam samples behind respective specimens of sample 2.



(a) (b)

Figure 3: Composite fabric/foam specimens after small-scale simulated match testing (a) sample 6 fabric; (b) PU foam underlying sample 2, before (left) and after (right) water-soaking.

Figure 4 shows a plot of limiting oxygen index (LOI) versus damaged length (FaDL) before the water soak treatment and Figure 5 after the 30 min, 40°C water-soaked for fabrics listed in Table 2.

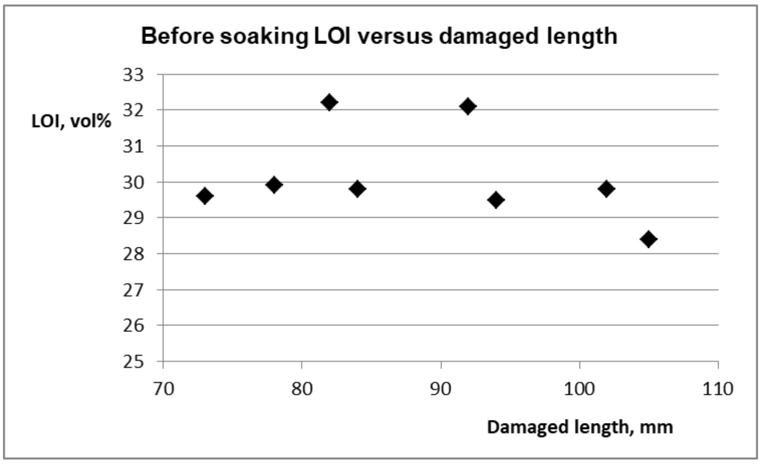


Figure 4: LOI versus damaged length for the plasma/UV-exposed fabrics

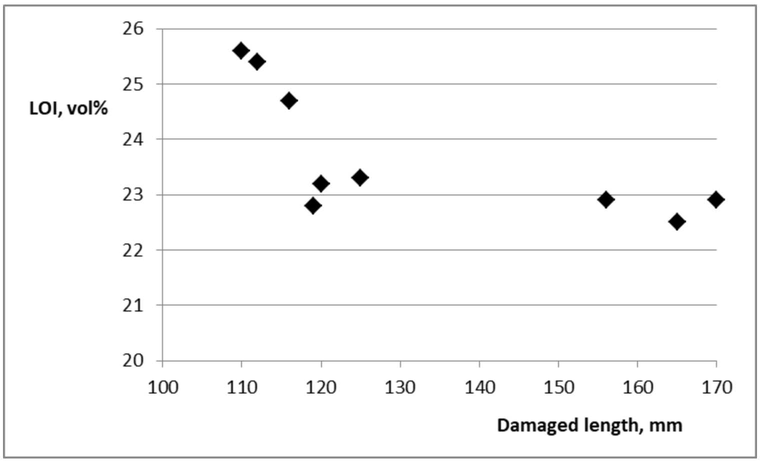


Figure 5: LOI versus damaged length for the 30 min, 40°C water-soaked, plasma/UV-exposed fabrics

In Figure 4, there is no real trend other than that all fabrics before water-soaking have LOI values > 28 vol% and damaged lengths ≤ 105mm. After water-soaking, Figure 5 shows there is a definite initial trend such that when the LOI value drops below 26 vol%, there appears to be an almost inverse linear relationship with increasing damaged length occurring until a value of 23 vol% is reached. While LOI changes little as the damaged length increases further, even for LOI values of about 22.5 vol%, fabrics subjected to the simulated match test still give acceptable values ≤ 180 mm.

3.2 Thermal analysis

Figure 6 shows typical TGA responses in air for woven twill fabric 1 comprising 80/20 viscose/linen, for untreated and FR-impregnated, plasma/UV-exposed samples before water-soaking and after water soaking. The discontinuity in the untreated sample at about 450°C is a consequence of the ignition of the cellulosic char at this temperature. The reduction in the onset temperature of major volatilisation and related maximum rate loss temperature (T_{max1}) in the 300-350°C region and increase in char evident at about 450°C are a consequence of the FR present.

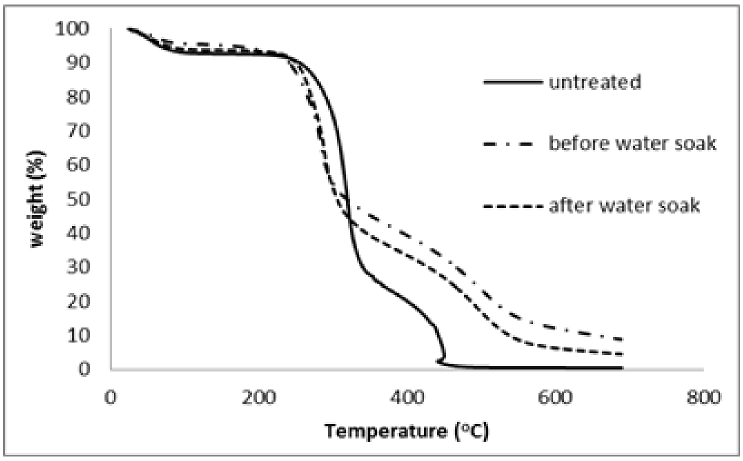


Figure 6: TGA response in air of fabric 1, untreated and after flame retardant, plasma/UV-exposed before and after water-soaking

These effects are typical of the behaviour of condensed phase active phosphorus- and nitrogen-containing flame retardants present on cellulosic fibres first observed by Tang and Neill over 50 years ago [20] and so indicate that the plasma/UV laser treatment has not influenced the

Peer-reviewed version available at Fibers 2018, 6, 31; doi:10.3390/fib6020031

flame retardant mechanism. After water-soaking, the apparent T_{max1} value increases slightly and the increase in char is reduced as a consequence of some loss of FR during water-soaking.

Each of the nine untreated fabrics is cellulosic-based and of similar area density and construction. However, they have different manufacturing histories and, as jacquard designs (e.g. check versus stripe), have differently dyed weft and warp yarns as a consequence. Such differences often promote slight variations in thermal decomposition data. Table 3 lists all the TGA data the nine fabrics and includes the maximum volatilisation and char oxidation mass loss rate temperatures, T_{max1} and T_{max2} respectively. Residue values at 400 and 550°C are included which represent char levels before and after oxidation respectively. T_{onset} values are within a range of 57-86°C reflecting the onset of moisture loss with T_{max1} values covering a much smaller range of 330-340°C. This indicates that each of the untreated fabrics has a very similar decomposition behaviour in spite of their varying manufacturing histories. Maximum rate temperatures of char oxidation, T_{max2}, are also similar covering the range 435-464°C, although in the 450-460°C region, samples combust leaving virtually no residue (≤ 1%).

It is also evident that the behaviours of the flame retardant formulation on all nine cellulose-based fabrics after FR impregnation and plasma/UV exposure before water soaking are similar in that the temperatures of maximum volatilisation, T_{max1}, cover the range 294-342°C, (see Table 1), although when plotted as a function of add-on % in Figure 7, a clear and expected inverse trend is observed. Again, this shows that the condensed phase mechanism of the applied flame retardant is not influenced by the plasma/UV exposure and that the shift to lower temperatures of T_{max1} with increasing FR add-on % is a expected.

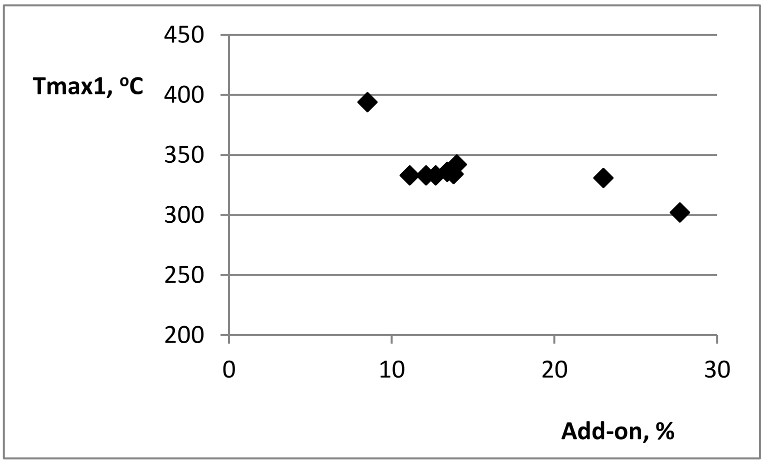


Figure 7: Plot of T_{max1} versus percentage add-on for fabrics before water-soaking

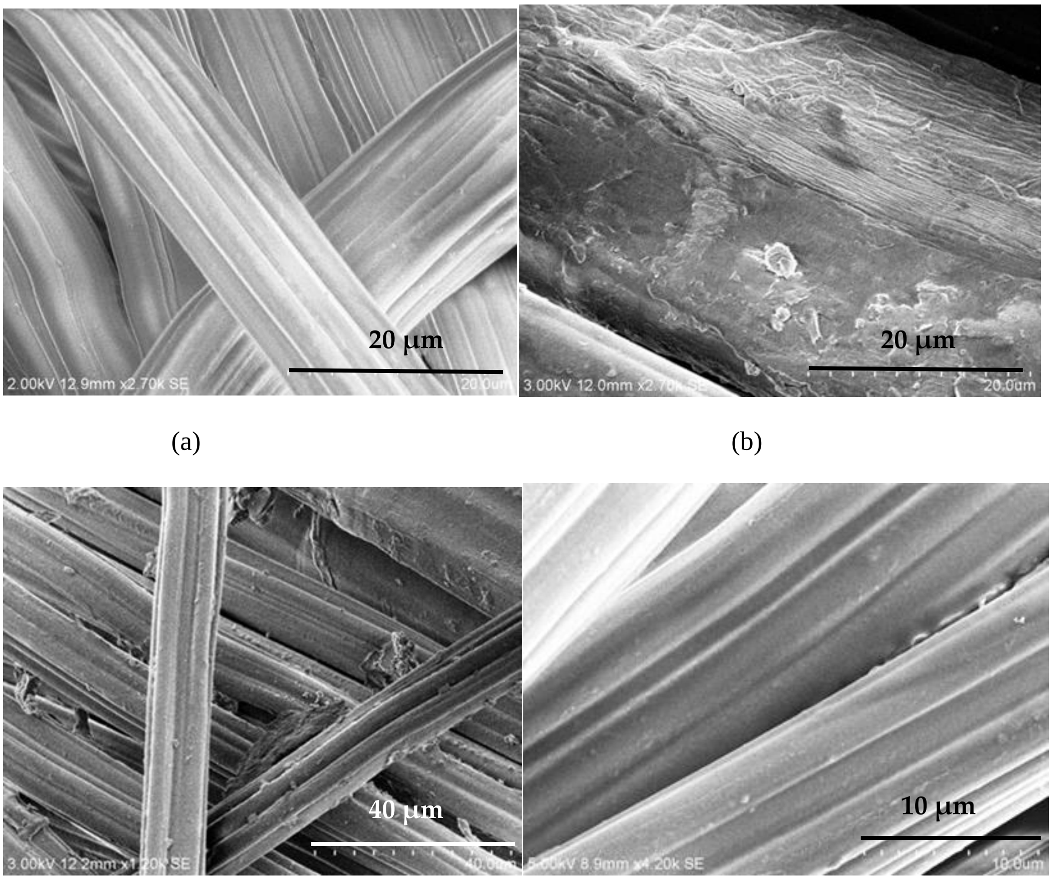
After water soaking, the T_{max1} range is much less at 307-326°C, suggesting only a small amount of loss of flame retardant has occurred. However, the reduced LOI values after water-soaking and increased damaged length values disagree with this conclusion, as does the effect of water soaking on char values at 450°C. Before water-soaking, the latter are in the range 37-42% whereas after water-soaking, 31-37%, which clearly indicates that loss of some flame retardant has occurred, indicated also in the difference in damaged lengths for water-soaked, sample 6 specimens shown in Figure 3(a).

Table 3: TGA data in air from each fabric, untreated and after plasma/UV exposure before and after water-soaking

Samples		**T_{onset} (5% weight loss)**	**T_{max1}, °C**	**T_{max2}, °C**	**Residue at 400°C, %**	**Residue at 550°C, %**
1.	Untreated	60	330	450	20	0.5
	Before soak	147	334	500	39	15
	After soak	67	320	496	33	8
2.	Untreated	57	330	453	19	0.6
	Before soak	91	333	500	37	13
	After soak	79	317	494	31	7
3.	Untreated	64	335	454	20	1
	Before soak	89	333	500	38	14
	After soak	78	326	500	31	6
4.	Untreated	62	336	454	20	1
	Before soak	168	294	498	42	19
	After soak	85	320	497	34	10
5.	Untreated	65	334	452	20	0.9
	Before soak	107	336	500	40	16
	After soak	91	317	491	32	7
6.	Untreated	60	334	460	21	0.2
	Before soak	116	333	500	41	17
	After soak	113	319	496	35	10
7.	Untreated	86	340	464	18	0
	Before soak	191	302	500	40	15
	After soak	216	312	500	37	11
8.	Untreated	82	336	436	19	0
	Before soak	217	331	497	42	19
	After soak	225	307	497	35	8
9.	Untreated	64	330	435	19	0
	Before soak	136	342	494	40	16
	After soak	82	321	494	37	12

3.3 Fibre surface morphologies

Scanning electron micrographs in Figures 8(a) and (b) respectively show the typical striated morphology of viscose fibres and a much coarser flax fibre, as a bundle ultimate fibres, in fabric sample 6 prior to any flame retardant impregnation and plasma/UV exposure. The former are in the majority appear to be in the majority judging by their dominance in the SEM images at lower magnifications. The viscose fibres will have typical skin-core structures with both phases showing lower levels of crystallinity [21, 22, 23] than the flax fibres present [22, 24]. This coupled with the fact that the flax fibre ultimate bundles will still have lignin present [18, 25] suggests that these will be more resistant to surface morphological damage than the former. Consequently the major focus here will be examination of the viscose fibre surfaces for topographical changes generated by their exposure to plasma/UV energy. Figure 8(c) shows the same sample after flame retardant treatment and plasma/UV laser treatment and Figure 8(d) shows the latter specimen after having been subjected to a 40^{o}C water soak.



(a) (b)

(c) (d)

Figure 8. SEM micrographs of sample 6 comprising both viscose and flax fibres; (a) no treatment – viscose fibres, (b) no treatment –flax fibre bundle, (c) flame retardant impregnation and subsequent plasma/UV laser exposed viscose fibres and (d) as for (c) but after water-soaking at 40^{o}C

Relative to Figure 8(a), the viscose fibres pre-impregnated with flame retardant and plasma/UV-exposed show the presence of considerable surface debris, which after water soaking at 40^{o}C, has largely been removed. The surfaces of viscose fibres in Figure 8(d) are smooth and very similar to those untreated ones in Figure 5(a), which would suggest that the exposure to plasma at 2kW and UV at 308 nm in a 95% nitrogen/5% carbon dioxide atmosphere has had no major etching effect at the magnification and resolution used. Such etching effects are well documented in the plasma literature for polyester and polypropylene fibre exposure under both inert and oxidising conditions, with the latter generating the greater level of surface erosion or etching [26]. There is very little literature with regard to the effect of plasma exposure on viscose fibre surfaces, whether under vacuum or atmospheric conditions and examples of the majority of these tend be in

Peer-reviewed version available at Fibers 2018, 6, 31; doi:10.3390/fib6020031

oxygenated atmospheres most often at low [27, 28] where introduction of oxygenated functionalisation [27, 29] occurs as a precursor to surface morphological change [28]. Of the few studies in which nitrogen is used, there appears to be little or no observable changes to fibre surface morphologies under SEM examination [27, 30]. Interestingly, Ibrahim et al [31] claim to have observed that pretreatment of cotton, linen and viscose substrates with a 5kW output atmospheric plasma under nitrogen applied for 45 s results in a remarkable increase in their nitrogen content, as a direct consequence of incorporation of nitrogen-rich polar functional groups, especially $–NH_2$ groups at the modified fibre surface in addition to the inherent cellulosic –OH groups. Their SEM micrographs showed little evidence of surface damage to either viscose or linen fibres present. The fabrics in this work were exposed for much lower times of about 0.1 s and so based on this latter work, the level of surface damage and reaction to form nitrogen-containing compounds would be expected to be less by about two orders of magnitude.

4. Discussion and Conclusions

This paper has assessed the ability of a novel MLSE technology to confer an acceptable level of durability on a range of cellulosic, furnishing-grade fabrics to which a non-durable flame retardant has been applied. Their ability to pass a simulated match test over PU foam, which is a requirement for UK domestic furnishing fabrics after a 30 min, 40^{o}C water soak procedure, has been used a the measure of their behaviour in this respect. The proprietary flame retardant has been shown to be non-durable if applied simply by a pad-dry process, but is acceptably durable if then subjected to a 3 min, 150^{o}C cure and then tested after water-soaking.

The analysis of the resistance to ignition over PU foam of nine commercial FR-impregnated, cellulosic woven fabrics of slightly varying area density, shows that subjecting fabrics to the plasma/ UV laser processing confers a similar, if not higher degree of water soak durability compared to the heat-cured control sample. LOI values before and after water soaking show that all fabrics after soaking had values ≥ 22.5 vol%, which were greater than the value for the water-soaked, heat-cured sample (21.9 vol%). Thermal analysis of the nine fabrics showed that the flame retardant activity of the applied retardant was as expected for a typical condensed phase formulation and so had not been affected by exposure to the plasma/UV laser source.

Scanning electron microscopy indicated that negligible changes to surface topography of the viscose fibres occurred during plasma/UV excimer processing of the commercial viscose/line blended fabrics.

Future work will investigate the changes in surface chemistry using techniques such as XPS, radical trapping and EPR to assess possible mechanisms by which durability of flame retardant species present on the fabric or introduced into the plasma zone directly may be achieved in terms of the underlying chemical processes involved.

Acknowledgements: The authors wish to thank the Cotton Industry War Memorial Trust for sponsoring the PhD programmes of S.E. and M.A. and to Messrs Graham Downhill and Pravin Mistry of MTIX Ltd., Huddersfield, England, for additional financial assistance, use of the MLSE equipment and supply of commercial fabrics.

Author Contributions: A.R.H and B.K.K had overall responsibility for supervising the work and together with S.E. designed the experiments. S.E. undertook the sample preparation, flammability testing and TGA experiments and M.A. undertook all the scanning electron microscopy work. A.R.H. and B.K.K. undertook the analysis of results and A.R.H. wrote the paper.

Conflicts of Interest: The authors declare that although MTIX Ltd., were part sponsors of this project and supplied the commercial fabrics, they had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. McAllister, D.L. Brominated flame retardants: current issues and future prospects. In *Flame Retardants '92,* The Plastics and Rubber Institute, Ed., London, UK: Elsevier, 1992, pp.149-154; ISBN 1-85166-758-X
2. Horrocks, A.R. Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions. *Polym Degrad Stab* **2011**, 96, 377-392
3. Horrocks, A.R. Overview of traditional flame-retardant solutions. In *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions*, Alongi, J.; Horrocks, A.R; Carosio, F.; Malucelli, G., Eds.; Smithers Rapra: Shawbury, UK, 2013; pp.123-178
4. Consumer Protection Act (1987), the Furniture and Furnishings (Fire) (Safety) Regulations, 1988, SI1324 (1988), 1988; amended in 1989, 1993 and 2010, HMSO, London, UK
5. Alongi J.; Carioso F.; Malucelli G. Smart (nano)coatings. In *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions*, Alongi, J.; Horrocks, A.R; Carosio, F.; Malucelli, G., Eds.; Smithers Rapra: Shawbury, UK, 2013; pp 263-318,
6. Horrocks, A.R. Flame Retardant finishes. In *Textiles: Current Developments and Future Trends,* Bahners, T.; Mittal, K., Eds.; Scrivener Publishing LLC: Beverly, MA, USA, 2017; pp.69-128
7. Leistner, M.; Abu-Odeh, A.A.; Rohmer, S.C.; Grunlan, J.C. Water-based chitosan/melamine polyphosphate multilayer nanocoating that extinguishes fire on polyester-cotton fabric. *Carbohydr Polym* **2015**, 130, 227–232
8. Haile, M.; Leistner, M.; Sarwar, O.; Toler, C.M.; Henderson, R.; Grunlan. J.C. A wash-durable polyelectrolyte complex that extinguishes flames on polyester-cotton fabric. *RSC Adv* **2016**, 6, 33998-34004
9. Shishoo, R., Ed. *Plasma Technologies for Textiles*, Woodhead Publishing: Cambridge, UK, 2007
10. Herbert T. Atmospheric-pressure cold plasma processing technology. In *Plasma Technologies for Textiles*, Shishoo, R., Ed.; Woodhead Publishing: Cambridge, UK, 2007; pp. 79-128
11. Horrocks, A.R.; Nazaré, S.; Masood, R.; Kandola, B.K.; Price, D. Surface modification of fabrics for improved flash-fire resistance using atmospheric pressure plasma. *Polym Adv Technol* **2011,** 22, 22–29
12. Tata, J.; Alongi J., Frache, A. Optimization of the procedure to burn textile fabrics by cone calorimeter: Part II. Results on nanoparticle-finished polyester. *Fire Mater* **2012,** 36, 527-537)
13. Carosio, F.; Alongi, J.; Frache A. Influence of surface activation by plasma and nanoparticle adsorption on the morphology, thermal stability and combustion behavior of PET fabrics. *Eur Polym* **2011**, 47, 893-902

Peer-reviewed version available at *Fibers* **2018**, *6*, 31; doi:10.3390/fib6020031

14. Totolin, V.; Sarmadi, M.; Manolache, S.O.; Denes F.S. Environmentally friendly flame-retardant materials produced by atmospheric pressure plasma modifications. *J Appl Polym Sci* **2012**, 124,116–122
15. Edwards B.; El-Shafaei, A.; Hauser, P; Malshe. P. Towards flame retardant cotton fabrics by atmospheric pressure plasma-induced graft polymerization: Synthesis and application of novel phosphoramidate monomers. *Surf Coat Technol* **2012**, 209, 73-79
16. Mistry, P. (assigned to MTIX Ltd., UK). Treating Materials with combined Energy Sources. US Patent 9605376 B2, 28 May 2017.
17. Heywood, D., Ed. *Textile Finishing.* Bradford, UK: Society of Dyers and Colourists, 2003
18. Peters, R.H. *Textile Chemistry, Volume 2,* Amsterdam/London/New York: Elsevier, 1967, pp. 91-92
19. Wang, M.Y.; Horrocks A.R.; Horrocks, S.; Hall, M.E.; Pearson, J.S.; Clegg S. Flame retardant textile back-coatings. Part 1: Antimony-halogen system interactions and the effect of replacement by phosphorus-containing agents. *J Fire Sci* **2000**, 18, 265-294
20. Tang, W.K.; Neill, W.K. Effect of flame retardants on pyrolysis and combustion of α-cellulose. J. Polym. Sci. Part C **1964**, 6, 65-81
21. Moncrieff, R.W. *Man-made Fibres, 6th Edition.* London: Newnes-Butterworth, 1975 pp. 194-200. ISBN 0 408 00129 1; see also *Identification of Textile Materials, 7th Edition*, Manchester: Textile Institute, 1975 pp. 95-100. ISBN 0 900739 18 5
22. Hearle, J.W.S. *Physical Properties of Textile Fibres, 2nd Edition*, Manchester: Textile Institute, 1975, pp. 1-50. ISBN 1 870812 41 7
23. Colom, X.; Carrillo, F. Crystallinity changes in lyocell and viscose-type fibres by caustic treatment. *Europ. Polym. J.* **2002**, 38, 2225-2230
24. Duchemin, B.; Thuault, A.; Vicente, A.; Rigaud, B.; Fernandez, C.; Eve, S. Ultrastructure of cellulose crystallites in flax textile fibres. *Cellulose* **2012**, 19, 1837- 1854. https://doi.org/10.1007/s10570-012-9786-1
25. Ross, K.; Mazza, G. Characteristics of lignin from flax shives as affected by extraction conditions. *Int..J. Mol. Sc.i* **2010**, 11, 4035-4050. doi:10.3390/ijms11104035.
26. Gotoh, K. Surface functionalisation of synthetic textiles by atmospheric plasma. In *Textile Finishing. Developments and Future Trends.* Mittal, K.; Bahners, T., Eds.; Scrivener Publishing LLC: Beverly, MA, USA, 2017; pp. 237-260
27. Vesel, A.; Mozetic, M.; Strnad, S.; Peršin, Z.; Stana-Kleinschek, K.,; Hauptman, N. Plasma modification of viscose textile. *Vacuum,* **2009**, 84, 79-82
28. Kan, C.W.; Yuen, C.W.M. Influence of low temperature plasma treatment on the properties of tencel and viscose rayon fibers. IEEE Trans Plas Sci. 2009, 37, 1615-1619
29. Peršin, Z.; Vesel, A.; Kleinschek, K.S.; Mozetič, M. Characterisation of surface properties of chemical and plasma treated regenerated cellulose fabric. *Text. Res. J.* **2012**, 82,. 2078-2089
30. Kramar, A.D.; Žekić, A.A.; Obradović, B.M.; Kuraica, M.M.; Kostić, M.M. Study of interaction between nitrogen DBD plasma-treated viscose fibers and divalent ions Ca^{2+} and Cu^{2+}. *Cellulose* **2014**, 21, 3279-3289
31. Ibrahim, N.A.; Eid, B.M.; Abdel-Aziz, M.S. Effect of plasma superficial treatments on antibacterial functionalization and coloration of cellulosic fabrics. *Appl. Polym. S*ci. **2017**, 392, 1126-1133